Products and methods for ring dyeing a yarn and/or surface dyeing a fabric are provided. The product and method discloses the application of a dye binding composition including a urethane based polymer to a textile yarn, fabric, or garment. The dye binding composition is engineered so that the composition is positionned or near the surface of the yarn, producing a ring dyed material. The dye binding composition can be colored with selective dyes that bind to the composition but generally do not have affinity for textile substrate. Garments created using this fabric can be abraded to remove surface polymer and color in different locations of the garment, creating an antiqued appearing garment. Dyes of different classifications can be used to produce novel performance and coloration effects in textile materials and garments. This process has been demonstrated on yarn (for a denim-like appearance), knitted and woven fabrics, and garments.
RING DYED POLYMER TREATED MATERIALS

Background

[0001] Color has been applied to textiles over the ages. Natural colorants derived from plants and earthen surroundings were used before a dyestuff industry came into being. Issues with dye fixation, durability, light fastness, colorfastness, and depth of color all remained challenges. As the chemistry of dyes became known and a synthetic approach to engineering dyes to adhere to specific fibers abounded, dyes were created with different mechanisms to become attached to various fiber classes. For cellulosic materials, vat dyes were rendered soluble with reducing materials, and subsequently fixed through oxidization once the dye had penetrated the fiber. Also used were metalized mordants that when applied to a natural fiber could be coupled with a water soluble colorant to precipitate the dye once in the fiber. To capitalize on the solubility of dye components for coloring textiles, naphthol dyes were applied and upon coupling with a companion base, an insoluble colorant resulted - trapped within the fiber matrix.

[0002] As film forming materials were introduced into the dyeing process, new methods to apply colorants to textiles through padding and printing methods became possible. In this dyeing application, the polymeric binder and colorant were generally mixed, applied together, and the pigment color generally left on the surface. Attempts to incorporate other colorants in this mixture generally resulted in poor colorfastness or light fastness performance issues.

[0003] There have been many attempts to create "ring dyed" yarns. The most common and prevalent is that of the dyeing of indigo to produce denim. By multiple steps of dipping and oxidizing the dye onto yarn, the dye penetrates only partially into the yarn bundle. The resultant "ring dyeing" creates light and dark highlights on abrasion points once a garment is sewn and processed using chemical and physical abrasive means before and during a laundering process.

[0004] Ring dyeing is also generally achieved with the application of pigment dyes mixed with binders. This approach has resulted in fabric with stiff handle and marginal rub-fastness performance; however, with advances in acrylic polymer chemistry featuring co and ter polymer blends with lower $T_g$ values, softer and more durable polymers have been created. Even with advances to improve performance, color choice and depth of shade versus rub fastness performance remain challenges. Efforts to improve rub fastness performance

Summary

[0005] The following presents a simplified summary of one or more embodiments of the invention in order to provide a basic understanding of such embodiments. This summary is not an extensive overview of all contemplated embodiments, and is intended to neither identify key or critical elements of all embodiments, nor delineate the scope of any or all embodiments. Its sole purpose is to present some concepts of one or more embodiments in a simplified form as a prelude to the more detailed description that is presented later.

[0006] In a first aspect, a dye binding composition for a ring dyed material is provided, the composition comprising a urethane based polymer having a solids percentage in the composition of between 0.5% and 50% by weight. In some embodiments, the solids percentage in the composition is between 2.0% and 12.0%. In some embodiments, the composition further includes a cationic material. In still further embodiments, the cationic material is selected from the group consisting of guanidine and urethane. In yet still further embodiments, the composition further includes a UV inhibitor. In some embodiments, the urethane based polymer is a polyurethane dispersion.

[0007] In a second aspect, a ring dyed yarn including at least one fiber; and a dye binding composition for a ring dyed material is provided, the composition comprising a urethane based polymer having a solids percentage in the composition of between 0.5% and 50% by weight. In some embodiments, the yarn includes at least one dye configured to selectively dye the dye binding composition positioned on at least a portion of the surface of the fiber. In further embodiments, at least some of the dye binding composition is positioned on at least a portion of the surface of the fibers. In a still further embodiment, the fiber is selected from the group consisting of cotton, wool, silk, hemp, flax, polyester, rayon, acetate, nylons, spandex, olefins, polyethylene, polyethylene, and polypropylene.

[0008] In a third aspect, a fabric including fibers; a dye binding composition for a ring dyed material, the composition comprising a urethane based polymer having a solids percentage in the composition of between 0.5% and 50% by weight, wherein at least some of the dye binding composition is positioned on at least a portion of the surface of the fibers; and at least one dye configured to selectively color the dye binding composition positioned on at least a portion of the surface of the fibers is provided. In some embodiments, the dye binding composition further includes a cationic material selected from the group consisting of
guanidine and urethane. In still further embodiments, the at least one dye does not directly dye the fibers. In some embodiments, the fabric comprises denim. In some embodiments, the fibers include at least one of cotton fibers and synthetic fibers.

[0009] In a fourth aspect, a garment including fabric comprising fibers; a dye binding composition for a ring dyed material, the composition comprising a urethane based polymer having a solids percentage in the composition of between 0.5% and 50% by weight, wherein at least some of the dye binding composition is positioned on at least a portion of the surface of the fibers; and at least one dye configured to selectively dye the dye binding composition positioned on at least a portion of the surface of the fibers is provided. In some embodiments, the garment includes a first surface area comprising the dye binding composition that has been dyed with the at least one dye and a second surface area that is free of the dye binding composition.

[0010] In a fifth aspect, a method of producing ring dyed or surface dyed fiber, yarn, fabric, or garment is provided, the method including applying a dye binding composition for a ring dyed material to at least one of the fiber, yarn, fabric, or garment, the composition comprising a urethane based polymer having a solids percentage in the composition of between 0.5% and 50% by weight; heating the fiber, yarn, fabric, or garment to cause the dye binding composition to mobilize to a surface of the fiber, yarn, fabric, or garment; and applying at least one selective dye to the at least one of the fiber, yarn, fabric, or garment, wherein the selective dye is selective for the dye binding composition.

[0011] In some embodiments, the dye binding composition and the selective dye are applied simultaneously. In some embodiments, the dye binding composition and the selective dye are applied sequentially. In further embodiments, the method further includes abrading at least a portion of the surface of the garment to remove at least some of the dye binding composition that has been dyed with the at least one dye such that the garment has first areas comprising fibers that comprise the dye binding composition that has been dyed with the at least one dye and second areas comprising fibers that do not include the dye binding composition. In some embodiments, the abrading is performed based on at least one of: sanding; application of diatomaceous earth; and application of pumice stones to the garment. In still further embodiments, the heating the dye binding composition is performed using at least one of a curing oven, steam cans, and hot flue. In still further embodiments, the selective dye is applied using at least one of thermosol dyeing on a continuous dye range or tenter frame, pad steaming on a continuous pad/steam range or flash ageing machine, jet dyeing, jigger dyeing, beam dyeing, pad/dry/thermosol dyeing, and printing.
Other aspects and features, as recited by the claims, will become apparent to those skilled in the art upon review of the following non-limited detailed description of the invention in conjunction with the accompanying figures.

**Brief Description of the Drawings**

Having thus described embodiments of the invention in general terms, reference will now be made to the accompanying drawings, which are not necessarily drawn to scale, and wherein:

FIG. 1 is a diagram showing the impact of shade on chemical application at varying dye concentrations, in accordance with an embodiment of the disclosure.

**Detailed Description**

Embodiments of the present invention will now be described more fully with reference to the accompanying examples and drawings, in which some, but not all, embodiments of the invention are shown. Indeed, the invention may be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure may satisfy applicable legal requirements. Like numbers refer to like elements throughout.

Where possible, any terms expressed in the singular form herein are meant to also include the plural form and vice versa, unless explicitly stated otherwise. Also, as used herein, the term "a" and/or "an" shall mean "one or more," even though the phrase "one or more" is also used herein. It should also be understood that while some embodiments describe the methods or products as comprising one or more elements, the methods or elements may also consist of or consist essentially of the elements disclosed herein.

As disclosed herein, a dye binding composition for preparing a ring dyed yarn and/or a surface dyed material is provided. In an embodiment, the surface dyed material is prepared with the ring dyed yarn. In some embodiments, the dye binding composition includes a polymer and/or additives that are engineered to either provide a minimum or maximum degree of migration to position the composition within or on a fiber surface depending on molecular weight and monomer selection. The polymer is generally applied in an aqueous media and can be formulated from a number of monomers in the urethane, guanidine, azetidinium, and vinyl halogen families to form polymer emulsions. The solids added on to the textile substrate can range from 0.5% to 50% by weight; but generally 2.0% to 12.0%, percent is desired. Additionally, the polymer has good film forming properties, is
durable to laundering conditions, has the ability to incorporate materials that can provide targeted dyestuff attraction and durability, and/or is capable of fixing the dye in its matrix.

In some embodiments, the dye binding composition comprises a urethane based polymer with a molecular weight ranging from 1,000 to 400,000 g/mole. In an embodiment, the urethane based polymer has a molecular weight ranging from 2,000 to 200,000 g/mole. The urethane based polymer is designed to attract and hold selective dyes; however, in some embodiments, additional materials can be added as discussed below. The urethane based polymer, in some embodiments, comprises a polyurethane dispersion. The term "polyurethane dispersion" as used herein describes stable mixtures of polyurethane polymers in water. Polyurethane polymers are generally characterized by their monomer content and most commonly involve the reaction of a diisocyanate with a polyl and chain extender. The polyurethane dispersion can be a stable aqueous mixture of any known polyurethane. Typically, the polyurethanes suitable for use in the aqueous polyurethane dispersions are the reaction products (a) an isocyanate compound having at least two isocyanate (~NCO) functionalities per molecule; and (b) a polyl having at least two hydroxy functionalities per molecule and a molecular weight ranging from 250 to 10,000 g/mole.

Exemplary polyl include hydroxy-containing or terminated polyethers, polyesters, polycarbonates, polycaprolactones, polythioethers, polyetheresters, polyolefins, and polydienes. Suitable polyether polyols for the preparation of polyether polyurethanes and their dispersions include the polymerization products of cyclic oxides such as ethylene oxide, propylene oxide, tetrahydrofuran, or mixtures thereof. Polyether polyols commonly found include polyoxyethylene (PEO) polyols, polyoxypropylene (PPO) polyols, polyoxytetramethylene (PTMO) polyols, and polyols derived from the mixture of cyclic oxides such as poly(oxyethylene-co-polypropylene) polyols. Typical molecular weight of polyether polyols can range from 250 to 10,000 g/mole.

Suitable polyester polyols for the preparation of polyester polyurethanes and their aqueous dispersions include hydroxy-terminated or containing reaction products of ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1,4-butandiol, furan dimethanol, polyether diols, or mixtures thereof, with dicarboxylic acids or their ester-forming derivatives. Modified polyether polyurethanes such as polyetherester polyurethanes and polyethercarbonate polyurethanes may also be suitable polyurethanes for the preparation of aqueous polyurethane dispersions. These modified polyether polyurethanes can be derived by incorporating additional polyester polyols or polycarbonate polyols into polyether polyols during the polyurethane manufacturing. The polyurethane dispersion as component in the
compositions of the dye binding composition is selected from polyether polyurethanes, polyester polyurethanes, polycarbonate polyurethanes, polyetherester polyurethanes, polyethercarbonate polyurethanes, polycaprolactone polyurethanes, hydrocarbon polyurethanes, aliphatic polyurethanes, aromatic polyurethanes, and combinations thereof.

Polyurethane dispersion as used herein encompasses both conventional emulsions of polyurethane polymers, for example where a preformed polyurethane polymer is emulsified into an aqueous medium with the addition of surfactants and application of shear, and also includes stable mixtures of self-dispersing polyurethane polymers. These polyurethane dispersions are generally free of external surfactants because chemical moieties having surfactant like characteristics have been incorporated into the polyurethane polymer and therefore are "self emulsifying" or "self dispersing." Representative examples of internal emulsifier moieties that can be incorporated into the polyurethane dispersions useful in the present invention include ionic groups such as sulfonates, carboxylates, and quaternary amines, as well as nonionic emulsifier groups such as polyethers.

In an embodiment, an isocyanate-terminated polyurethane prepolymer is made from isocyanates, polyols, optional chain extender, and at least one monomer containing a hydrophilic group to render the prepolymer water dispersible. The polyurethane dispersion can then be prepared by dispersing the isocyanate-terminated polyurethane prepolymer in water with other polyisocyanates. Further chain extension can be affected by the addition of chain extenders to the aqueous dispersion. Depending on the choice of the hydrophilic group used to render the polyurethane polymer water dispersible, an additional reaction step may be needed to convert the hydrophilic group to an ionic species, for example converting a carboxyl group to an ionic salt or an amine to an amine salt or cationic quaternary group.

For dyeing with selective dyes, materials that can attract targeted dyes within the polymeric matrix are incorporated into the dye binding composition. In some embodiments, the dye binding composition comprises cellulose esters including cellulose acetate, cellulose propionate, cellulose butyrate, and combinations thereof. In other embodiments, the dye binding composition comprises the polymer and the cellulose ester. In further embodiments, the total solids of the dye binding composition is 50%, where the concentration of one or more of the cellulose esters is in the range of 1.0% to 25% solids and the concentration of the polymer is 25% to 49% solids. The one or more cellulose esters, in some embodiments, comprise finely ground powder having a particle size ranging from 0.5 microns to 10 microns. In other embodiments, the finely ground powder of the cellulose esters have a particle size ranging from 1 micron to 3 microns. In further embodiments, the
cellulose ester is added to the dye binding composition in powder form. The total solids of the emulsion may vary between 10% and 60% in concentrated form, with the ratio of the polymer to the one or more cellulose esters remaining between 2% and 50% of the total solids percentage.

[0024] In some embodiments, the dye binding composition is applied to fibers, yarns, fabrics, and garments in concentrations ranging from 0.5% to 50% solids; however, with greater percent solids come greater expense and greater stiffness. In one embodiment, the percent solids range to be applied to the fibers, yarns, fabrics, or garments is between 2.0 and 12.0%. In further embodiments, the percent solids range to be applied to the fibers, yarns, fabrics, or garments is between 3.0 and 10.0%. The dye binding composition, including the percentage of solids in the composition, is specifically engineered to produce a dye binding composition that causes the polymer and/or selective dye to migrate to the surface for use in producing ring dyed yarns and/or surface dyed fabrics.

[0025] Yarns and fabrics can be constructed from any of a host of textile fiber, particularly natural fibers including cotton, wool, silk, hemp, flax, or synthetic fibers including polyesters, rayon, acetate, acrylics, nylons (aromatic and aliphatic), modacrylics, spandex, olefins inclusive of super high molecular weight polyethylene, polyethylene, polypropylene, etc., or combinations of two or more of these fibers. In some embodiments, the yarn contains fiber comprised of 100% cotton. In other embodiments, the yarns comprise cotton fibers blended with non-cotton fibers. The blend of fibers, in some embodiments, is at least 50%, cotton fibers.

[0026] In some embodiments, the dye binding composition further includes a UV inhibitor to improve light fastness performance, such as hindered amine light stabilizers (HALS). The light stabilizer can be added to the polymer mixture prior to application or after the polymer has cured either as a part of a dye mixture or alone. Both methods have shown effectiveness at improving lightfastness performance. Several low and high molecular materials are commercially available from companies including Cytec, Clariant, Great Lakes, and Ciba/Huntsman. An exemplary UV inhibitor includes a high molecular weight material that can be incorporated into the bath and that will eventually migrate to the surface of the film as the polymer film is formed upon drying. One Example is TINUVIN® 622 from CIBA® Chemical Company with a molecular weight of around 4000. These UV inhibitors can also be added to the final finishing bath to coat the surface of the polymer before or after the application of dye. UV absorbing materials are also available that can serve a similar
purpose through a different mechanism typically in the benzotriazole family and are available from Cytec.

[0027] In further embodiments, the dye binding composition comprises a cationic polymer that is incorporated into the urethane matrix. Such embodiments are useful for dyeing with acid dyes or acidified reactive dyes. The cationic polymer comprises guanidine and/or urethane. The guanidine and urethane can be combined to create a polymeric film that is cationic depending upon the percentage of the guanidine that has been incorporated into the matrix. In some embodiments, the dye binding composition comprises guanidine and a urethane based polymer. In further embodiments, the total percent solids of the dye binding composition is 50% solids, where the guanidine makes up 5% to 45% solids of the total solids percentage of the dye binding composition and the urethane based polymer makes up 45%, to 5% of the total solids percentage of the dye binding composition. In one embodiment, the urethane based polymer is present in the dye binding composition at a greater percentage than the cationic material. In a further embodiment, the urethane based polymer is present in the dye binding composition at a lesser percentage or at an approximately equal percentage (e.g., plus or minus 5%) of the cationic material.

[0028] In the application process of the dye binding composition, process conditions and chemical concentrations dictate the resulting appearance and degree to which penetrative dyeing or ring dyeing occurs. In the case in which penetrative dyeing is desired, drying of the polymer is done slowly or anti-migrating agents are incorporated into the mix prior to the drying process. When fabrics with the same percent solids add on are compared, fabrics that are dried slowly result in a shade after dyeing that is lighter than the shade after dyeing for fabrics that are dried at a more rapid rate. It is believed that this result is a direct result of the polymer being on the surface of the substrate. However, the intent of this technology is to engineer dye binding compositions that cause a polymer and/or dye to migrate to the surface of a material, creating ring dyed yarns and/or surface dyed fabrics.

[0029] The mix to be applied to the textile substrate is generally prepared by blending the dye binding composition with water having a temperature range of 80° to 100° Fahrenheit. In an embodiment, the pH of the water/polymer mixture is not less than 6.0 and not greater than 8.0 after the addition of the polymer; however, pH levels slightly outside this range have not been shown to be detrimental. Anti-migrating agents and UV inhibitors may be added at this time if desired. The polymer percent solids concentration range of the dye binding composition is, in some embodiments, from 1% to 25% solids. In one exemplary
embodiment, the dye binding composition has a percent solids concentration range of between 2% and 12% solids depending on hand and depth of color considerations.

The dye binding composition is formulated based on the yarn, fabric, or garment wet pickup in order to provide the appropriate targeted percent solids add on of between 2.0% and 12%. For the application of this chemical mixture to cotton, pad wet pickups will generally vary from 45% to 220% depending on pad nip pressures, post vacuuming of fabric, bath viscosity, and/or absorbency of the padded material. Percent wet pickup is calculated as the \([(\text{fabric wet weight after padding})-(\text{fabric dry weight before padding})] / (\text{fabric dry weight before padding}) \times 100\). For example, the wet pickup of most 100% cotton fabrics ranges from 85 to 100%, so to achieve a solids add-on of 3%, a bath concentration of 3% solids (6% of the dye binding material with 50% active solids material) with a wet pick-up of 100% would yield the appropriate solids addition. Lower moisture add on applications as low as 10% have been demonstrated using foaming techniques; however, the main body of the work has been done with more conventional chemical application techniques. Using foaming techniques, wet pickup levels generally are controlled between 20 and 40% depending upon the amount of moisture needed on the fabric for finishing and the appearance desired.

Once the dye binding composition has been applied to the yarn or fabric, the evenness and rate of drying determines the amount of chemical that migrates to the fabric surface. The faster the fabric is dried, the greater the polymer migration to the surface. This impacts the degree of ring dyeing that will result from the application. For more controlled, slower drying, the fabric can be processed through pre-dryers prior to drying and curing on a tenter frame. For a penetrative dyeing in which minimal polymer migration is desired, fabric can be processed on a tenter frame such that the fabric is only partially dried. This can be accomplished by lowering the tenter zone temperatures and increasing the speed of the fabric. The moisture level of the fabric should be controlled to between 8 and 15%. Final drying and curing is achieved in subsequent processing.

For a ring-dye look, more rapid drying is used for the polymer of the dye binding composition to migrate to the yarn or fabric surface. This is achieved by processing the fabric or yarn at higher temperatures and curing the polymer on the initial tenter pass. This drying can also be achieved in a curing oven, steam cans, hot flue, or other heat source that promotes the movement of water and the polymer to the surface.

In the case of applying the chemical to yarn, yarns may be coated and the polymer of the dye binding composition dried such that the yarns are not broken from being
stuck together after drying. The dye binding composition can be applied to scoured yarn, scoured & bleached yarn, or yarn in its raw state. Each condition provides a different appearance with the raw yarn providing the greatest ring dyed characteristic. Bath concentrations are also different under each condition because of the absorbency of the yarn for the polymer/water mixture; however, targeted solids addition range from 2.0% to 12.0% depending upon the size of the yarn being treated.

There are many ways in which the yarn can be coated. One method is to process the yarn through a pad with the dye binding composition comprising the mixture of polymer, water, and auxiliaries. The bath temperature can be adjusted to between 65° and 190° F; however, the most consistent results occur when the bath temperature is controlled to between 80° and 100° F. Drying can be done using a forced air oven, pre-dryers, a thermosol oven, hot flue oven, microwave or steam cans, or a combination of any of the above. Treated yarns are collated on either a loom beam or a section beam for future processing. A resulting section beam comprised of treated yarns can be combined with many other beams, sized with an easily removed material such as starch or polyvinyl alcohol, or if sufficient polymer has been applied, not sized at all. By employing a combination of these application techniques, using the treated yarns in the warp direction, and subsequently weaving the fabric with raw, scoured, bleached, or dyed filling yarn, the resultant fabric can then be dyed with dyes targeted to dye the polymeric material of the dye binding composition. Dyes are selected for their propensity to not stain cotton - both in the dyeing stage and in the washing stage when the polymeric material is being applied to cotton or cotton blends and a ring dyed appearance is desired. In a further embodiment of application of chemical to yarn, chemical can be applied to the yarn by passing it through a foaming unit allowing both chemical and moisture to be metered onto the fabric. This technique minimizes chemical waste and allows specific levels of the dye bonding polymer to be applied to the yarn.

Filling yarn selection will determine the processing steps that follow. Most denim fabrics directed to the men and boy's denim market contain no stretch yarns, such as spandex. For the women's market, stretch yarns are generally employed in the filling direction. The dyeing and finishing processes required to develop and maintain the stretch characteristics must be carefully controlled to prevent degradation of the elastic effect of the spandex or other stretch material.

Once the fabric has been woven, the fabric will appear as most other undyed, greige fabric. Dye can be applied either in fabric form or garment form depending upon the dye binding composition selected. Exemplary dyes include acid dyes and selectively reactive
dyes for the polymer containing guanidine or other cationic materials, and disperse dyes for any of the dye binding compositions. One advantage of dyeing in fabric form is the ability to see the color and shade of the fabric before going to the customer. In addition, fabric panels can be prepared and laundered to ensure that the shade of the fabric is consistent before constructing garments and laundering them to create denim appearing garments. This approach allows the flexibility to produce denim appearing fabric and garments in multiple colors, depth of color, and engineered color retention depending on the polymer selected and the penetration of the material during processing.

[0037] There are a number of ways in which this resulting denim fabric can be dyed. In one embodiment, the polymer of the dye binding composition is engineered to accept selective dyes. One dyeing method is to apply dyes in a pad, dry the fabric, and heat the fabric to between 390° and 425° F for a minimum of 30 seconds depending on the selective dye. In an embodiment, the dyes are designed to sublime (transform from a solid state to a gaseous state) between these temperatures. In the gaseous state, the dyes are selectively attracted to the polyurethane polymer and/or the cellulose acetate material within the polymeric matrix, and generally not to the cellulosic fibers of the fabric. Subsequent washing is generally effective at removing selective dye not fixed within the polymeric matrix if the dyes are properly chosen and the proper washing conditions are utilized. Care must be used with this approach if stretch fibers are incorporated within the fabric because spandex can be reset or degraded at these elevated temperatures.

[0038] The fabric is finished by the application of sewing lubricants and water soluble hand-builders if needed. These are generally applied in a pad or foamed onto the fabric prior to drying on a tenter frame. The final process involves preshrinking the fabric and adding a uniform skew in the direction of the twill line. This prevents twisted legs in finished garments, and ensures that the shrinkage of the fabric when wet processed does not exceed 3%. Before the sanforization process, fabric shrinkage in the warp or lengthwise direction for high cotton blends ranges from 8% to 12%.

[0039] Another method of applying color to the treated fabric is to apply the selective dye in a pad and steam the fabric for a period of between 30 seconds and 3 minutes. The polymer and cellulose acetate generally will dye under these conditions depending upon the dye selection and polymer selection. This steaming process may be used for stretch fabrics for which the substrate will be dyed in fabric rather than garment form.

[0040] For stretch fabrics, the finishing process may include a heatsetting step to stabilize the width of the fabric. The application of finishing chemicals including a UV
stabilizer can occur in this stage. Spandex or stretch polyesters in the filling direction will have a tendency of staining or becoming colored in this application; therefore it is better to have a core spun cotton spandex stretch yarn than one comprised of a composite polyester yarn such as LYCRA® T-400® by INVISTA™ or filling yarn comprised of poly-butylene terephthalate. The best results have been demonstrated on core spun products consisting of cotton with a spandex core.

[0041] One significant advantage to this process is that it bypasses the need to dye the yarn in rope form on a denim range, apply size, and then spend time, energy, and chemical resources to remove all of the size and some of the color to create a finished garment. In addition, the amount of selective dye needed to achieve saturated shades ranges from 0.5 to 2.0% OWG instead of the higher 3 to 5 percent OWG indigo concentrations desired for denim.

[0042] By using the dye binding composition in the processes described hereinabove, garments can be laundered in cold water for lesser periods of time and with fewer chemicals depending on the desired appearance after laundering. The elimination of amylase enzymes to remove starch, cellulase enzyme to degrade the fabric surface, hypochlorite bleach or potassium permanganate to remove color, and the resulting byproducts from these processes have been shown to produce a positive environmental impact resulting from reduced solids generation and energy usage during the wet processing of garments. Furthermore, the elimination of these chemicals and processing at lower temperatures also results in monetary savings.

[0043] One additional option for the dye binding composition is to dye the fabric after garments are sewn using selective dyes in the wet processing step. For example, garments are placed in a laundering machine, water added to produce a 4:1 to 20:1 liquor to goods ratio, the pH adjusted to 4.0 with acetic acid, 0.5% and 3% OWG (on weight of goods) selective dye added, the machine heated to 190°F at a rate of 5°F per minute, the temperature held for 60 minutes, the bath dropped, garments rinsed with warm water for 5 minutes two times, softener added, water extracted, and the garments dried at 140°F for 40 minutes. Other methods of using selective dyes in the wet processing step are possible.

Application of the polymer to woven and knitted fabrics.

[0044] There are a vast number of iterations of how this chemistry can be applied to produce new and innovative products to meet the many fashion and environmental needs of the market. In a woven finishing plant, fabric can be dyed in a number of ways. These
include but are not limited to: thermosol dyeing on a continuous dye range or tenter frame, pad steaming on a continuous pad/steam range or flash ageing machine, jet dyeing, jigger dyeing, beam dyeing, pad/dry/thermosol dyeing, and printing. Fabric can also be dyed using a high pressure steamer in which superheated steam is used to achieve temperatures approaching 220° F. This technology offers new design and merchandising opportunities that can create unique and fashion forward fabric and garment concepts. The embodiments presented herein address many of the performance deficiencies inherent in many products on the market today, and provides significant environmental advantages to the current processes. A number of these ideas are advanced below. The general process is as follows:

[0045] 100% cotton or Polyester/cotton blended fabric in greige form is received and is desized, scoured, bleached, and/or mercerized and readied for dyeing. These processes can be performed to provide an absorbent, dyeable fabric.

[0046] The prepared fabric is padded with the dye binding composition comprising the polymer to achieve a polymer percent solids concentration of between 0.5% and 10% solids. In one embodiment, the polymer percent solids concentration is between 2.0% and 7.5% and is calculated as described above.

[0047] Fabric is dried using one or more methods including predryers, tenter frames, dry cans, forced air ovens, electric elements, microwave energy or a combination of the same. This drying step will cause a film to form. Curing of the polymer will result at between 250° and 320° F.

[0048] Once the polymer is cured, dye can be applied by pad/roll/extract. Fixation of the dye to the polymer can be accomplished for polyester dyes by steaming at 212° to 219° F for 30 seconds to 3 minutes or thermosol dyeing at between 380° and 425° F for 30 to 45 seconds depending on the dye selection. For the condition in which a cationic material is incorporated into a polymeric matrix, the pad/steam option using acid dyes or selectively reactive dyes at pH levels below 5.0 can be incorporated.

[0049] Fabric can be dyed by other methods; however, care must be exercised to avoid abrasion in fabric form unless this is desired for novel effects in garment form. In this case, dyeing could be accomplished in a dye jet. In the case of knits, this is the preferred method of dye application other than in garment form. If a soft flow jet is used such as a Gaston County FUTURA® or other similar machine, knits can be dyed with a minimum amount of abrasion in fabric form.

[0050] One additional dyeing method particularly valid for this approach is that of jigger dyeing. Jigger dyeing has the advantage of allowing dye to be applied to fabric in
batches by the continuous rolling and rerolling of fabric from one side of the machine to the
other with dye liquor exchange occurring during the transferring process. This process
allows for the heating of dye liquor, keeps the liquor to fabric ratio low, and allows for
evenness of dyeing as long as too much excess dye is not incorporated into the bath. There
are a finite number of dye sites available within the polymer matrix thereby limiting the depth
of shade. For this application, dye selection is important in controlling the shade. Efforts to
match strike rates of the selective dye onto the polymer have been found to dictate whether
shade continuity can be controlled from one lot to the next.

[0051] In one embodiment, the dyeing process is not conducted in fabric form for
fabric in which the color is to be applied in garment form.

[0052] The dyed fabric can now be finished by padding softeners onto the fabric,
framing to width while drying, and removing residual shrinkage through the sanforization
process.

[0053] Once garments are constructed, wet processing can follow thereby creating a
garment with abrasion at the seams and highs and lows of color in the flat areas of the
garment.

[0054] Environmental attributes of this process specifically when applying the
mixture to yarns prior to weaving have demonstrated that biodegradable materials in the
entire process can be reduced between 80 and 90 percent. Furthermore, water and energy use
can be reduced between 50 and 70 percent to achieve comparable-appearing garments after
wet processing steps in garment form.

[0055] Additional application methods and embodiments of this technology include
that with the selection of the targeted polymeric urethanes or urethane mixtures, it is possible
to combine the urethane mixture and dye in a single mixture and subsequently apply this to a
fabric substrate. The dye has been shown to congregate with the urethane mixture in solution
and migrate with the urethane during drying leaving the fiber below undyed. This is
specifically demonstrated when the substrate is cotton or when the dye has a greater affinity
for the polymeric mixture than the substrate.

[0056] Further, the addition of a fluorochemical produces a fabric with excellent
water repellent properties; however, the resulting treated substrate is difficult to dye by
conventional continuous dyeing methods. Adding the dye with the urethane mixture and the
fluorochemical successfully produced a colored, water repellent, dyed substrate. This process
was successful in treating para and meta aramids, olefins, cotton, and blends as outlined
above.
When these polymeric urethanes have UV inhibitors added and are applied to light sensitive materials such as KEVLAR® or other para-aramid and NOMEX® or other meta-aramid fibers, not only is the durability of the material improved, but the material can be dyed on the surface.

Application of polymeric urethanes and mixtures in multiple application and drying steps have demonstrated that the depth of shade can be enhanced up to 125% when compared to a single application at the same polymeric solids loading.

There are numerous variations of this process that can result in unique fabrics and garments with enhanced performance characteristic and/or design interests. Some have been outlined in the Examples.

Examples

Example #1  (Treatment of Woven Fabrics)

An 8.2 oz/yd² 3x1 left hand twill 100% cotton fabric with a greige construction of 108 ends per inch x 56 picks per inch was desized, scoured, bleached and mercerized. A solution containing 3% solids was prepared by the addition of 6% of the dye bonding composition (the 50% total solids content resulting from the combination of 45% solids aqueous polyurethane and 5% solids cellulose acetate) and water at 80° F. The fabric was padded through a mangle with a hard rubber roll and steel roll with a pressure set at 40 psi. The fabric wet pickup was 88% resulting in solids add on to the fabric of 2.6%. The fabric was processed through an 8 zone gas fired tenter at 40 yards per minute with each zone set at 380° F. The fabric was completely dried and cured at the exit of the tenter frame.

Example #1A  (Dyeing of treated fabric in garment form)

Mock pant legs were prepared and laundered as follows: 2.0 kg of treated pant legs were loaded into a 35 pound Milnor sample machine. 30 liters of water were added to the machine resulting in a 15:1 liquor to goods ratio. The pH was adjusted to 4.0 by the addition of 10 ml of acetic acid. DIANIX® Lum Yellow 10G (0.8% OWG) and DIANIX® Lum Red 4B-E (0.2% OWG) were diluted in 1 liter of hot 160° F water and stirred for 2 minutes to disperse the powdered dyes into solution. The dyes were added to the bath while the garments were being agitated. The washer was heated at a rate of 5° F per minute until reaching 180° F. The machine was held at this temperature for 1 hour before dropping the water, rinsing, and applying 10 ml of Ampak Softener Flekes, a cationic softener. A
fluorescent orange color resulted and only slight abrasion evidenced by a slight difference in color was observed at the seams.

Example #1B (Dyeing treated fabric in garment form adding an abrasive material)

[0062] 1.0 Kg from Example #1A and 1.0 kg of diatomaceous earth were added to a 35 lb Milnor machine and processed for 1 hour with a 20:1 liquor to goods ratio at 80° F. There was only marginal abrasion at the seams. The garments were rinsed and 1 kg of pumice stones was added and the process repeated for 30 minutes. Excellent abrasion was observed at the seams and the pant leg hems. The fabric was abraded and hairy, so the garments were laundered for an additional 20 minutes with a cellulase acid enzyme at 125° F. Garments were heated to 160° F with soda ash to deactivate the enzyme, rinsed, and additional softeners added at 120° F and a pH of 4.5. The garments were then extracted, dried, and reviewed. Abrasion at the seams was clearly evident, the pant leg hand was soft, and the white cotton could be clearly seen at the highly abraded points. One side of the leg was then hand sanded and feathering was possible simulating wear. This result clearly demonstrated the ring dyed property imparted from this dye bonding composition and subsequent processing.

Example #1C (Dyeing of treated fabric in fabric form on a pad/steam range)

[0063] Fabric from Example #1 was processed in the lab through a dye bath containing 10 grams/liter of DIANIX® Royal Blue CC (pH of 4.0 adjusted with acetic acid).

[0064] The pad steam range provided a dwell time of 50 seconds at a steamer temperature of 218° F. Fabric was rinsed, extracted, and dried on a hot head press. A medium royal blue fabric resulted. 1.0 kg of pant legs were loaded into an 80 pound Milnor sample washing machine. 75 liters of water and 3.0 kg of pumice stone were added as an abrasive. The garments were processed at 80° F for 40 minutes, rinsed, and processed with 1.2% OWG (on weight of garments) of an acid enzyme (SEYCOZYME TCE®) Sydel Wooley & Company a pH of 4.0 at 125° F for 20 minutes to remove the surface hairs, the acid enzyme denatured as previously described, rinsed twice, softened as described above, extracted, and dried at 140° F for 40 minutes. The resulting pant legs were a royal blue shade and displayed abrasion at the seams exemplified by a loss of color in those areas. The fabric was tested for lightfastness, colorfastness, and ozone fading. The washfastness (American Association of Textile Chemists and Colorists test method "AATCC" 61 2A) results showed
some staining on nylon and acetate and almost no staining on cotton and polyester fibers. The shade change was between a 3.0 and 3.5 rating.

**Example #1D (Sublimation Printing of treated Woven fabric)**

[0065] Treated fabric from Example #1 was selected. A transfer paper was printed with color from four dot matrix printers with low energy disperse dyes. The printed paper was placed on the fabric face, heated to 400° F by passing the paper and fabric sandwich over heated steel rollers. The printed design was transferred to the polymer on the fabric surface. Fabric was laundered through five AATCC 135 III Ai cycles (machine wash warm with 105° F water, dry at hot temperature) to access color retention. Less than 25% of the color was lost. Some abrasion of the fabric was observed.

**Example #2 (Treatment of previously dyed fabric)**

[0066] An 8.2 oz/yd² 3x1 left hand twill 100% cotton fabric with a greige construction of 108 ends per inch x 56 picks per inch was desized, scoured, bleached, and mercerized. This fabric was continuously dyed into an almond yellow color using a three dye reactive dye combination. This fabric was cut into 1 yard 12 inch strips for lab processing.

[0067] A solution containing approximately 3% solids was prepared by adding 6% of dye bonding composition (50% solids) with 0.5% TINUVIN® 622 from CIBA® Chemical Company and water at 80° F. The dyed fabric was padded through a lab padder set at 40 psi resulting in a fabric wet pickup of 90%>, and dried with predryers and dry cans.

[0068] A dye bath containing 5 gram/liter DIANIX® Orange SG and 0.2 grams/liter DIANIX® Red CC was prepared by diluting 5 grams DIANIX® Orange SG and 2.0 grams of DIANIX® Red CC dye to 1.0 liter and adjusting the pH to 4.0 with acetic acid. Dye was padded onto the fabric resulting in a wet pickup of close to 100%. After steaming the fabric for 40 seconds at 212° F, washing and drying of the dyed fabric completed the process. Only the surface of the fabric was dyed to a chestnut brown color. When the fabric was cut or torn, the center of the fabric was clearly still the almond color.

[0069] Fabric swatches were assembled into miniature pant legs with seams characteristic of 5 pocket jean construction. 1.0 kg of chestnut brown and 4.0 kg of white bull denim ballast garments were loaded into an 80 pound Milnor sample washing machine. 75 liters of water and 2.5 kg of pumice stone added as an abrasive. The garments were processed at 80° F for one hour, rinsed twice, softened as described above, extracted, and dried at 140° F for 40 minutes. The resulting garments had the almond color showing
through on the seams and slightly in the flat areas of the mock pant legs resulting in an
antique looking garment.

Example #3  (Yarn Dyeing to produce blue and colored denim fabric)
[0070] An 8/1 rough spun ring spun yarn was selected for treatment. 1.0 kg of the
yarn was scoured and bleached and 1.0 kg of the yarn was used as spun. A mixture
comprising the dye bonding composition containing 3% solids was prepared using the
urethane polymer previously described and water at 80° F. The solution was padded onto
each yarn using a single end size application apparatus. A wet pickup of the scoured and
bleached yarn was 120% resulting in a solids add-on of 3.6%. The wet pickup of the
untreated yarn was 90% resulting on a solids add-on of 2.7%. Both samples were dried by
passing through a forced hot air oven at 100 m/min for 3 minutes at 90 degrees C. Both yarns
were smooth to the touch.
[0071] Denim fabric was woven by inserting 50 and 58 picks per inch picks of the
treated yarn in the filling direction across a 4.5/1 100% cotton warp with 32 ends/inch in a
3x1 left hand twill construction. The fabric width was 59 inches off the loom.

Example #3A  (Denim fabric colored during the laundering process)
[0072] Garments were constructed without further processing. In constructing pant
legs and a garment for color evaluation, the pattern markers were rotated 90° so that the
treated yarn was in the lengthwise direction of the pant leg. Prior to construction into
garments, the fabric was heated to 325° F for 3 minutes to ensure that the polymer was
sufficiently cured.
[0073] 5.0 kg of pant legs were loaded into an 80 pound Milnor sample washing
machine. 75 liters of water (15:1) were added and 15 ml of acetic acid used to adjust the pH
to 4.0. 100 g of DIANIX® Blue UN-SE (2.0% OWG) was prediluted into 1.0 liters of 160° F
water before adding to the washer. The temperature was increased at 5° F per minute until
reaching 180° F. After holding for one hour at 180° F, the water was emptied and the
garments rinsed at 120° F for 5 minutes through two rinses. 50 grams of Ampak Softener
Flekes were added to soften the garments. The garments were extracted and dried at 160° F
for 50 minutes. The finished pant legs had a denim-like appearance with abrasion
characterized by areas in which there was little or no color at the seam areas, pockets, and
waist band. The dye did not stain the untreated cotton filling yarns or the fiber underneath
the polymer matrix.
Example #3B  (Denim fabric colored with multiple colors)

Example #3A was repeated except instead of dyeing a blue denim color, orange, red, fluorescent yellow, and green colors were dyed using the dye combinations in Table 1:

Example #3C  (Denim fabric dyed prior to constructing garments)

Fabric from Example #3 was taken and cut in the width direction into 12 inch strips 59 inches long. A dye bath was prepared by diluting 20 grams of DIANIX® Blue UN-SE in one liter of 120° F water. The pH was adjusted to 4.0 by adding 1.0 gram of acetic acid. Fabric was padded through the dye solution and steamed for 40 seconds at 212° F, rinsed through boxes at 160° F, and dried in a forced air oven. The same fabric was padded through an identical dye bath as above, dried on pre-dryers and dry cans, and heated to 400° F for 30 seconds. Mock pant legs were constructed and laundered at 80° F for 60 minutes with 1 g/1 non-ionic surfactant and rounded pumice stones in a 35 pound Milnor washer to enhance abrasion. The bath was dropped, refilled, softener added, heated to 120° F for 5 minutes, extracted and dried. The resulting mock pant legs had abrasion at the seams and a denim-like appearance with negligible staining of the untreated cotton fiber.

Example #4  (Application of dye to fibers that are difficult to dye)

Cut resistant gloves constructed from a composite yarn containing DYNEEMA® (super high molecular weight polyethylene manufactured by DSM Dyneema LLC) and nylon. Garments were weighed and prepared for treatment. Previous efforts to color this undyeable fiber were met with failure.
A bath was prepared by mixing 300 grams of the dye bonding composition comprised of a 50% solids urethane solution to 5 liters of 80° F water creating a 3% solids solution. 1kg of garments were dipped into the bath and soaked for 1 minute. The garments were removed, extracted, and 40% of the urethane solution remained. The garments were dried at 160° F for 30 minutes in a gas fired drier. Treated garments were dyed as follows:

Example #5

An 8.2 oz/yd² 3x1 left hand twill 100% cotton fabric with a greige construction of 108 ends per inch x 56 picks per inch was desized, scoured, bleached and mercerized. A solution containing 4.1% solids was prepared by the addition of 6.9% of the dye bonding composition consisting of the urethane material and water at 80° F. 10 linear yards of fabric 12 inches in width was padded in the lab through a mangle at a nip pressure set to 20 psi. The fabric wet pickup was 72% resulting in solids add on to the fabric of 3.0%. The fabric was processed by passing the fabric through a forced air oven set at 375° F for 2 minutes and 5 seconds. With this treated fabric, a number of dyes were evaluated for colorfastness, lightfastness, and dye durability. Dye was applied by padding and squeezing excess dye from the fabric achieving a wet pickup of around 75%. Fabric was steamed for 50 seconds at 218° F with saturated steam. Dyed fabric was rinsed with hot 165° F water and 0.01% surfactant to remove excess dye. Fabric was dried and colorfastness performance assessed. Results of a number of dyes evaluated have been illustrated below in Table 2:

<table>
<thead>
<tr>
<th>Dye Name</th>
<th>Concentration</th>
<th>Colorfastness Testing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2

Evaluation of Dyes for Fastness and Performance
[0080] For assessing performance of the tested material, grading is done on a scale of 1.0 to 5.0. A rating of 1.0 indicates significant color change; a rating 5.0, no color change. Ratings of 3.5 and above are generally considered good. For the dyes listed above, several would be unsuitable for this application. A dye that has poor washfastness such as DIANIX® Lum Red G may appear a poor candidate if only assessing washfastness; however, if a fluorescent red is required, this dye may be the only option available. For dyes with poor lightfastness, chemical additives can be incorporated into the polymeric mixture to improve performance. For dyes with poor ozone fastness, materials are available after wet processing that can improve this performance. Dyes assessed in this fashion have been selected as candidates for this process.

Example #5A - Dyeing with multiple techniques
[0081] To assess the impact of dye technique on colorfastness performance, the treated fabric was processed in three ways in the lab and the colorfastness properties assessed:

Dye Process 1: 10 g/l dye padded, steamed, washed, and dried.

Dye Process 2: 10 g/l dye padded, predried, can dried, and thermosol dyed at 416° F for 50 seconds, washed, and dried.


[0082] Colorfastness results are depicted in Table 3.
### Table 3

<table>
<thead>
<tr>
<th>Trial</th>
<th>Description of Dye Method</th>
<th>Disperse Navy GFE Concentration (g/l)</th>
<th>Colorfastness Testing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>120° F Washfastness</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AATCC 61-2A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Shd Chg Cotton Polyester Dry Wet 20 hours</td>
</tr>
<tr>
<td>Dye Process #1</td>
<td>Pad Steam</td>
<td>10.0</td>
<td>3.0 4.5 3.0 4.5 2.5 4.5</td>
</tr>
<tr>
<td>Dye Process #2</td>
<td>Pad Thermosol</td>
<td>10.0</td>
<td>3.0 3.5 2.0 4.5 2.5 3.0</td>
</tr>
<tr>
<td>Dye Process #3</td>
<td>Pad Steam / Pad Thermosol</td>
<td>10.0</td>
<td>3.0 3.5 2.5 4.5 2.5 2.0</td>
</tr>
</tbody>
</table>

The first two techniques were successful at producing an acceptable dyeing. The pad steam option appears to provide the best lightfastness and washfastness result likely from minimizing dye staining of the untreated cotton and keeping excess dye from the fabric surface.

Example #6 - Treatment of cotton Stretch Fabrics

A 7.8 oz/yd² 3x1 Left Hand Twill 99/1 Cotton/Spandex fabric with a finished construction of 109 ends per inch x 50 picks per inch comprising a 20/1 Ring Spun Warp and a 10/1 open end + 14/1 + 70 denier spandex filling was prepared by a desize, caustic scour, bleach, mercerize process before dyeing. The fabric was processed by applying a urethane mixture adjusted to a pH of 5.8 with acetic acid with 4.1 percent solids. A wet pickup of 72% resulted in a solids pickup on the fabric of 3.0 percent. Moisture was reduced to about 45% before the fabric was dried and cured on dry cans.

Example #6A
Fabric was dyed into a multitude of shades on a pad steam range. Preliminary work in the lab revealed that at a 3.0% chemical application level, most medium shades were able to be matched. One color selected was Spiced Orange. The dye formulation contained:

**TABLE 4**

<table>
<thead>
<tr>
<th>Dye Auxiliary</th>
<th>Concentration (grams/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIANIX® Scarlet CC</td>
<td>10.0</td>
</tr>
<tr>
<td>DIANIX® Orange SG</td>
<td>2.0</td>
</tr>
<tr>
<td>Barasol (surfactant)</td>
<td>0.5</td>
</tr>
<tr>
<td>Acetic Acid (20%)</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Fabric was processed at 75 yards per minute by applying the Spiced Orange dye formulation through a Kuster pad with a measured pickup of 75%. The dyes were fixed after processing through a tight laced steamer at 216° F for 50 seconds. Very little excess dye was observed during the washing process. The fabric was dried, finished, and sanforized to remove shrinkage.

The fabric was tested for a number of physical and colorfastness performance parameters as depicted below. Washfastness performance was better before than after finishing. The chemical formulation in finishing is likely the cause. Fabric was made into garments and wet processed. Washfastness performance improved after wet processing with only a 15 to 20% reduction in shade except on the seams and hand sanded areas.

**TABLE 5**

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Test Method</th>
<th>Test Result</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>ASTM D-3776</td>
<td>7.35</td>
<td>oz/yd²</td>
</tr>
<tr>
<td>Width</td>
<td></td>
<td>64.5</td>
<td>inches</td>
</tr>
<tr>
<td>Construction</td>
<td>ASTM D-3775</td>
<td>Ends 128</td>
<td>per inch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Picks 52</td>
<td></td>
</tr>
<tr>
<td>Tensile</td>
<td>ASTM D-5034</td>
<td>Warp 169</td>
<td>lbs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Filling 77</td>
<td></td>
</tr>
<tr>
<td>Elmdendorf Tear</td>
<td>ASTM D1424</td>
<td>6.6</td>
<td>lbs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.2</td>
<td></td>
</tr>
</tbody>
</table>
Seam Slippage  ASTM D-434  54  55  lbs
Needle cutting  ASTM D-1906  0  4  Cuts
Shrinkage  AATCC 135 IVAi  -2.45 -7.4 percent
Stretch & Growth  ASTM D-3 107  Growth  Stretch
Initial  1.3  10.6 percent
After 3 launderings  5.6  17.5 percent
Pilling (Random Tumble)  ASTM D-35 12  30  60 minutes
  4.0  3.0 Grade

| TABLE 6 |

**Colorfastness Test Results - Spiced Orange**

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Test Method</th>
<th>Test Result</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washfastness</td>
<td>AATCC 61-2A</td>
<td>Shade Chg</td>
<td>Cotton</td>
</tr>
<tr>
<td>After dyeing</td>
<td>4.0</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>After Finishing*</td>
<td>3.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>After Garment Wash</td>
<td>4.0</td>
<td>4.0</td>
<td>4.5</td>
</tr>
<tr>
<td>Perspiration*</td>
<td>AATCC 15</td>
<td>4.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Cold Water Bleeding*</td>
<td>AATCC 107</td>
<td>4.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Crocking*</td>
<td>AATCC 8</td>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Gas Fading*</td>
<td>AATCC 23</td>
<td>4.5</td>
<td>1 cycle</td>
</tr>
<tr>
<td>Lightfastness*</td>
<td>AATCC 16</td>
<td>3.5</td>
<td>20 hours</td>
</tr>
<tr>
<td>Ozone*</td>
<td>AATCC 109</td>
<td>4.5</td>
<td>2 cycles</td>
</tr>
</tbody>
</table>

*After finishing test results

Example #6B - Wet processing of Spiced Orange Garments

[0088] Fabric was constructed into a womenswear jean cut in a size 6. Four sets of garment increments, each set consisting of three garments and weighing 1.0 kg, were processed to evaluate the impact of wash procedure on overall appearance and aesthetic. The wash procedures included:

A) A Rinse Wash - 20 minute wash at 120° F with softener

B) A 20 minute Enzyme Wash - A 20 minute wash at 125° F with acid enzymes followed by a 10 minute softening step at 120° F Softening step

C) A 20 minute Stonewash + 20 minute Enzyme Wash - A 20 minute wash at 100° F with a 2:1 Pumice Stone to garment ratio followed by a rinse, a 20 wash at 125° F with acid enzymes followed by a 10 minute softening step
D) A 40 minute Stonewash + 20 minute Enzyme Wash - A 40 minute wash at 100° F with a 2:1 Pumice Stone to garment ratio followed by a rinse, a 20 minute wash at 125° F with acid enzymes followed by a 10 minute softening step

[0089] The rinse wash was effective at softening the fabric and little to no abrasion was observed. The color appeared similar to that of a garment constructed from a piece dyed fabric. In several garments, the thigh portion of the garment was presanded prior to laundering. In all cases, these sanded areas appeared lighter and worn with white, undyed cotton apparent in the more heavily sanded areas. Garments that were enzyme washed for 20 minutes had a shade drop of about 10% and a slight bit of abrasion on the side seams, belt loops, and bottom hems of each leg. The sanded areas were clearly lighter than the unsanded areas.

[0090] Adding stonewashing to the process provided an abraded look generally seen in ring dyed or surface dyed fabrics. The abrasion was greater after 40 minutes than 20 and both garments had excellent abrasion without any significant destruction to the integrity of the garment. Generally, to achieve a comparable abraded appearance in similar garments using classical dyeing techniques, more than twice the stone washing is required and physical damage to the garment is generally observed.

[0091] The areas of the garments that were hand sanded prior to stonewashing were nearly white in the more heavily sanded areas. This color differentiation results because the dyes selected do not redeposit on the fabric once in solution during processing. Finally, after the garments were processed, softened, and dried, additional highlights could be readily created by hand sanding after wet processing. This ability adds a new dimension to the options available to the wet processor and the designer looking for new and innovative garments.

Example #7 - Yarn Treatment of 100% Cotton and the Environmental Impact

[0092] A raw 20/1 Ring Spun 100% cotton warp comprised on 4260 ends was processed through a box containing a urethane mixture consisting of 9% solids. After the yarn was dipped and excess material removed with squeeze rolls set at 45 psi, a wet pickup of 105%, was measured resulting in a 9.45%> solids add on to the yarn. Each yarn was separated while wet and dried at 150° F for 50 seconds followed by steam cans set at 275° F to ensure that the fabric is dry and the polymeric matrix cured. Under these conditions, no steam was observed on the cans indicating that the yarn was completely dry before reaching the cans.
Treated yarn was wound onto a loom beam and woven on a Picanol air jet loom. Fabric was woven at 71 inches with 60 ends per inch and 60 picks per inch in a plain weave construction to produce a fabric that once dyed, would produce a chambray effect. The chambray effect is exemplified by a plainweave construction less than 6 oz/yd² in which only the warp or lengthwise yarn is dyed and the filling yarn remains white. Chambray is generally seen in indigo colors in which the warp yarns have been dyed on an indigo dye range. Colored chambrays are generally not available because of dye minimums, the ability to match color, and the associated expense. Chambrays produced from this invention can be prepared by scouring and bleaching the treated fabric through normal preparation processes. Absorbancy of prepared fabric was less than one second from the time a drop of water touches the fabric surface to when it dissipates. The whiteness of treated and untreated fabric after preparation cannot be differentiated.

Example #7A - Preparation and dyeing of treated yarn

Fabric from Example #7 is scoured on a continuous bleach range by applying a scouring formulation comprising 4% sodium hydroxide solution with EDTA type chelating agents (ethylene diamine tetra-acetic acid) with an alkaline stable surfactant system. The scouring process was completed by steaming the fabric for 10 minutes and rinsing. The fabric was then bleached with a bleaching formulation comprising hydrogen peroxide, sodium hydroxide, an organic stabilizer and a chelating agent for 25 minutes before being washed and dried. It is important to note that the dye binding composition disclosed herein unexpectedly permits this process of scouring and bleaching to occur without loss of dye quality on the material. In contrast, dyeing procedures known in the art would result in extensive loss of dye on the material if processed with a scouring and bleaching formulation.

Fabric was dyed a navy color on a steam range at 75 yards/min using a formulation consisting of 7.0 g/liter DIANIX® Navy CC and 2.0 g/liter of Black CA-B with a KUSTER® pad with a 75% WPU. The dyes become fixed by passing the fabric through a tight laced steamer at 216° F for 50 seconds and then washing. The fabric produced from this trial was a fabric with chambray appearance and aesthetic produced using 100% cotton yarn. This is achieved by selecting dyes that do not dye cotton so only the coating on the warp yarns become dyed. Efforts to minimize dye staining of the cotton have been achieved through rigorous washing after the steamer. The colorfastness performance and specifically the lightfastness performance is a function of the effectiveness of removing surface dye from the untreated cotton portion of the blend. The initial lightfastness of this trial tested in
accordance with AATCC 16-E after 20 hours was 1.5. The same dye formulation on a solid fabric treated sample has an initial lightfastness of 3.5. Additional washing with special soaps enabled the lightfastness performance to improve to between a 2.5 and 3.0, depending on the amount of fugitive dye remaining. As the lightfastness performance improved, so also did the overall washfastness. Prepared fabric was dyed in the lab in a variety of colors including yellows, oranges, blues, violets, tans, khakis, greens, browns, plums, and greys.

The significance of this process is:

1) Large number of colors are possible
2) Shade matching can be done quickly
3) Minimums become less problematic
4) Wash down of fabric remains on hue
5) Significant environmental impact

Example #8 - The environmental impact

Based on wet processing results from fabrics from Examples #3 and #7, and upon procedures well established in the industry used in the production of washed-down indigo denim jeans, the environmental impact of each was determined. Conditions including prescouring, bleaching, yarn dyeing, and wet processing of finished garments were a part of the assessment. With the indigo denim, an assumption was made that the wet processing would include desizing, permanganate spraying, bleaching, abrasion with neutral cellulase enzymes and an abrasive material, softening, and drying. From the results in Table #7, the impact of this invention on the environmental footprint of wet processing is significant.

<table>
<thead>
<tr>
<th>The Environmental Impact of Urethane Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Indigo Blue Jeans versus Urethane Produced Colored Denim</strong></td>
</tr>
<tr>
<td>Total processing (fabric through finished garment)</td>
</tr>
<tr>
<td>Biodegradable materials (% by weight)</td>
</tr>
<tr>
<td>Alkali (% by weight)</td>
</tr>
<tr>
<td>Chlorine (% by weight)</td>
</tr>
<tr>
<td>Heavy Metals (Manganese ppm)</td>
</tr>
<tr>
<td>Wet processing in garment form</td>
</tr>
<tr>
<td>Time (min/garment)</td>
</tr>
<tr>
<td>Energy (Kcals/garment)</td>
</tr>
</tbody>
</table>
Table #7 is illustrative of the impact of the invention on biodegradable waste products associated with textiles in general, and denim specifically. Processing of Indigo denim garments generally requires the removal of a sizing material generally in the form of starch. This alone represents around 6% of the total weight of the denim. Amylase and cellulase enzymes, cellulose, and dye round out the remaining percentage. The majority of the material removed from the Urethane processed fabric results from cellulose degradation promoted by cellulase enzymes. This results in nearly an 80% reduction of biodegradable solids when compared with normal processing. The aesthetic character of the Urethane processed fabric or yarn is achieved without the use of typical oxidative materials like hypochlorite bleaches or potassium permanganate materials. This eliminates the need for heavy metals like manganese in the process. Finally, most wet-processing can be done at lower temperatures with fewer rinses resulting in a 40 to 60% reduction of time, water, and energy to process garments incorporating this technology.

Example #9 - Impact of chemical concentration on the depth of shade and processes to achieve shades when greater dye uptake is desired

During the development process, there appeared to be a limit to the amount of dye that the urethane material can incorporate into the surface matrix. This level was thought to be dependent upon the concentration of urethane solids applied to the fabric. Application of solids at the 3.0%, 5.0%, and 6.5% levels revealed that there was little to no benefit of increased solids on depth of color with the application technique of chemical mixture described in Example #5. There was a linear effect of color build for all four chemical level applications when dye concentration was increased from 5 grams per liter to 15 grams per liter when evaluating DIANIX® Blue S-BG. (See FIG. 1). When solids are applied in multiple steps of application/cure, the dye yield doubles at 5% solids and increases 250% at 6.5% solids. This increased color yield enables darker colors to be realized.

In FIG. 1, the standard strength is set to 100% for the lightest swatch. All swatches are compared to that lightest swatch. For all of the dyeings made from fabric that had a single application of chemical, dye yield was fairly linear up to 15 g/l and an increase from 5.0 g/l to 15 g/l resulted in an 80% increase in strength.

When additional chemical solids are applied in a second pass, two results occur: first, the slope of the dye yield changes with increased dye concentration from an 80%
strength increase, to 140%. Second, the dye yield for the two pass application with 5.0% solids nearly doubles and in the case for the two pass application with 6.5% solids, the depth of shade increases 2.5 fold.

When greater depth of shade is desired, fabric may be processed by a dual pass method.

Example #10 - Treatment of fabric with specialized yarns to achieve a vintage appearance after wet processing with pumice stones.

A 10.8 oz/yd² 98/2 cotton spandex with a greige construction of 80 ends per inch x 46 picks per inch and a finished construction of 93 ends per inch and 48 picks per inch comprising an Amsler Ring Spun 9.75 warp yarn and a 10/1 + 70 denier spandex was prepared by desizing, scouring, bleaching, and mercerizing the fabric. The Amsler spinning technique creates yarn that mirrors much of the inconsistency in yarn prevalent before sophisticated yarn production techniques creating uniform yarn were introduced. The Amsler spinning technique creates slubs in the yarn. This fabric was treated as described in Example #5. Fabric was dyed as described in Example 5A - Dye Process #1 through a pad steam range through a dye formulation consisting of 10 g/l of DIANIX® Blue S-BG. The dyed fabric was thoroughly washed, dried, and constructed into denim-like pant legs. The legs were laundered in a Washex 250 lb machine with pumice stones for 50 minutes at 90° F to assess the impact of the stones on the seams and on the slub portion of the Amsler warp yarns. The resulting laundered pant legs demonstrated excellent abrasion at the seams and the thick places on the uneven warp yarns. Negligible coloration of the cotton yarn underneath the abraded high points in the yarn was observed. (When laundering indigo denim, this problem is a major concern). After drying, the resultant pant legs were somewhat hairy from the abrasive effect of the pumice stones. Some additional hand sanding was done to demonstrate an even greater contrast between the slubs and the surface of the fabric. A modified technique was used to assess stretch and growth by leaving one of the seams in the pant leg to provide sufficient length in the filling to do the measurements. Other than this modification, the laundered garment was tested in accordance with ASTM D-3107. Stretch was 24% and growth was 5.2%.

Example #11 - Combination of treated and untreated yarns to create novel selvedge designs for denim and chambrays
[00102] 16 ends of 20/1 from the yarn treated from Example #7 were taken and combined with 12 ends of 20/1 yarn from fabric that had been desized, scoured, bleached, and mercerized. The yarns were configured across a 12 inch template approximately 0.5 mm apart from one another with 6 treated yarns, followed by 6 untreated yarns, followed by 2 treated yarns, 6 untreated yarns and 6 treated yarns for a total of 28 yarns. A 16/1 Ring spun yarn that had been scoured, bleached, and mercerized was woven in a plainweave construction with 30 yarns per inch. Two inches were woven with a needle by hand. The tails of the ribbon were sewn to leader fabric and processed through a pad steam as described in Example #5A - Dye Process #1. The dye formulation consisted of 7.0 g/l of DIANIX® Blue S-BG. The resulting 2 inch ribbon was about one half inch. Where the untreated warp yarn and white filling yarn were together, two white stripes with a fine dyed stripe resulted. This clearly demonstrated that stripes will be possible to create when fabric is continuously dyed with the appropriate dyes. Some staining on the white yarn was observed; however, a clear contrast was demonstrated between the treated and untreated yarn.

Example #12 - Treatment of Flame resistant fabrics imparting color to fibers difficult to dye. [00103] A 55/45 Protex C modacrylic/combed cotton 6.9 oz/yd² plainweave woven fabric was desized, scoured, and bleached prior to treatment. Fabric was treated as described in Example #5. Fabric was dyed to produce a bright firehouse red shade with the pad steam process described in Example #5A-Dye Process #1 using the attached formulation:

| Table 8 |
|-----------------|------------------|
| Firehouse Red   |                  |
| Dye Auxiliary   | Concentration (grams/liter) |
| DIANIX® Rubine CC | 5.0                 |
| DIANIX® Orange SG | 1.0                |
| Barasol (surfactant) | 0.5                |
| Acetic Acid (20%) | 0.2                |

[00104] Fabric was tested for vertical flammability. The results indicated that the addition of the urethane did not change the after flame and char length performance when tested in accordance with ASTM D-6413 initially and after three launderings in accordance with AATCC 135 IV-Ai. (120° F with detergent). This is the same laundering procedure used to assess dimensional stability in the warp and filling directions. Char length in both warp and filling direction were less than 4 inches and afterflame was less than 0.5 seconds.
As described in this example, application of the treatment to KEVLAR® was successful in producing a red shade; however, the color was much more yellow than the protex cotton blend because of the differences in color of the treated substrate. The KEVLAR® was golden yellow before treatment and red orange after treatment. Based upon the results from the dyeing of these materials separately, a 50/40/10 Protex C/Combed Cotton/para-aramid is being constructed and will be dyed this same red shade for potential commercial use.

Example #13 - Treatment of polypropylene

A 30 inch 4.0 oz/yd² plain weave woven fabric with 24 ends and 24 picks comprised of 625 denier polypropylene yarns was treated by padding a urethane mixture containing 4.1 percent solids through a mangle set at 20 psi. A wet pickup of 60 percent was measured resulting in a solids add on to the substrate of 2.5%. Fabric was dried and cured in a dispatch oven at 180° F for 5 minutes. Fabric was dyed as described in Example #5A - Dye Process #1 with the following formulation producing a saturated Gray shade.

Table 9

<table>
<thead>
<tr>
<th>Gray</th>
<th>Concentration (grams/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye Auxiliary</td>
<td></td>
</tr>
<tr>
<td>DIANIX® Black CA-B</td>
<td>5.0</td>
</tr>
<tr>
<td>Barasol (surfactant)</td>
<td>0.5</td>
</tr>
<tr>
<td>Acetic Acid (20%)</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Exemplary embodiments include:

A denim-like fabric and garment comprised of cotton or cotton/synthetic fiber produced from the application of a dye bonding composition comprised of a mixture of polymers of the urethane, guanidine, and vinyl halogen families with or without additives that sequester dye in which the polymer combination is preferentially dyed over the cellulosic fiber. The preferential dyeing of the polymer combination over the cellulosic fiber produces ring dyed yarns that can subsequently be abraded in garment form.

In some embodiments of the denim-like fabric and garment, yarn or fabric is dyed prior to, during, or after the fabric is woven with dyes that are not substantive to the cellulosic material. In this embodiment, the dyes do not have the propensity of reacting with or sticking to cellulose. In the case in which the dye bonding composition is comprised of a urethane alone or mixed with a cellulose ester, selective dyes such as disperse dyes are
preferred. In the case in which the dye bonding composition is comprised of a urethane combined with guanidine creating a cationic polymer, acid or reactive dyes of the vinyl sulfone or monochloro hydrazine family that also stain cotton can be used. In the case in which polyester is blended with cotton in these blends, using a cationic polymer is the preferred approach.

[00109] In some embodiments of the denim-like fabric and garment, the dye bonding composition comprises a urethane emulsion polymer blended with powdered cellulose acetate in a urethane emulsion polymer to powdered cellulose acetate ratio ranging from 90:10 to 50:50 or a urethane emulsion polymer to powdered cellulose ratio ranging from 90:10 to 75:25. This blend is contained in an aqueous solution containing 50% solids which is further diluted prior to application to yarn, fabric, or garments.

[001 10] The fabric and garment can be dyed in yarn form, fabric form, or garment form with selective dyes that have preferential attraction to cellulose acetate and/or the urethane polymer.

[001 11] In some embodiments, a process by which fiber, yarn, fabric, and garments can be produced through the application of a dye bonding composition comprising at least one polymer, wherein the dye bonding composition is preferentially dyed over the cellulosic fiber, producing ring dyed yarns that can subsequently be abraded in garment form is provided.

[001 12] In some embodiments of the process, the yarn or fabric is dyed prior to, during, or after the fabric is woven with dyes that are not substantive to the cellulosic material. In the case in which the dye bonding composition is comprised of a urethane mixed with a cellulose ester, selective dyes are preferred. In the case in which the dye bonding composition is comprised of a urethane combined with guanidine creating a cationic polymer, acid or reactive dyes of the vinyl sulfone or monochloro hydrazine family that also stain cotton can be used. In the case in which polyester is blended with cotton in these blends, using a cationic polymer is the preferred approach.

[001 13] In some embodiments, the process includes dyeing cotton knit or woven fabrics varying in weight from 3 to 14 oz/yd² with reactive, sulfur, vat, or naphthol dyes to precolor the substrate. Subsequently, the dye bonding composition is applied as described above, and then the cured dye bonding polymer matrix is dyed a different color with selective dyes that affix to the polymer matrix but do not color or stain the dyed color underneath the polymer. The dyeing of the polymer can be done in garment form or fabric form. Fabric can be dyed by jigger, pad/dry/thermosol, pad/steam, and/or jet dyed. The garments produced
from this process are abraded during wet processing with various abrasive materials including pumice stones, sand, plastic abrasive balls, etc., resulting in garments that have abrasion at seams, back pockets, hems, and the like that allow the original color to show through creating tonal effects.

[0014] In further embodiments, the process includes applying the dye bonding composition comprised of the urethane polymer material to fibers, yarns, fabrics, or garments which contain materials difficult to dye including DYNEEMA®, KEVLAR®, polybenzimidazole (PBI), PBO® and blends thereof, providing a film on the surface of the materials to which dye binders can attach. This dye bonding composition can be dyed with selective dyes and the polymeric matrix can further be dyed with pigments and other colorants that adhere through the action of acrylic and other binding polymeric materials.

[0015] While certain exemplary embodiments have been described and shown in the accompanying drawings, it is to be understood that such embodiments are merely illustrative of and not restrictive on the broad invention, and that this invention not be limited to the specific constructions and arrangements shown and described, since various other updates, combinations, omissions, modifications and substitutions, in addition to those set forth in the above paragraphs, are possible.

[0016] Those skilled in the art may appreciate that various adaptations and modifications of the just described embodiments can be configured without departing from the scope and spirit of the invention. Therefore, it is to be understood that, within the scope of the appended claims, the invention may be practiced other than as specifically described herein.
WHAT IS CLAIMED IS:

What is claimed is:

1) A dye binding composition for a ring dyed material, the composition comprising a urethane based polymer having a solids percentage in the composition of between 0.5% and 50% by weight.

2) The dye binding composition for the ring dyed material of claim 1, wherein the solids percentage in the composition is between 2.0% and 12.0%.

3) The dye binding composition for the ring dyed material of claim 1 or claim 2, the composition further comprising a cationic material.

4) The dye binding composition for the ring dyed material of claim 4, wherein the cationic material is selected from the group consisting of guanidine and urethane.

5) The dye binding composition for the ring dyed material of claim 1 or claim 2, the composition further comprising a UV inhibitor.

6) The dye binding composition for the ring dyed material of claim 1 or claim 2, wherein the urethane based polymer is a polyurethane dispersion.

7) A ring dyed yarn comprising:
   at least one fiber; and
   a dye binding composition for a ring dyed material, the composition comprising a urethane based polymer having a solids percentage in the composition of between 0.5% and 50% by weight.

8) The ring dyed yarn of claim 7, further comprising at least one dye configured to selectively dye the dye binding composition positioned on at least a portion of the surface of the fiber.
9) The ring dyed yarn of claim 7 or claim 8, wherein at least some of the dye binding composition is positioned on at least a portion of the surface of the fibers.

10) The ring dyed yarn of claim 7 or claim 8, wherein the fiber is selected from the group consisting of cotton, wool, silk, hemp, flax, polyester, rayon, acetate, nylons, spandex, olefins, polyethylene, polyethylene, and polypropylene.

11) A fabric comprising:
   fibers;
   a dye binding composition for a ring dyed material, the composition comprising a urethane based polymer having a solids percentage in the composition of between 0.5% and 50%, by weight, wherein at least some of the dye binding composition is positioned on at least a portion of the surface of the fibers; and
   at least one dye configured to selectively color the dye binding composition positioned on at least a portion of the surface of the fibers.

12) The fabric of claim 11, wherein the dye bind composition further comprises a cationic material selected from the group consisting of guanidine and urethane.

13) The fabric of claim 11 or claim 12, wherein the at least one dye does not directly dye the fibers.

14) The fabric of claim 11 or claim 12, wherein the fabric comprises denim.

15) The fabric of claim 11 or claim 12, wherein the fibers comprise at least one of cotton fibers and synthetic fibers.

16) A garment comprising:
   fabric comprising fibers;
   a dye binding composition for a ring dyed material, the composition comprising a urethane based polymer having a solids percentage in the composition of between 0.5% and 50%, by weight, wherein at least some of the dye binding composition is positioned on at least a portion of the surface of the fibers; and
at least one dye configured to selectively dye the dye binding composition positioned on at least a portion of the surface of the fibers.

17) The garment of claim 16, wherein the garment comprises a first surface area comprising the dye binding composition that has been dyed with the at least one dye and a second surface area that is free of the dye binding composition.

18) A method of producing ring dyed or surface dyed fiber, yarn, fabric, or garment, the method comprising:
   
   applying a dye binding composition for a ring dyed material to at least one of the fiber, yarn, fabric, or garment, the composition comprising a urethane based polymer having a solids percentage in the composition of between 0.5% and 50% by weight;
   
   heating the fiber, yarn, fabric, or garment to cause the dye binding composition to mobilize to a surface of the fiber, yarn, fabric, or garment; and
   
   applying at least one selective dye to the at least one of the fiber, yarn, fabric, or garment, wherein the selective dye is selective for the dye binding composition.

19) The method of claim 18, wherein the dye binding composition and the selective dye are applied simultaneously.

20) The method of claim 18, wherein the dye binding composition and the selective dye are applied sequentially.

21) The method of claim 18, claim 19, or claim 20, further comprising:
   
   abrading at least a portion of the surface of the garment to remove at least some of the dye binding composition that has been dyed with the at least one dye such that the garment has first areas comprising fibers that comprise the dye binding composition that has been dyed with the at least one dye and second areas comprising fibers that do not include the dye binding composition.

22) The method of claim 21, wherein the abrading is performed based on at least one of:
   
   sanding;
   
   application of diatomaceous earth; and
   
   application of pumice stones to the garment.
23) The method of claim 18, claim 19, or claim 20, wherein the heating the dye binding composition is performed using at least one of a curing oven, steam cans, and hot flue.

24) The method of claim 18, claim 19, or claim 20, wherein the selective dye is applied using at least one of thermosol dyeing on a continuous dye range or tenter frame, pad steaming on a continuous pad/steam range or flash ageing machine, jet dyeing, jigger dyeing, beam dyeing, pad/dry/thermosol dyeing, and printing.
Impact of Shade on Chemical Application

% Dye Strength

Dye Concentration (g/l)

○ Single Pass at 3.0%, 5.0%, and 6.5% chemical application
△ Double pass at 3.0% on the first pass & 2.0% on the second pass (5.0% solids)
◊ Double pass at 3.0% on the first pass & 3.5% on the second pass (6.5% Solids)

Note: 3.0% single pass at 5.0% was determined to be 100% and all strength measurements are relative to this standard.

FIG. 1
A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - D06P 1/00; D06M 11/00; D06B 11/00 (2013.01)
USPC - 8/490, 554, 550, 606, 115.51, 918

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)
IPC(8): D06P 1/00; D06M 1 1/00; D06B 1 1/00 (2013.01)
USPC: 8/490, 554, 550, 606, 115.51, 918

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>WO 201 1/153296 A1 (SCOTT, JC et al.) 08 December 201 1; paragraphs [0001], [0010], [0015], [0027]-[0031], [0033], [0036]; claim 9</td>
<td>1, 3/1, 5/1, 6/1, 7-8, 9/7-8, 10/7-8, 11, 13/1 1, 15/1 1, 16, 18-20, 23/18-20, 24/18-20</td>
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<td>Y</td>
<td>US 5,700,867 A (ISHIYAMA, M et al.) 23 December 199 7; column 2, lines 15-20; column 3, lines 15-25</td>
<td>2, 3/2, 4, 5/2, 6/2, 12, 13/12, 14/11-12, 15/12, 17, 21/18-20, 22/21/18-20</td>
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<td>Y</td>
<td>US 5,221,288 A (KAMATA, M et al.) 22 June 1993; column 2, lines 15-20; column 3, lines 65-68; column 5, lines 65-68</td>
<td>4, 12, 13/12, 14/12, 15/12</td>
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<td>Y</td>
<td>US 4,740,213 A (RICCI, F) 26 April 1988; column 2, lines 44-48; claims 1-2, 4</td>
<td>14/1-12, 17, 21/18-20, 22/21/18-20</td>
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<td>A</td>
<td>US 2006/0089453 A1 (PAJERSKI, A) 27 April 2006; entire document</td>
<td>1, 2, 3/1-2, 4, 5/1-2, 6/1-2, 7-8, 9/7-8, 10/7-8, 11, 12, 13/1 1, 14/1 1-12, 15/1 1-12, 16-20, 21/18-20, 22/21/18-20, 23/18-20, 24/18-20</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

* 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
17 January 2014 (17.01.2014)

Date of mailing of the international search report
03 FEB 2014

Name and mailing address of the ISA/US
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