The present invention relates to a method of dyeing polymeric substrates having pendent carboxyl groups, especially polyamides. The method comprises applying to a substrate a reactive dye solution and heating the substrate in the presence of a magnesium donor at a pH of greater than 9.0, such that the reactive dye forms a covalent bond with the carboxyl groups on the substrate. A dye composition for dyeing a polymeric substrates having pendent carboxyl groups is also disclosed.
REACTIVE DYE COMPOSITION AND METHOD OF DYEING POLYAMIDE MATERIALS

FIELD OF THE INVENTION

[0001] The present invention relates generally to a method and composition for dyeing a substrate. More specifically, the present invention relates to a method of dyeing a substrate, such as Type 6 nylon; Type 6,6 nylon; cationic dyeable Type 6 nylon; cationic dyeable Type 6,6 nylon; Nomex® and Kevlar®, with a reactive dye.

BACKGROUND OF THE INVENTION

[0002] Textile designers, especially those who create carpet and upholstery fabric designs, have a need for a pre-dyed nylon yarn which can be combined with an undyed nylon yarn to produce a textile product, such as a tufted carpet or an upholstery fabric. Such a textile product can then be subjected to a further dyeing operation so as to apply a color to the undyed nylon portion of the product which is different from the color or colors of the pre-dyed yarn. The availability of a pre-dyed nylon yarn permitting such processing would make possible styling and design effects in the finished textile product which cannot be achieved in any other way.

[0003] The problem presented is that, most pre-dyed nylon yarn cannot withstand exposure to typical further dyeing treatments which involve subjecting the textile product to an aqueous dyebath having a high temperature; e.g., at or near 220°F. Such exposure causes the coloring in the pre-dyed fiber to at least partially wash out and/or bleed onto the undyed yarn, compromising the final color of that yarn. In addition, the pre-dyed fiber takes on some of the color presented by the further dyeing operation, thereby altering the original color of the pre-dyed fiber.

[0004] To a small extent, this problem can be overcome by employing as the pre-dyed yarn solution-dyed nylon; i.e., nylon into which pigment is incorporated at the time the filaments are produced. The coloring in solution-dyed nylon will not wash out or bleed during further dyeing treatment. However, solution-dyed nylon yarns are available in only a few solid colors, and hence reliance on their use severely limits the creation of designs. Optimum styling effects require pre-dyed yams, both solid color and multicolor dyed yarns, available in a wide range of colors.

[0005] In an attempt to meet this need, American Hoechst Corporation developed bifunctional fiber reactive dyes for use with nylon which are sold under the trademark Remalan. A characteristic of these dyes is that they are treated with a process Hoechst calls “previnylization” which allows them to act as both acid and fiber reactive dyes at different stages of the dyeing process. The Remalan dyes initially form an ionic bond with the amine groups in nylon fiber, similar to the bonds formed when acid dyes are applied to nylon. The nylon yarn is washed and then treated with an alkali solution, specifically trisodium phosphate, which increases the pH of the dye and activates the fiber reactive portion of the dye. The dyed yarn is dried and then autoclaved, the high temperature and pressure, and alkali exposure, inducing a reaction between the amine groups of the nylon and the fiber reactive portion of the Remalan dye to create covalent bonds between the dye and amine groups. Thus, the term “bifunctional” dye, as used herein is intended to refer to a dye which exhibits the characteristics of both acid dyes, in their ability to form ionic bonds, and fiber reactive dyes, in their ability to form covalent bonds. As a result of these strong ionic and covalent bonds, nylon yarn carrying Remalan dye can withstand a further dyeing process without washing out or bleeding onto adjacent nylon yarns.

[0006] However, a problem which remains when the American Hoechst technology is employed is that the amine groups, which must be available in the nylon to form ionic and covalent bonds with the Remalan dyes, remain capable of forming ionic bonds with acid, premetalized, and mordant dyes used to color the undyed nylon in the second dyeing process. Thus, if for example, a designer wishes to use a pre-dyed nylon yarn, which has been printed with red and yellow areas using Remalan dyes, so as to provide red and yellow accents in the final nylon carpeting, and the second dyeing process involves coloring the undyed nylon blue, the treatment of the carpeting with the blue dye will inevitably cause the pre-dyed Remalan red and yellow colors to become purple and green.

[0007] To aid in understanding the present invention, it should be pointed out that nylon refers to a variety of long chain, high molecular weight polyamide fibers. Two types of these fibers are of interest to the commercial textile industry; e.g., carpeting and upholstery fabrics.

[0008] Type 6 nylon is made by the polymerization of e-caprolactam. A characteristic of this type of nylon is that it has a very open structure easily penetrated by dyestuff solutions and print pastes, and hence readily dyeable with dark shades. However, the open structure of the fiber makes it more susceptible to having the dye washed out of it, and hence gives the fiber relatively poor washfastness properties. Major producers of Type 6 nylon in the United States are Honeywell Nylon, Inc. and BASF Corp.

[0009] Type 6,6 nylon is produced by the polymeric reaction between hexamethylene diamine and adipic acid. This results in a hydrophilic but much more closed fiber structure and hence slower than Type 6 nylon to absorb dye solutions and print pastes. Consequently, it is more difficult to dye Type 6,6 nylon with dark shades. However, the tighter structure of the fiber gives it much better wash and bleed fastness than is obtained when Type 6 nylon is used. Major producers of Type 6,6 nylon are Invista, Wichita, Kans., and Solutia, Inc., St. Louis, Mo.

[0010] In addition to the differences in dye absorption properties caused by the different degrees of openness of the fiber structures, each nylon manufacturer has offered for commercial sale a range of nylon yams which have been modified to accept different depths of colors. The modification involves the number of reactive groups, or amine ends, which are introduced into the fiber when it is originally spun or produced. The number of amine groups can vary with different yarn producers, but a typical index is as follows: deep dyeable nylon; i.e., nylon that is capable of being dyed to very deep shades, may have an index number of 75, indicating the relatively high proportion of amine groups in the yarn; regular nylon may have an index number of 40; light dyeable nylon may have an index number of 18; and cationic dyeable nylon will have an index number of 0. With reference to cationic dyeable nylon, the index number of 0 does not indicate that there are no amine groups in the nylon. The nylon does contain amine groups, but by adding
sulfonic acid to the fiber during the manufacturing process, the amine groups are effectively neutralized leaving the fibers with a negative charge which causes them to resist acid dyes and to form ionic bonds with cationic dyes.

[0011] The Remalan dyes of American Hoechst Corporation can be used successfully with deep dyeable, regular, and light dyeable Type 6 nylon as well as deep dyeable and regular Type 6.6 nylon. However, Remalan dyes do not provide good color yield when used with light dyeable Type 6.6 nylon. Since deep dyeable, regular, and light dyeable Type 6 nylon, and deep dyeable and regular Type 6.6 nylon have relatively high contents of amine ends, these fibers, when pre-dyed do not react well when subjected to a second dyeing operation. Specifically, when these pre-dyed fibers are subjected to a second dyeing operation with acid, premetalized, and mordant dyes, which are used to dye the undyed nylon in the textile product by means of high temperature aqueous dye solutions, the pre-dyed colors tend to be stained by these dyes and hence the original color is compromised. Thus, it will be seen that the very fibers with which Remalan dyes work effectively are those which cannot be successfully used in textile products which must undergo a second dyeing operation.

[0012] Therefore, in order to provide a maximum range of textile design possibilities, it would be desirable to be able to apply dyes, such as Remalan dyes, to cationic dyeable nylon, since such fibers has no available amine ends and hence will resist taking on acid, premetalized, or mordant dyes during a second dyeing operation.

[0013] U.S. Pat. No. 5,445,653 (the disclosure of which is incorporated herein by reference) discloses a method of dyeing cationic dyeable Type 6 and Type 6.6 nylon and light dyeable Type 6.6 nylon, so that the dyed fiber will resist taking on further dye and will have a high degree of wash and bleed fastness when the dyed fiber is subjected to a further high temperature aqueous dye bath. The disclosed method comprises providing a bifunctional fiber reactive dye solution capable of forming both ionic and covalent bonds with the amine groups of the nylon fiber, the dye solution having a pH no higher than 1.5. Then, applying the dye to the fiber with a degree of wet pick up exceeding 100% by weight of the fiber, contacting the fiber with an alkaline solution, and thereafter autoclaving the fiber.

[0014] Surprisingly, it has been found that it is not necessary to use relatively expensive bifunctional dyes to bond the dye to the amine group of the polyamide. Instead, in accordance with the present invention, it has been found that more economical fiber reactive dye can be covalently bonded to the pendant carboxyl groups of polyamides, such as Type 6 nylon; Type 6.6 nylon; cationic dyeable Type 6 nylon; cationic dyeable Type 6.6 nylon; Nomex® and Kevlar® as well as the pendant carboxyl groups of wool and silk.

SUMMARY OF THE INVENTION

[0015] The present invention relates to a method and composition for dyeing a substrate made from a synthetic or natural polymeric material having pendant carboxyl groups, such as polyamides, silk and wool. The method comprises applying to the substrate a reactive dye solution and heating the substrate in the presence of a magnesium donor compound at a pH of greater than 9.0, such that the reactive dye forms covalent bonds with the pendant carboxyl groups on the polymeric substrate. More specifically, method comprises contacting Type 6 nylon; Type 6.6 nylon; cationic dyeable Type 6 nylon; cationic dyeable Type 6.6 nylon; Nomex® or Kevlar® with a reactive dye solution and heating the polycrystalline substrate in the presence of a magnesium donor compound at a pH of greater than 9.0, such that the reactive dye forms covalent bonds with the pendant carboxyl groups on the polycrystalline substrate.

[0016] In an alternate embodiment, there is disclosed a reactive dye composition. The composition comprises a reactive dye, a magnesium donor compound and a pH adjusting component in an amount sufficient to adjust the pH of the dye composition to greater than 9.0.

[0017] In another alternate embodiment, there is disclosed polymeric substrates, fibers, yarns, sheets, ribbons and other textile materials dyed with the reactive dye composition of the present invention.

[0018] Accordingly, it is an object of the present invention to provide an improved method and composition for dyeing substances, fibers, yarns, fabrics (woven and unwoven), tufted fabrics, sheets, ribbons and other textile materials.

[0019] Another object of the present invention is to provide a method of covalently bonding a fiber reactive dye to a carboxyl group of a polymeric substrate.

[0020] Yet another object of the present invention is to provide a method of dyeing Type 6 nylon; Type 6.6 nylon; cationic dyeable Type 6 nylon; cationic dyeable Type 6.6 nylon; wool; silk; Nomex® and Kevlar® that is relatively easy and inexpensive.

[0021] A further object of the present invention is to provide a method of dyeing Type 6 nylon; Type 6.6 nylon; cationic dyeable Type 6 nylon; cationic dyeable Type 6.6 nylon; wool; silk; Nomex® and Kevlar® with fiber reactive dyes.

[0022] These and other objects, features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

DETAILED DESCRIPTION OF THE DISCLOSED EMBODIMENTS

[0023] The present invention relates to a method of dyeing a substrate wherein the substrate is made from a polymeric material having pendant carboxyl groups. Polymeric materials having pendant carboxyl groups include, but are not limited to polyamides, silk and wool. Preferred polyamides useful in the present invention include, but are not limited to, Type 6 nylon; Type 6.6 nylon; cationic dyeable Type 6 nylon; cationic dyeable Type 6.6 nylon; Nomex® and Kevlar®. Substrates made from these materials can be in the form of fibers, yarns, woven fabrics, nonwoven fabrics, tufted fabrics, sheets, ribbons or other textile materials.

[0024] As indicated above, Type 6 nylon is made by the polymerization of e-caprolactam and is commercially available from Allied-Signal Corp. and BASF Corp. Type 6 nylon has the following chemical structure:
Type 6,6 nylon is produced by a polymeric reaction between hexamethyline diamine and adipic acid and is commercially available from E.I. duPont and Monsanto Corp. Type 6,6 nylon has the following chemical structure:

![Type 6 Nylon](image)

[0025] Type 6,6 nylon is produced by a polymeric reaction between hexamethyline diamine and adipic acid and is commercially available from E.I. duPont and Monsanto Corp. Type 6,6 nylon has the following chemical structure:

[0026] Cationic dyeable Type 6 and Type 6,6 nylon is made by replacing nylon monomer with sulfonated nylon forming monomer. See U.S. Pat. Nos. 4,579,762 and 3,389,172 (the disclosures of which are both incorporated herein by reference). Cationic dyeable Type 6 nylon and cationic dyeable Type 6,6 nylon are commercially available from Solutia and Invista. Kevlar® is a carboxyclic aromatic homo- or copolymer having chain extending bonds from each aromatic nucleus which are coaxial or parallel and opposite in direction. Kevlar® is disclosed in U.S. Pat. No. 3,671,542 (the disclosure of which is incorporated herein by reference). Nomex® is a polycarbonamide disclosed in U.S. Pat. No. 3,287,324 (the disclosure of which is incorporated herein by reference). Both Kevlar® and Nomex® are commercially available from E.I. duPont.

[0027] The reactive dyes are dyed in accordance with the present invention and are dyed with reactive dyes. A reactive dye is a colored compound which has a suitable group capable of forming a covalent bond between a carbon atom of the dye ion or molecule and an oxygen, nitrogen or sulfur of a hydroxy, an amino or a mercapto group respectively of the substrate. Rys and Zollinger, "The Theory of Colouration of Textiles," Dyers Company (1975). Reactive dyes all rely on many of the same chromophoric groups as acid and direct dyes for their color, although the azo chromophore, \(-\text{N} \equiv \text{N}-\), is by far the most important. Any of the following chromophores can be used: mono and diazo (metalized or unmetalized), triphenoxazine and phthalocyanine. Reactive dyes, especially bright blues, often depend on anthraquinone derivatives. Other chromophores are well known to those skilled in the art and can be used in the present invention.

[0028] All reactive dyes contain sodium sulfonate groups for solubility, and dissolve in water to give colored sulfonate anions and sodium cations. Most reactive dyes have from one to four of these sulfonate groups. Reactive dye molecules have several specific structural (reactive) features. These are of two principal types: carbon-nitrogen (heterocyclic) ring structures and masked vinyl sulfones.

[0029] The reactive dyes can have various types of reactive functions. By way of example and not limitation, reactive dyes having the following reactive functions can be used in the present invention and are commercially available: Dichlorotriazine (DCT) types of dyes are available from ICI Americas Inc. under the brand name PROcion® MX. Monochlorotriazine (MCT) types of dyes are available from Ciba-Geigy Corp. under the brand names CIBACRON® and CIBACRON® F; from ICI Americas Inc. under the brand name PROcion® HE; and from Sandoz Corp. under the brand name DRIMAREN® P. Vinyl sulfone (VS) types of dyes, are available from Hoechst Celanese Corp. under the brand name REMAZOL® and from Sumitomo Corp. of America under the brand name SUMIFIX®. Trichloropyrimidine (TCP) types of dyes are available from Sandoz Corp. under the brand name DRIMAREN® Z and from Ciba-Geigy Corp. under the brand name CIBACRON® T-E. Dichloronaphthoxazine (DCQ) types of dyes are available from Bayer Corp. under the brand name LEVAFIX® E. Difluorochloropyrimidine (DFCP) types of dyes are available from Bayer Corp. under the brand names LEVAFIX® E-A. Monochlorotriazine (FT) types of dyes are available from Ciba-Geigy Corp. under the brand name CIBACRON® F and from Bayer Corp. under the brand name LEVAFIX® E-N. Fluorochloromethyl pyrimidine types of dyes are available from Bayer Corp. under the brand name LEVAFIX® PN.

[0030] The chromophore portion of the reactive dye can be any colored species meeting the appropriate requirements for fastness, solubility, tintorial value, ecology and economy. Azo dyes comprise the majority, with anthraquinone and phthalocyanine comprising most of the other blue dyes. Metallized (sometimes referred to as "pre-metallized") and formazan dyes are also important blue dyes. Other blue dyes are oxazine and thiazine dyes. Yellow dyes are generally monoozo and most have pyrazolone or pyridone couplings. Orange dyes are generally monoozo derived from couplings to pyrazolones or of slightly substi-
tuted phenyl and napthyl groups. Many red dyes are based on H-acid, while others are substituted phenyl and napthyl or metallized systems. Violet dyes are also metallized monoazo dyes. Brown and black dyes generally are disazo with some exceptions for metallized or polycyclic structures. Green dyes are obtained by bridging an anthraquinone blue chromogen with a yellow chromagen, or from phthalo cyanine.

[0031] Examples of dichlorotriazynyl reactive dyes are shown below.

Metallized monoazo - C.I. Reactive Red 6

Anthraquinoid - C.I. Reactive Blue 4

[0032] Examples of vinyl sulfone reactive dyes are shown below:

Bifunctional masked vinyl sulfonyl reactive dye - C.I. Reactive Black 5

[0033] Examples of trichloropyrimidine reactive dyes are Drimarene Navy X-CN and C.I. Reactive Blue 214.
Examples of monochlorotriazine reactive dyes are Procion Turquoise H-A, C.I. Reactive Blue 71 and the compounds shown below:

![Procion Blue H-EGN - Bis(monochlorotriazine) - Triphenodioxazine Chromophore](image)

Examples of dichloroquinoxaline reactive dyes are Levafix Brilliant Blue E-B and C.I. Reactive Blue 29.

Examples of monofluorotriazine reactive dyes are C.I. Reactive Blue 182 and Cibacron Blue F-R shown below:

![Procion Red H-3B](image)

Examples of difluoropyrimidine reactive dyes are Levafix Brilliant Blue E-BRA and C.I. Reactive Blue 114. Examples of difluorochloropyrimidine reactive dyes are Drimarene Blue K-2RL and C.I. Reactive Blue 209.

The reaction between the reactive dye solution and the carboxyl groups of the substrate is believed to be as follows:

\[
\text{S--C--B--N} + \text{Cl} \overset{\text{MgSO}_4, \text{NaOH}}{\text{260°F. Hess}} \text{S--C--B--N+} + \text{H}.
\]
Since it is intended that the reactive dye solution be as concentrated as possible consistent with good shelf stability, it is preferred to include a stabilizer capable of retarding precipitation and crystallization of any components or impurities in the solution for a reasonably long, commercially practical shelf life of about 6 months. Various types of stabilizers include, for example without limitation, amineopolysphosphonates, available from Monsanto Company, for example as DEQUEST® chelates, designations 2000 (aminotrimethylene phosphonic acid (ATM)), 2006 (aminotrimethylene phosphonic acid, pentasodium salt (Na4ATMP)), 2010 (hydroxyethylidene diphosphonic acid (HEDP)), 2015 (hydroxyethyldene diphosphonic acid, tetrasodium salt (Na4HEDP)), 2060 (diethyleneetraminepenta(methylene phosphonic acid) (DTMP)), 2066 (diethyleneetraminepenta(methylene phosphonic acid, hexasodium salt (Na6DTMP)), and others. Other known crystalization inhibitors are polyvinylpyrrolidone (PVP) and polyacrylic acids.

Other additives and adjuvants that do not adversely affect the performance of the reactive dye solution can be used as desired. Such optional ingredients include for example, without limitation, thickeners, wetting agents, defoamers, dye bath lubricants, and the like. All of such additives or adjuvants are well known to those skilled in the art and further details about the type of such additives, the amounts in which they are used and their method of inclusion within the reactive dye solution of the present invention or the dye bath containing it, need not be explained in detail herein.

The method of dyeing a substrate according to the present invention generally comprises the steps of: (a) providing an aqueous reactive dye solution, including an Mg²⁺ donor compound, (b) contacting the substrate with the reactive dye solution, and (c) heating the substrate in contact with the dye solution to a sufficient temperature and for a sufficient time, such that the reactive dye forms a covalent bond with the pendant carboxyl groups of the substrate. The temperature to which the substrate in contact with the dye solution should be heated is any temperature that permits the formation of the covalent bond between the reactive dye and the substrate in a commercially practical period of time; preferably approximately 220° to 280° F; more preferably approximately 260° F. The length of time for which the substrate in contact with the dye solution should be heated is that length of time that permits the formation of the covalent bond between the reactive dye and the substrate; preferably approximately 1 minute to 2 hours; most preferably approximately 5 minutes.

The reactive dye solution of the present invention can be applied to a substrate by various methods well known to those skilled in the art, such as by batch, continuous, spore dye, pad, print, and exhaust. Variations of reaction conditions can be undertaken without undue experimentation by those skilled in the art using available equipment and typical processing parameters. The total wet pick up of the reactive dye solution by the substrate is less than 100% by weight; preferably, approximately 20% by weight to approximately 90% by weight; most preferably approximately 50% by weight.

After the reactive dye has been covalently bonded to the substrate, the substrate can be rinsed and dried in a manner well-known in the art.

The following examples are illustrative of the present invention and are not intended to limit the scope of the invention as set forth in the appended claims. The following ingredient were used for all examples.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fourgum 5352</td>
<td>Viscosity control agent which is a blend of acrylic copolymer and polysaccharide</td>
</tr>
<tr>
<td>Fouractive yellow MX-3RA</td>
<td>Reactive Orange 86</td>
</tr>
<tr>
<td>Fouractive Red MX-813</td>
<td>Reactive Red 11</td>
</tr>
<tr>
<td>Fouractive Blue MX-6OC</td>
<td>Blend of Azo Reactive Blue dyes</td>
</tr>
<tr>
<td>Arrosalt 2327</td>
<td>25% magnesium sulfate aqueous solution</td>
</tr>
<tr>
<td>Arrofix NB-12</td>
<td>Sulphonated phenolic formaldehyde condensate fixative</td>
</tr>
<tr>
<td>Arrofix ARS-7</td>
<td>Methacrylic polymer fixative</td>
</tr>
<tr>
<td>Arrotext 2446</td>
<td>fluorochemical resin emulsion</td>
</tr>
<tr>
<td>Arrocon 2298</td>
<td>43% potassium hydroxide aqueous solution</td>
</tr>
</tbody>
</table>


**EXAMPLE 1**

One liter of reactive dye bath solution is made by combining the following components with mixing in aqueous solution:

- 10 g/l synthetic gum Fourgum 5352;
- 10 g/l Fouractive yellow MX-3RA;
- 15 g/l Arrosalt 2327;
- 50 g/l Arrofix NB-12;
- 25 g/l Arrotext 2446; and
- distilled water sufficient to make 1 liter.

The pH of the solution is then adjusted with alkali Arrocon 2298 to 10.0.

This dye bath is then applied on a Type 6 nylon yarn sock to simulate Knit-de-Knit with applicator rollers. The total wet pick up is 80%. The sock is dried and then autoclaved for 15 minutes at 260° F. The sock is then washed and rinsed with clean water and dried. The dyed portions of the sock are colorfast and are not dyed another color by acid dyes.
EXAMPLE 2

One liter of reactive dye bath solution is made by combining the following components with mixing in aqueous solution:

- 10 g/l synthetic gum Fourgum 5352;
- 10 g/l Fourreactive yellow MX-3RA;
- 5 g/l Fourreactive Red MX-8B;
- 5 g/l Fourreactive Blue Mx-4GC;
- 15 g/l Arrosalt 2327;
- 20 g/l Arrofix ARS-7;
- 10 g/l Arrotex 2446; and
- distilled water sufficient to make 1 liter.

The pH of the solution is then adjusted with alkali Arrocon 2298 to 12.0.

This dye bath is then applied on a Type 6,6 nylon yarn sock to simulate Knit-de-Knit with applicator rollers. The total wet pick up is 80%. The sock is dried and then autoclaved for 15 minutes at 260° F. The sock is then washed and rinsed with clean water and dried. The dyed portions of the sock are colorfast and are not dyed another color by acid dyes.

EXAMPLE 3

A sock made from cationic dyeable Type 6,6 nylon from Solutia is dyed in a pressurized handiometer using the following procedures. A portion of the sock weighing 10 grams is added to a beaker along with 0.2 grams of Fourreactive Blue MX-4GC and 5 ml of Arrosalt 2327. Distilled water is added to bring the volume to 150 ml. The pH is adjusted to 10.5 with Arrocon 2298. The contents of the beaker are then brought to 260° F. for 30 minutes. The cooled sample is then rinsed and dried. The dyed sock is colorfast.

EXAMPLE 4

One liter of reactive dye bath solution is made by combining the following components with mixing in aqueous solution:

- 10 g/l synthetic gum Fourgum 5352
- 10 g/l Fourreactive yellow MX-3RA
- 15 g/l Arrosalt 2327
- distilled water sufficient to make 1 liter.

The pH of the solution is then adjusted with alkali Arrocon 2298 to 10.0.

This dye bath is then applied to a woven Kevlar® fabric to simulate a print applicator. The total wet pick up is 80%. The fabric is dried and then autoclaved for 15 minutes at 260° F. The cooled sample is then rinsed and dried. The dyed Kevlar® fabric is colorfast.

EXAMPLE 5

One liter of reactive dye bath solution is made by combining the following components with mixing in aqueous solution:

- 10 g/l synthetic gum Fourgum 5352
- 10 g/l Fourreactive yellow MX-3RA
- 15 g/l Arrosalt 2327
- distilled water sufficient to make 1 liter.

The pH of the solution is then adjusted with alkali Arrocon 2298 to 10.0.

This dye bath is then applied on a knitted Nomex® fabric to simulate a print applicator. The total wet pick up is 80%. The fabric is dried and then autoclaved for 15 minutes at 260° F. The cooled sample is then rinsed and dried. The dyed Nomex® fabric is colorfast.

EXAMPLE 6

One liter of reactive dye bath solution is made by combining the following components with mixing in aqueous solution:

- 10 g/l synthetic gum Fourgum 5352
- 10 g/l Reactive Orange 86 (Dichlorotriazine)
- 15 g/l Arrosalt 2327
- distilled water sufficient to make 1 liter.

The pH of the solution is then adjusted with alkali Arrocon 2298 to 10.0.

This dye bath is then applied to a Type 6 nylon knitted sock to simulate a print applicator. The total wet pick up is 80%. The sock is dried and then autoclaved for 15 minutes at 260° F. The cooled sample is then rinsed and dried. The dyed sock is colorfast.

EXAMPLE 7

One liter of reactive dye bath solution is made by combining the following components with mixing in aqueous solution:

- 10 g/l synthetic gum Fourgum 5352
- 10 g/l Reactive Yellow 17 (vinyl sulfone)
- 15 g/l Arrosalt 2327
- distilled water sufficient to make 1 liter.

The pH of the solution is then adjusted with alkali Arrocon 2298 to 10.0.

This dye bath is then applied to a Type 6 nylon knitted sock to simulate a print applicator. The total wet pick up is 80%. The sock is dried and then autoclaved for 15 minutes at 260° F. The cooled sample is then rinsed and dried. The dyed sock is colorfast.
EXAMPLE 8

One liter of reactive dye bath solution is made by combining the following components with mixing in aqueous solution:

- 10 g/l synthetic gum Fourgun 5352
- 10 g/l Reactive Yellow 145 (Bifunctional: Vinyl sulfone and monochlorotrizine)
- 15 g/l Arrosalt 2327
- Distilled water sufficient to make 1 liter.

The pH of the solution is then adjusted with alkali Arroco 2298 to 10.0.

This dye bath is then applied to a Type 6 nylon knitted sock to simulate a print applicator. The total wet pick up is 80%. The sock is dried and then autoclaved for 15 minutes at 260° F. The cooled sample is then rinsed and dried. The dyed sock is colorfast.

EXAMPLE 9

One liter of reactive dye bath solution is made by combining the following components with mixing in aqueous solution:

- 10 g/l synthetic gum Fourgun 5352
- 10 g/l Reactive Yellow 84 (Monochlorotrizine)
- 15 g/l Arrosalt 2327
- Distilled water sufficient to make 1 liter.

The pH of the solution is then adjusted with alkali Arroco 2298 to 10.0.

This dye bath is then applied to a Type 6 nylon knitted sock to simulate a print applicator. The total wet pick up is 80%. The sock is dried and then autoclaved for 15 minutes at 260° F. The cooled sample is then rinsed and dried. The dyed sock is colorfast.

What is claimed is:

1. A method of dyeing a substrate of a polymeric material having pendent carboxyl groups, said method comprising:
   - contacting said substrate with an aqueous reactive dye solution; and
   - heating said substrate in the presence of a magnesium donor compound at a pH of greater than 9.0, such that said reactive dye forms a covalent bond with said carboxyl groups on said substrate.
2. The method of claim 1 further comprising the step of drying the substrate before the heating step.
3. The method of claim 1 further comprising the step of drying the substrate after the heating step.
4. The method of claim 1, wherein said polymeric material is a polyamide.
5. The method of claim 1, wherein said polymeric material is Type 6 nylon; Type 6,6 nylon; cationic dyeable Type 6 nylon; cationic dyeable Type 6,6 nylon; Kevlar or Nomex.
6. The method of claim 1, wherein said polymeric material is wool or silk.
7. The method of claim 1, wherein said magnesium donor compound comprises a magnesium salt.
8. The method of claim 1, wherein said magnesium donor compound is magnesium sulfate or magnesium hydroxide.
9. The method of claim 1, wherein said pH is approximately 10 to approximately 13.
10. The method of claim 1, wherein said reactive dye solution comprises a reactive dye selected from dichlorotrizazinyl reactive dye, vinyl sulfone reactive dye, monochlorotrizine reactive dye, monofluorotrizine reactive dye, dichlorotrizazinyl reactive dye, dichloroquinotiazinyl reactive dye, or mixtures thereof.
11. The method of claim 1, wherein said substrate is a fiber.
12. The method of claim 1, wherein said substrate is a yarn.
13. The method of claim 1, wherein said substrate is a fiber, a yarn, a woven fabric, a nonwoven fabric, a tufted fabric, a sheet, or a ribbon.
14. The method of claim 1, wherein said substrate is heated to a temperature of approximately 220° to 280° F.
15. The method of claim 1, wherein said substrate is heated to a temperature of approximately 260° F.
16. A fiber dyed by the process of claim 1.
17. A yarn dyed by the process of claim 1.
18. A tufted fabric dyed by the process of claim 1.
19. A textile material dyed by the process of claim 1.
20. A textile material having a pre-dyed fiber or yarn therein pre-dyed by the process of claim 1.
21. A carpet having a pre-dyed fiber or yarn therein pre-dyed by the process of claim 1.
22. A method of dying a substrate of a polymeric material having pendent carboxyl groups, said method comprising:
   - contacting said substrate with an aqueous dye solution comprising:
     - a reactive dye; and
     - an Mg⁺² donor compound, said aqueous dye solution having a pH of greater than 9.0; and
heating said substrate while contacting said aqueous dye solution to a temperature of approximately 220° to 280° F.  

23. The method of claim 22 further comprising the step of drying the substrate before the heating step.  

24. The method of claim 22 further comprising the step of drying the substrate after the heating step.  

25. A substrate of a polyamide material having pendent carboxyl groups dyed with a reactive dye solution, whereby said fiber reactive dye solution forms a covalent bond with said carboxyl groups on said substrate.  

26. The substrate of claim 25, wherein said substrate is selected from Type 6 nylon; Type 6,6 nylon; cationic dyeable Type 6 nylon; cationic dyeable Type 6,6 nylon; Kevlar and Nomex.  

27. A dye composition comprising in aqueous solution:  

a reactive dye;  
a magnesium donor; and  
a pH adjusting component in an amount sufficient to adjust the pH of said dye composition to greater than 9.0.  

28. The dye composition of claim 27, wherein said reactive dye comprises a reactive dye selected from dichlorotriazinyl reactive dye, vinyl sulfone reactive dye, monochlorotriazine reactive dye, monofluorotriazine reactive dye, trichloropyrimidine reactive dye, difluorochloropyrimidine reactive dye, dichloroquinazoline reactive dye, or mixtures thereof.  

29. The dye composition of claim 27, wherein said magnesium donor comprises a magnesium salt.  

30. The dye composition of claim 27, wherein said magnesium donor is selected from magnesium sulfate and magnesium hydroxide.  

31. The dye composition of claim 27, wherein said pH adjusting component in an amount sufficient to adjust the pH of said dye composition to approximately 10 to approximately 13.  

32. The dye composition of claim 27, wherein said pH adjusting component is an alkali metal hydroxide or an alkali metal carbonate.  

33. The dye composition of claim 27, wherein said pH adjusting component is sodium hydroxide or potassium hydroxide.  

34. The dye composition of claim 27, wherein said pH adjusting component is sodium carbonate, sodium bicarbonate, potassium carbonate or potassium bicarbonate.  

35. A dye composition comprising:  

approximately 0.01% to 10% by weight of a reactive dye selected from dichlorotriazinyl reactive dye, vinyl sulfone reactive dye, monochlorotriazine reactive dye, monofluorotriazine reactive dye, trichloropyrimidine reactive dye, difluorochloropyrimidine reactive dye, dichloroquinazoline reactive dye, or mixtures thereof;  

approximately 0.01% to 10% by weight magnesium sulfate;  
an amount of sodium hydroxide sufficient to adjust the pH of said dye composition to greater than 9.0; and  
water in an amount sufficient to make the dye composition 100% by weight.  

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