CELLULOSIC TEXTILES TREATED WITH HYPERBRANCHED POLYETHYLENEIMINE DERIVATIVES

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ABSTRACT

The present disclosure is directed to cellulosic textiles treated with h-PEI derivatives, such derivatives possessing the general structure shown below:

\[(R)_{x} \text{A} \cdot \text{PEI} \cdot \text{A} \cdot \text{R}^{y}\]

where R is a non-hyperbranched hydrocarbon group (for example, such as alkyl, alkenyl, arylalkyl, and arylalkenyl groups, where the number of carbon atoms in the linear portion of the hydrocarbon is between 5 and 30 carbon atoms), where x is a number from 1 to about 10,000 (depending on the Mₙ of the h-PEI), where h-PEI is a hyperbranched polyethyleneimine, where A is a small organic “capping” compound having from 1 to 4 carbon atoms, where y is a number from 0 to 10,000, and wherein R is present in an approximate amount of between about 20% and about 75% by weight of the h-PEI derivative. The chemical treatment imparts durable colorfastness, softness, wrinkle resistance, and reduced drying time to substrates treated therewith.
CELLULOSIC TEXTILES TREATED WITH HYPERBRANCHED POLYETHYLENEIMINE DERIVATIVES

TECHNICAL FIELD

[0001] The present disclosure is directed to the field of hyperbranched polyethyleneimine derivatives useful for treating textile substrates. More specifically, this disclosure relates to treatments used to provide substantially permanent retention of dye color in textiles (that is, colorfastness), particularly in cellulosic textile substrates. In addition to improving the colorfastness of these substrates, the present chemical treatment further enhances the substrate by increasing softness and reducing drying time and wrinkling.

[0002] The present disclosure is directed to a molecule having a hyperbranched polyethyleneimine core to which is attached, at a minimum, one or more hydrocarbon groups. Optionally, linking compounds may connect the hydrocarbon groups to the hyperbranched polyethyleneimine core. Additionally, other organic compounds may also be used to “cap” the branches of the hyperbranched polyethyleneimine that are unreacted with hydrocarbon groups.

BACKGROUND

[0003] Poor washfastness (that is, the leaching and bleeding of dye stuffs from fabrics), along with poor crockfastness (the removal of dye from fabric when it is abraded), are two significant problems that to one degree or another must be overcome for any dyed or printed good to be used commercially. Some loss of dye is expected to take place from dyed textiles during washing and/or abrasion with all categories of dyes, including sulfur dyes, direct dyes, vat dyes (for example, indigo), and reactive dyes. Sulfur dyes, which are used to produce black denim products, are notoriously poor at retaining their intended color.

[0004] One area where colorfastness is of particular concern is the denim market. Color loss in denim apparel due to laundering is a significant issue to denim manufacturers and consumers, particularly with black denim products. Considerable efforts have been devoted to modifying existing manufacturing processes and chemical treatments to mitigate this long-standing problem, although with limited success thus far. A number of chemical compositions used in the process of denim have been found ineffective at preserving the colorfastness of the dyed substrates and, in some cases, have contributed to other undesirable effects, such as stiffness.

[0005] Typically, manufacturers use one or more quaternary salts attached to long-chain hydrocarbons to treat dyed denim fabrics. While these kinds of quaternary salts provide the treated fabric with a soft feel (also known as “hand”), they generally are not durable to laundering and are ineffective at preserving colorfastness.

[0006] Polymeric cationic materials previously have been used as dye fixing agents. Typically, these are linear molecules with positive charges distributed along the length of the molecular chain. Examples of these cationic fixing agents include BURCOFIX™ FM and BURCOFIX™ 195 (available from M. Dohmen USA of Greenville, S.C.); MURQUAT® 100 (available from Nalco of Naperville, Ill.); and CASSEOFIG® FRN, CARTAFIX® SWE Liq., and SANDOFIX® TP (all available from Clariant Corporation of Charlotte, N.C.). The issues with these kinds of products are that either they contain formaldehyde, which may be dangerous at certain levels, or they impart stiffness to the substrate, which is undesirable for apparel applications. Generally, they have only limited ability to preserve colorfastness to laundering.

[0007] More recently, dye fixatives, which are based on the cross-linking of hyperbranched polyethyleneimine (h-PEI) to the dye stuffs and/or the substrate, have been developed. Such fixatives are described in U.S. Pat. No. 6,497,733 and U.S. Pat. No. 6,679,924 (both assigned to Nano-Tex, LLC). The disclosures of which are hereby incorporated by reference. It has been found that the h-PEI compounds described in these patents have limited capability to preserve colorfastness, because the compounds are very hydrophilic and will actually cause color bleeding during processing. In addition, these compounds also attract hydrophilic detergents to the substrate surface during laundering, which tend to strip dyes away from the textile surface. Finally, another problem with these h-PEI compounds is that they increase stiffness to the substrate.

[0008] Yet another use for polyethyleneimine-based compounds in treating textile substrates is described in U.S. Pat. No. 7,141,077 to Detering et al., the disclosure of which is hereby incorporated by reference. In this patent, hydrophobically modified polyethyleneimines and polyvinylamines are used to impart wrinkle resistance to cellulose-containing substrates. In this instance, the polyethyleneimines are water-soluble or water-dispersible polyamines. Because the compounds have been modified to introduce only a limited amount of hydrophobicity (i.e., because they are intended to be hydrophilic enough to maintain water solubility), the treatment lacks wash durability and offers little benefit to the washfastness of the substrate. In fact, the compounds actually may lead to significant color bleeding during fabric processing. Additionally, because the treated substrate may lack the desired degree of softness for certain applications, a separate softening agent may be necessary.

[0009] Thus, a need exists for a wash-durable dye fixing agent—particularly for cellulosic substrates—that preferably imparts benefits such as softness and wrinkle resistance. The present treatment provides a solution to such needs providing a specific hyperbranched polyethyleneimine structure, which is linked to one or more hydrocarbon groups having linear portions of between 5 and 30 carbon atoms and which may additionally be linked to one or more organic “capping” compounds.

SUMMARY

[0010] This disclosure is directed to treatments for dyed textile goods that will improve their fastness properties. More particularly, this disclosure is directed to certain chemical treatments that, when placed on the dyed textile, allow the dye to be permanently or substantially permanently affixed to the fabric, while providing additional benefits in terms of wrinkle resistance and reduced drying time.

[0011] The present treatment comprises a hydrophobically modified hyperbranched polyethyleneimine compound, also known as a “hyperbranched polyethyleneimine derivative.” The hyperbranched polyethyleneimine derivative comprises at least one hyperbranched polyethyleneimine (a “hydrophilic component”) that has been linked to one or more hydrocarbon groups having between 5 and 30 carbon atoms linearly arranged (“hydrophobic component(s)”; which may be linked to the hyperbranched polyethyleneimine using any of a number of different linkages). In another embodiment, the
chemical treatment also comprises one or more additional organic “cap” compounds attached to the hyperbranched polyethyleneimine core.

[0012] Preferably, the hydrophobic components (that is, hydrocarbon groups and optional linking compounds) are electrophilic, so that they react with the nucleophilic hyperbranched polyethyleneimine molecule. Preferably, the hydrophobic components are present in an amount of from about 20% to about 75% of the weight of the final compound (that is, the hyperbranched polyethyleneimine derivative), thereby imparting softness to the treated substrates. Any of a number of acceptable linking groups may be used to link the hydrocarbon groups to the hyperbranched polyethyleneimine, as will be described herein, or the hydrocarbon groups may link directly to the hyperbranched polyethyleneimine molecule.

[0013] The disclosure is further directed to the process for treating dyed textiles and other webs with the present chemical treatment, wherein the chemical treatment is applied to at least a portion of the fiber, yarn, textile, or composite. In a presently preferred embodiment, the dyed fabric is placed into the chemical treatment (e.g., by dipping), then padded and dried in a single continuous process.

[0014] This disclosure is further directed to the dyed fibers, yarns, fabrics, textiles, finished goods, or nonwovens (encompassed herein under the terms “textiles” and “webs”) treated with the subject hyperbranched polyethyleneimine derivatives. Such textiles and webs exhibit a greatly improved colorfastness and resistance to fading, even after multiple launderings. Further, such treated textiles also exhibit increased softness and reduced wrinkling and drying time.

DETAILED DESCRIPTION

[0015] The present chemical treatment is especially well-suited for use with cellulose substrates. The term “cellulose” refers to those fibers made from the carbohydrates contained in the cell walls of plants. Most often, the term “cellulose” refers to cotton substrates, although flax, ramie, linen, jute, hemp, bamboo, rayon, acetate, and triacetate substrates also fall into this classification. Substrates containing combinations of cellulose fiber types may be successfully treated with the present chemical treatment. Other natural fibers, such as wool and silk, may also benefit from the present chemical treatment.

[0016] Of principal utility in the present chemical treatment is the hyperbranched polyethyleneimine (h-PEI) molecule, which may also be referred to herein as the hydrophilic component of the compound. In schematic terms, the h-PEI molecule can be described as having a central core surrounded by a plurality of molecular branches, with each branch projecting outward from the core and having a highly reactive end group. It is to be expected that partial linkage of the branches to themselves often occurs. The molecule typically exhibits a very high charge density per area, meaning that there are a high number of positive charges clustered densely together around the molecular core. This configuration makes the molecule very capable of interacting with a wide range of other molecules, many of which will be described herein. The number of molecules that may be attached to the h-PEI molecule depends on the number average molecular weight (Mn) of the h-PEI, which reflects the number of branches available for attachment.

[0017] For the applications that are contemplated herein, hyperbranched polyethyleneimines having a number average molecular weight (Mn) of between about 300 and about 2 million are preferred, with Mn of between about 1,000 and about 75,000 being more preferred.

[0018] To the h-PEI molecule are attached at least one, and preferably more than one, hydrocarbon groups to increase the hydrophobicity of the resulting compound (i.e., the h-PEI derivative). These hydrocarbon groups, together with any linking compounds which may be used to attach them to the h-PEI molecule, are collectively referred to as the “hydrophobic components” of the dye-reactive molecule. These hydrocarbon groups may be linear molecules or may contain branched or aromatic portions, which have an electrophilic group capable of reacting with the nucleophilic h-PEI. Preferably, regardless of the structure of the hydrocarbon, the linear portion of the hydrocarbon group contains between about 5 and about 30 carbon atoms and, more preferably, contains between about 10 and about 24 carbon atoms. Mixtures of various length hydrocarbons may also be used.

[0019] Examples of electrophilic hydrocarbons include, without limitation, carboxylic acids, ketene dimers, formates, acetyl halides (such as acetyl chloride), esters, anhydrides, alkyl halides, epoxides, isocyanates, and the like. Preferred examples include stearic acid, hydroxy stearic acid, isostearic acid, and palmitic acid.

[0020] The weight ratio of h-PEI to hydrophobic groups is from about 5:1 to about 1:10 and, more preferably, is from about 2:1 to about 1:5, depending on the Mn of the h-PEI. Most preferably, weight ratios of h-PEI to hydrophobic group from about 1:1 to about 1:4 are used.

[0021] The present h-PEI derivatives possess the structure shown below:

(R)-h-PEI-(A),

where R is a non-hyperbranched hydrocarbon group (for example, such as alkyl, alkenyl, arylalkyl, and arylalkenyl groups, where the number of carbon atoms in the linear portion of the hydrocarbon is between 5 and 30 carbon atoms), where x is a number from 1 to about 10,000 (depending on the Mn of the h-PEI), where h-PEI is a hyperbranched polyethyleneimine, where A is a small organic “capping” compound having from 1 to 4 carbon atoms, where y is a number from 0 to 10,000, and wherein R is present in an approximate amount of about 20% and about 75% by weight of the molecule.

[0022] It is understood that, in the synthesis of molecules such as the general structure provided above, the actual product exhibits a polydispersity (a distribution of ratios) and the molar ratio of each molecule will vary somewhat around the target ratio.

[0023] Optionally, small organic molecules (generically shown as “A” in the structure above) may be used to “cap” the unreacted branches of the hyperbranched polyethyleneimine. Generally speaking, the capping molecule “A” has between one and four carbon atoms. Any caps that will react with the amine (NH or NH2) portion of the h-PEI molecule may be used, including, without limitation, epoxides, anhydrides, esters, acids, carbonates, sulfates, formates, isocyanates, and mixtures thereof. Specific examples of such caps include, without limitation, ethylene oxide, propylene oxide, methyl bromide, acetic acid, vinyl sulfonates, trifluoroacetic acid, and succinic anhydride. Mixtures of different “cap” molecules may be used.

[0024] Ethylene oxide (EO) or propylene oxide (PO) chains are especially useful as capping compounds in the present treatment to prevent the treated substrate from yel-
lowing when exposed to high manufacturing temperatures (for example, temperatures greater than 350°F). The addition of such chains is not required to achieve the colorfastness and other benefits of the present treatment, but merely to impart additional benefits.

One potentially preferred R group has a $C_{12}H_{25}$ structure, which in the above structure forms a stearamide. When using this R group and an h-PEI having an $M_n$ of 1200, representative molar ratios of h-PEI to R are 1:2, 1:4, 1:6, 1:8, 1:10, and 1:12. Similarly, when the $M_n$ of the h-PEI molecule is about 10,000, representative molar ratios of h-PEI to R are 1:25, 1:60, 1:80, and 1:100. Finally, when the $M_n$ of the h-PEI molecule is about 75,000, representative molar ratios of h-PEI to R are 1:400, 1:500, and 1:600.

The chemical synthesis of the present treatment molecules is conducted by reacting the h-PEI molecule with a hydrophobic R-containing electrophilic molecule in the presence of nitrogen. It has been found that mechanical agitation of the reagents in a vessel under nitrogen at a temperature of about 150°C produces the h-PEI derivatives described herein. The time necessary to complete the reaction depends on the amount of reagents that are being reacted and the size of the reaction vessel. The resulting compounds, referred to herein as "h-PEI derivatives", are typically in the form of an oily liquid or waxy solid. Preferably, h-PEI derivatives exhibit hydrophobic agents present in an amount of at least 20%, more preferably, of at least 30%, and most preferably, of up to 75% of the weight of the h-PEI derivative.

To prepare a treatment bath for textiles using the h-PEI derivatives described herein, it is necessary to heat the h-PEI derivative to its melting point, so that it may be poured into a vessel where it is combined, via high speed and high shear agitation, with hot water. In this instance, the phrase “hot water” refers to water having a temperature equal to or greater than the melting point of the h-PEI derivative. Suitable equipment for achieving high speed and high shear agitation includes propeller-type mixers, Jago®-type agitators, homogenizers, roll mills, ball mills, microfluidizers, and the like. The dispersion that results from the forcible introduction of the h-PEI derivative into water is assisted and stabilized by addition of a solubilizing agent (e.g., an acid or a surfactant), the amount of which depends on the molecular weight of the h-PEI and the molar ratio of h-PEI to hydrophobic components. Acetic acid is one potentially preferred acidd for this purpose (excess acid being evaporated off during subsequent drying of the treated textile substrate). Amounts of greater than 0.1% acid, by weight of solution, may be used successfully. Preferably, the amount of acid will be in the range of about 0.1% to about 20% of the weight of the h-PEI derivative.

The fiber, the yarn, the fabric, or the finished garment is dyed in the normal manner and is then exposed (by methods known in the art such as by soaking, spraying, dipping, padding, foaming, exhausting, and the like) to the aqueous dispersion of the treatment chemistry. In some instances, it may be possible to introduce the treatment chemistry onto a garment by replacing the softening chemistry (normally applied during the laundering process) with the treatment described herein.

The treated web is then removed from the solution and dried, preferably at temperatures between room temperature and 400°F; more preferably, at temperatures between about 100°F and 380°F; and, most preferably, at temperatures between about 109°F and 220°F. The typical add-on weight of the h-PEI derivative is from about 0.1% of the weight of the fabric to about 10% of the weight of the fabric and, preferably, is from about 0.2% of the weight of the fabric to about 5% of the weight of the fabric.

The treated substrates exhibit improved color retention after multiple launderings. Additionally, and surprisingly, the substrates also have durable softness, reduced wrinkling after laundering/drying, and reduced drying time in a conventional home dryer.

Without wishing to be bound by theory, it is hypothesized that the h-PEI derivatives, because of their potentially high cationic charge density, are readily attracted to the anionic groups of the cellulose fibers or dyed, thereby forming multiple ionic bonds that render the complex molecule water-insoluble. The high density of these ionic bonds unites the chemistry and the textile substrate tenaciously, reducing the likelihood that detergent will attack and strip dyes from the textile. It is also believed that any dyestuffs, which ordinarily might be pulled away from the textile fibers during laundering, may be "captured" by the nano-sized core of the h-PEI derivative, in effect holding the dye against the substrate and preserving its dyed appearance. Finally, the long hydrocarbon chains of the h-PEI derivatives provide softness and wrinkle resistance to the textile substrate.

Preferably, when durability to laundering (e.g., for 10 or more washes) is desired, a cross-linking agent is incorporated into the aqueous solution or dispersion. Suitable cross-linking agents for this purpose include epoxides, chlorotrimines and their derivatives, azetidines, blocked isocyanates, and melamine derivatives, which may further enhance the durability of the treatment chemistry. Other finishing agents may also be used, although softeners are unlikely to be needed due to the softening effects of the treatment chemistry.

In order to further illustrate the present derivative and advantages thereof, the following specific examples are given, it being understood that the same are intended only as illustrative and are in no way limiting.

EXAMPLE 1

To a round-bottom flask with a mechanical agitator were added 100 grams of hyperbranched polyethyleneimine (sold under the name EPOMINE® SD012 by Summit Specialty Chemicals, New Jersey) and 50 grams of stearic acid (sold by Aldrich, Wis.). The hyperbranched polyethyleneimine had a $M_n$ of 1200. The mixture was heated under nitrogen, with agitation, at a temperature of about 150°C for 3 hours. At the end of the 3 hours, an aliquot was removed and analyzed using FT-IR, which indicated that no acid remained and that the reaction was complete. The resulting product was a waxy solid.

EXAMPLE 2

The same procedure, as described in Example 1, was followed, except that 100 grams of stearic acid were used. The resulting product was a waxy solid.

EXAMPLE 3

The same procedure, as described in Example 1, was followed, except that 250 grams of stearic acid were used. The resulting product was a waxy solid.

EXAMPLE 4

To a round-bottom flask with a mechanical agitator were added 100 grams of hyperbranched polyethyleneimine
(sold under the name EPOMIN® SP200 by Summit Specialty Chemical, New Jersey) and 120 grams of stearic acid (sold by Aldrich, Wis.). The hyperbranched polyethylenimine derivative had a M. of 10,000. The mixture was heated under nitrogen, with agitation, at a temperature of about 150°C. for about 3 hours. At the end of the 3 hours, an aliquot was removed and analyzed using FT-IR, which indicated that no acid remained and that the reaction was complete. The resulting product was a waxy solid.

EVALUATION OF EXAMPLES 1 AND 2

[0038] Commercially available black denim jeans (Lee® brand) were washed once with Tide® laundry detergent.

[0039] The h-PEI derivatives of Examples 1 and 2 were separately dispersed into hot water via high speed and high shear agitation. To solubilize the h-PEI derivatives, acetic acid was added to the dispersions to achieve a pH level of about 5. The h-PEI derivatives comprised about 2.0% by weight of dispersions.

[0040] The black denim fabric samples were dipped into the treatment dispersions (one sample in the dispersion of Example 1 and one in the dispersion of Example 2), passed through two nip rolls at 40 p.s.i. to remove excess water, dried in a dispatch oven at 320°F. for about 10 minutes (or until dry), and then steam-pressed and vacuumed. The treated fabric samples felt noticeably softer to the touch than the untreated fabric.

[0041] A comparative sample (Comparative Example A) was also prepared by dipping a sample of the same black denim fabric with a mixture containing 5% by weight of solution of HydroSoft® LDS, a supposedly quaternary ammonium softener, commercially available from Boehme-Filatex Corporation of North Carolina. Comparative Example A was also passed through nip rolls, dried, steam-pressed, and vacuumed, as described above.

[0042] The edges of the fabric samples (Examples 1 and 2 and Comparative Example A) were then sewn, and the samples were washed at 140°F. The samples were washed and dried ten times to evaluate color retention.

[0043] The L*a*b* color values for the samples were evaluated, using a Labscan XE from Hunter Labs after 0, 5, and 10 washes. The shade change (ΔE) was calculated by comparing the 5 and 10 wash readings with the initial measurement after zero washes. Such values are shown in TABLE 1. Smaller AE values are indicative of better color retention.

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>ΔE (after 5 washes)</th>
<th>ΔE (after 10 washes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1</td>
<td>0.39</td>
<td>0.81</td>
</tr>
<tr>
<td>Example 2</td>
<td>0.58</td>
<td>1.76</td>
</tr>
<tr>
<td>Comp. Example A</td>
<td>1.42</td>
<td>2.46</td>
</tr>
</tbody>
</table>

[0044] Thus, the h-PEI derivatives of Examples 1 and 2 were better at preserving color than Comparative Example A. The fabric of Comparative Example A became stiffer after laundering, as well as fading.

[0045] Next, the fabrics of Example 1, Example 2, and Comparative Example A were evaluated to determine the effect, if any, of the applied treatment on drying time.

[0046] The drying procedure is described as follows. Each fabric sample to be tested was die cut using a 3.5-inch diameter die cutter. The cut samples were soaked with water after having been treated and cured with the hyperbranched polyethylenimine derivative treatment described herein. The soaked samples were then removed from water and padded (with approximately 40 p.s.i. of pressure) to remove the excess liquid from the samples and to insure that all of the samples had approximately the same amount of initial moisture.

[0047] The drying of the samples was measured and recorded by an IR-200 Moisture Analyzer made by the Denver Instrument Company. The standby temperature of this machine was set at 60°C. The machine has an internal weight scale. Each wet sample was placed individually into the machine, which measured an initial weight and moisture content.

[0048] The temperature inside the machine was set at a constant temperature of 60°C, the scale recorder recording the actual weight and measuring the weight loss as moisture left the fabric. Measurements were recorded until the actual weight had varied less than 0.100 grams for about 30 seconds (which indicated that the fabric was completely dry). The machine then generated a print-out containing the sample identification, time elapsed, initial weight, final weight, total weight loss, and % moisture lost during the drying.

[0049] The drying times (minutes/seconds) are shown in TABLE 2.

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Drying Time (after 0 washes)</th>
<th>Drying Time (after 5 washes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1</td>
<td>10:10</td>
<td>25:19</td>
</tr>
<tr>
<td>Example 2</td>
<td>13:39</td>
<td>21:14</td>
</tr>
<tr>
<td>Comp. Example A</td>
<td>16:39</td>
<td>55:20</td>
</tr>
</tbody>
</table>

[0050] Thus, the data shows that the h-PEI derivatives of Examples 1 and 2 significantly reduce drying time, as compared to the treatment of Comparative Example A.

EVALUATION OF EXAMPLES 3 AND 4

[0051] In an alternate evaluation, a different commercially available black denim jean fabric (Wrangler® brand) was used. In this evaluation, the fabric was washed first with acidic water at 140°F. (where the pH of the water was about 4.5, having been adjusted to that level by the addition of acetic acid) for about 5 minutes and then dried.

[0052] The hyperbranched polyethylenimine derivatives of Examples 3 and 4 were separately dispersed into hot water via high speed and high shear agitation. To solubilize the h-PEI derivatives, acetic acid was added to the dispersions to adjust the pH to about 4. The h-PEI derivatives comprised about 0.7% by weight of the Example 3 dispersion and about 0.9% by weight of the Example 4 dispersion. Included with the h-PEI dispersions (Examples 3 and 4) was a cross-linking agent (sold under the name POLYCUPE® 1721X, from Hercules Inc. of Delaware), present in an amount of about 2.5% by weight of the dispersion.

[0053] The black denim fabric samples were dipped into the treatment dispersions (one sample in the dispersion of Example 3 and one in the dispersion of Example 4), passed through two nip rolls at 40 p.s.i. to remove excess water, dried in a dispatch oven at 220°F. for about 20 minutes (or until dry), and then steam-pressed and vacuumed. The treated fabric samples felt noticeably softer to the touch than the untreated fabric.
[0054] A comparative sample (Comparative Example B) was also prepared by dipping a sample of the same black denim fabric with a mixture containing 2.0% by weight of solution of HIPOSOFT® LDS, a quaternary ammonium softener, commercially available from Boonehme-Filatex Corporation. Comparative Example B was also passed through nip rolls, dried, steam-pressed, and vacuumed, as described above.

[0055] The edges of the fabric samples (Examples 3 and 4 and Comparative Example B) were then sewn, and the samples were washed at 120°F. The samples were washed and dried ten times to evaluate color retention.

[0056] The L*a*b* color values for the samples were evaluated, using a LabscanXE from Hunter Labs after 0, 5, and 10 washes. The shade change (ΔE) was calculated by comparing the 5 and 10 wash readings with the initial measurement. Such values are shown in TABLE 3.

<p>| TABLE 3 |</p>
<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>ΔE (after 5 washes)</th>
<th>ΔE (after 10 washes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 3</td>
<td>0.58</td>
<td>1.90</td>
</tr>
<tr>
<td>Example 4</td>
<td>0.67</td>
<td>2.03</td>
</tr>
<tr>
<td>Comp. Example B</td>
<td>2.27</td>
<td>5.06</td>
</tr>
</tbody>
</table>

[0057] Thus, the h-PEI derivatives of Examples 3 and 4 were better at preserving color than Comparative Example B. The fabric of Comparative Example B became stiffer after laundering, as well as fading.

[0058] A third comparative example (Comparative Example C) was prepared, using the same fabric as that of Example 1, except that a solution containing 1.5% by weight of solution of only h-PEI was used, instead of an h-PEI derivative. Such h-PEI was sold under the name EPOMIN® SP012 by Summit Specialty Chemical of New Jersey. The hydrophilic molecule was easily put into solution with water, without the addition of a solubilizing agent, such as acetic acid.

[0059] The fabric of Comparative Example C was prepared by dipping the fabric into the solution described above, passing it through nip rolls, drying, steam-pressing, and vacuuming, as described above. The resulting fabric was noticeably stiffer than the untreated fabric and the treated fabrics of Examples 1, 2, 3, and 4.

EXAMINES 5-11

[0060] To determine the necessary degree of hydrophobicity necessary to achieve the intended properties (i.e., reduced drying time and wrinkling, improved color retention) in the treated textile fabrics, a series of experiments was used to create compounds with various levels of amidation. The experiments were conducted following the procedure outlined in Example 1. The hyperbranched polyethyleneimine compounds that were used had a Mn of approximately 10,000. TABLE 4 also shows the amount of stearic acid (by weight %) used to produce the h-PEI derivatives and the degree of hydrophobicity resulting from the synthesis of such derivatives. The phrase “degree of hydrophobicity” refers to a calculated theoretical ratio of the amount of reacted amine groups present in the h-PEI derivative versus the total available reactive amine provided during the synthesis.

<p>| TABLE 4 |</p>
<table>
<thead>
<tr>
<th>Example ID</th>
<th>Hydrophobic Wt.% of Final Compound</th>
<th>Degree of Hydrophobicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative Ex. D</td>
<td>6.23</td>
<td>0.0100</td>
</tr>
<tr>
<td>5</td>
<td>20.0</td>
<td>0.0372</td>
</tr>
<tr>
<td>6</td>
<td>30.0</td>
<td>0.0630</td>
</tr>
<tr>
<td>7</td>
<td>42.6</td>
<td>0.1075</td>
</tr>
<tr>
<td>8</td>
<td>65.7</td>
<td>0.2580</td>
</tr>
<tr>
<td>9</td>
<td>72.7</td>
<td>0.3440</td>
</tr>
<tr>
<td>10</td>
<td>75.3</td>
<td>0.3870</td>
</tr>
<tr>
<td>11</td>
<td>84.1</td>
<td>0.6000</td>
</tr>
</tbody>
</table>

[0061] The h-PEI derivatives of Comparative Example D and Examples 5-11 were separately dispersed into hot water via high speed and high shear agitation. To solubilize the h-PEI derivatives, acetic acid was added to the dispersions to achieve a pH level of about 5. The h-PEI derivatives comprised about 0.25% by weight of dispersions. It should be noted that the product of Example 11 was incapable of being dispersed into water, even with the addition of a significant amount of solubilizing agent. Accordingly, the evaluation described below excludes fabric treated with the h-PEI derivative of Example 11.

[0062] The black denim fabric samples (Lee® brand) were dipped into the treatment dispersions (one fabric sample for each Example and the Comparative Example), passed through two nip rolls at 40 p.s.i. to remove excess, dried in a dispatch oven at 220°F. for about 8 minutes (or until dry), and then steam-pressed and vacuumed. The fabric samples of Examples 5-10 felt noticeably softer to the touch than the untreated fabric or the fabric of Comparative Example D.

[0063] The fabrics of Comparative Example D and Examples 5-10 were then wet with water. Drying time and moisture % were measured for each Example as initially produced and again after being washed once with TIDE® detergent at 105°F. and then dried.

[0064] The results are shown in TABLE 5 below.

<p>| TABLE 5 |</p>
<table>
<thead>
<tr>
<th>Example ID</th>
<th>Drying Time (min/sec)</th>
<th>Moisture %</th>
<th>Drying Time (min/sec)</th>
<th>Moisture %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>37/00</td>
<td>49.45</td>
<td>45/50</td>
<td>55.08</td>
</tr>
<tr>
<td>Comparative D</td>
<td>14/19</td>
<td>18.63</td>
<td>27/05</td>
<td>37.46</td>
</tr>
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<td>5</td>
<td>13/39</td>
<td>18.60</td>
<td>17/30</td>
<td>24.55</td>
</tr>
<tr>
<td>6</td>
<td>13/39</td>
<td>17.63</td>
<td>13/30</td>
<td>24.02</td>
</tr>
<tr>
<td>7</td>
<td>12/30</td>
<td>16.21</td>
<td>21/09</td>
<td>30.58</td>
</tr>
<tr>
<td>8</td>
<td>12/30</td>
<td>21.57</td>
<td>16/30</td>
<td>26.31</td>
</tr>
<tr>
<td>9</td>
<td>12/30</td>
<td>15.34</td>
<td>33/50</td>
<td>47.15</td>
</tr>
</tbody>
</table>

[0065] The results shown above indicate that the present chemical treatment improves drying time, particularly when the weight percentage of the hydrophobic components is between about 20% and about 75% and, more particularly, when the weight percentage of the hydrophobic components is between 30% and 73%.

We claim:
1. A treated textile substrate, said treated textile fabric comprises:
   (a) a cellulosic textile Substrate; and
   (b) a treatment applied to at least one side of said textile Substrate, said treatment comprising:
a water-insoluble hyperbranched polyethyleneimine derivative of the formula:

$$(R)_x \text{h-PEI-} (A)_y$$

where $R$ is a non-hyperbranched hydrocarbon group, said hydrocarbon group having at least one linear portion, said linear portion having between 5 and 30 carbon atoms; where $x$ is a number from 1 to 10,000; where h-PEI is a hyperbranched polyethyleneimine; where $A$ is an organic compound having from 1 to 4 carbon atoms; where $y$ is a number from 0 to 10,000; and wherein $R$ is present in an amount of between about 20% and about 75% by weight of said hyperbranched polyethyleneimine derivative.

2. The treated textile substrate of claim 1, wherein said substrate is a fabric.

3. The treated textile substrate of claim 1, wherein said treatment is applied to said substrate at an add-on level of between about 0.1% to about 10%, based on the weight of said substrate.

4. The treated textile substrate of claim 3, wherein said treatment is applied to said substrate at an add-on level of between about 0.2% to about 5%, based on the weight of said substrate.

5. The treated textile substrate of claim 1, wherein said h-PEI has a number average molecular weight ($M_n$) in the range of about 300 to about 2 million.

6. The treated textile substrate of claim 5, wherein said h-PEI has a number average molecular weight ($M_n$) in the range of about 1,000 to about 75,000.

7. The treated textile substrate of claim 1, wherein said linear portion of said $R$ group has between about 10 and about 24 carbon atoms.

8. The treated textile substrate of claim 1, wherein said h-PEI and said $R$ group are present, in a weight ratio, of from about 5:1 to about 1:10.

9. The treated textile substrate of claim 8, wherein said h-PEI and said $R$ group are present, in a weight ratio, of from about 2:1 to about 1:5.

10. The treated textile substrate of claim 9, wherein said h-PEI and said $R$ group are present, in a weight ratio, of from about 1:1 to about 1:4.

11. The treated textile substrate of claim 1, wherein said $A$ group is at least one compound selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, methyl, acetate, vinyl sulfonate, trifluoroacetate, and trialkyl silyl.

12. The treated textile substrate of claim 11, wherein said $A$ group is ethylene oxide or propylene oxide.

13. The treated textile substrate of claim 1, wherein said $R$ group has a $C_{17}H_{35}$ structure, resulting in a stearic amide linkage between said $R$ group and said h-PEI.

14. The treated textile substrate of claim 1, wherein said treatment further comprises a cross-linking agent.

15. A process of treating a textile substrate, said process comprising:

(a) providing a cellulosic textile substrate;

(b) providing a dispersion of hyperbranched polyethyleneimine derivative, said hyperbranched polyethyleneimine derivative being of the formula:

$$(R)_x \text{h-PEI-N-} (A)_y$$

where $R$ is a non-hyperbranched hydrocarbon group, said hydrocarbon group having at least one linear portion, said linear portion having between 5 and 30 carbon atoms; where $x$ is a number from 1 to 10,000; where h-PEI is a hyperbranched polyethyleneimine; where $A$ is an organic compound having between 1 to 4 carbon atoms; where $y$ is a number from 0 to 10,000; and wherein $R$ is present in an amount of between about 20% and about 75% by weight of said hyperbranched polyethyleneimine derivative.

16. The process of claim 15, wherein said textile substrate is a fabric.

17. The process of claim 15, wherein said solubilizing agent is acetic acid.

18. The process of claim 15, wherein said dispersion further comprises a cross-linking agent.

19. The process of claim 15, wherein heat is applied during step (i) or step (ii) to facilitate formation of said dispersion.

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