A method of dyeing a blend of modacrylic fiber and aramid fiber employing a cationic dye and dye assistant employs a concentration of dye assistants not greater than 10 grams per liter of dye bath.
DYEING OF MODACRYLIC/ARAMID FIBER BLENDS

FIELD OF THE INVENTION

[0001] This invention relates to dyeing of modacrylic/aramid fiber blends.

DESCRIPTION OF RELATED ART

[0002] The present invention is directed to dyeing of fiber blends particularly useful in fabrics not only possessing flame resistance but also one or more additional properties. Examples of additional properties include resistance to electrical arcing, a high level of tensile strength and abrasion resistance.

[0003] Sicorin et al. U.S. Pat. No. 4,066,395 discloses a process for dyeing or printing aromatic polyamide fibers with cationic dyes in an aqueous medium containing a carrier without ketone-forming carbonyl groups and an anionic assistant.


[0005] A need is present for dyeing specific blends of flame resistant fibers without excessive shrinkage of the fibers or undue stiffness solely due to the dyeing procedure.

SUMMARY OF THE INVENTION

[0006] The present invention relates to a method of dyeing a blend of modacrylic fiber and aramid fiber employing a cationic dye and a dye assistant wherein the modacrylic fiber is present in a range of 1 to 99 weight % and the aramid fiber is present in a range from 99 to 1 weight % on the basis of modacrylic and aramid fiber. The method comprises the step of

[0007] contacting the fiber blend at a temperature in a range from 70 to 100 degrees C. in an aqueous dye bath containing a cationic dye and a dye assistant present in an amount not greater than 15 grams per liter of dye bath, said dye assistant selected from the group consisting of aryl ether, benzyl alcohol, N-ethoxyethylpyrrolidone, N,N-dibutylformamide, N,N-dimethylbenzamide, hexadecyltrimethyl ammonium salt, N,N-dimethylbenzamide, N,N-diethyl-m-toluamide, N-ocetylpyrrolidone, a blend of N,N-dimethylcaprylamide and N,N-dimethylcapramide and mixtures thereof.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The starting material for the dyeing procedure of the present invention is a blend of modacrylic and aramid fibers. Normally the blend will be dyed with the fibers present as a yarn or as a yarn formed into a fabric. However it is within the scope of the dyeing procedure that the blend of fibers is dyed prior to formation such as into a yarn or fabric.

[0009] The composition of the starting material is a modacrylic/aramid blend comprising 1 to 99 weight % modacrylic fiber and 99 to 1% weight % aramid on a basis of the modacrylic and aramid components. An example of a preferred range based on these two components is 40 to 70 weight % modacrylic fiber, 5 to 20 weight percent p-aramid fiber and 10 to 40 weight % m-aramid fiber. This example of a preferred range results in a blend useful in a yarn and fabric to provide electrical arcing resistance and flame protection.

[0010] By “yarn” is meant an assemblage of fibers spun or twisted together to form a continuous strand, which can be used in weaving, knitting, braiding, or plaiting, or otherwise made into a textile material or fabric.

[0011] By modacrylic fiber it is meant acrylic synthetic fiber made from a polymer comprising primarily acrylonitrile. Preferably the polymer is a copolymer comprising 30 to 70 weight percent of a acrylonitrile and 70 to 30 weight percent of a halogen-containing vinyl monomer. The halogen-containing vinyl monomer is at one monomer selected, for example, from vinyl chloride, vinylidene chloride, vinyl bromide, vinylidene bromide, etc. Examples of copolymerizable vinyl monomers are acrylic acid, methacrylic acid, salts or esters of such acids, acrylamide, methacrylamide and vinyl acetate.

[0012] The preferred modacrylic fibers of this invention are copolymers of acrylonitrile combined with vinylidene chloride, the copolymer having in addition an antimony oxide or antimony oxides for improved fire retardancy. Such useful modacrylic fibers include, but are not limited to, fibers disclosed in U.S. Pat. No. 3,436,667 having 2 weight percent antimony oxide, fibers disclosed in U.S. Pat. No. 3,748,302 made with various antimony oxides that are present in an amount of at least 2 weight percent and preferably not greater than 8 weight percent, and fibers disclosed in U.S. Pat. Nos. 5,208,105 & 5,506,942 having 8 to 40 weight percent of an antimony compound.

[0013] As used herein, “aramid” is meant a polyamide wherein at least 85% of the amide (—CONH—) linkages are attached directly to two aromatic rings. Additives can be used with the aramid and, in fact, it has been found that up to as much as 10 percent, by weight, of other polymeric material can be blended with the aramid or that copolymers can be used having as much as 10 percent of other diamine substituted for the diamine of the aramid or as much as 10 percent of other diacid chloride substituted for the diacid chloride of the aramid. Suitable aramid fibers are described in Man-Made Fibers—Science and Technology, Volume 2, Section titled Fiber-Forming Aromatic Polymides, page 297, W. Black et al., Interscience Publishers, 1968. Aramid fibers are, also, disclosed in U.S. Pat. Nos. 4,172,938; 3,869,429; 3,819,587; 3,673,143; 3,354,127; and 3,094,511. M-aramid are those aramids where the amide linkages are in the meta-position relative to each other, and p-aramids are those aramids where the amide linkages are in the para-position relative to each other. In the practice of this invention the aramids most often used are poly(paraphenylene terephthalamide) and poly(metaphenylene isophthalamide).

[0014] It is understood that one or more additional fibers or components may be included with the modacrylic and aramid fibers. Two examples are an abrasion resistant fiber and an antistatic component which may be present as a fiber.

[0015] By abrasion resistant it is meant the ability of a fiber or fabric to withstand surface wear and rubbing. Preferably the abrasion resistant fiber is a nylon. By nylon
it is meant fibers made from aliphatic polyamide polymers; and polyhexamethylene adipamide (nylon 66) is the preferred nylon polymer. Othernylonssuch as polycaprolactam (nylon 6), polybutylcaprolactam (nylon 4), poly-9-aminononanoic acid) (nylon 9), polyenanthiolactam (nylon 7), polycaprylactam (nylon 8), polyhexamethylene sebacamide (nylon 6, 10), and the like are suitable. The abrasion resistant fiber, if present, typically comprises 2 to 15 weight percent of the yarn.

[0016] Illustrative examples of an antistatic component are steel fiber, carbon fiber, or a carbon coating to an existing fiber. The conductivity of carbon or a metal such as steel when incorporated in a yarn, fabric, or garment provides an electrical conduit to assist in dissipating buildup of static electricity. Static electrical discharges can be hazardous for workers working with sensitive electrical equipment or near flammable vapors. The antistatic component, if employed, may be present in an amount of 1 to 5 weight percent of the total yarn.

[0017] Yarns of this invention may be produced by any of yarn spinning techniques commonly known in the art such as, but not limited to, ring spinning, core spinning, and air jet spinning or higher air spinning techniques such as Murata air jet spinning where air is used to twist staple fibers into a yarn. Typically the single yarns produced by any of the common techniques are then plied together to form a ply-twisted yarn comprising at least two single yarns prior to being converted into a fabric.

[0018] The term fabric refers to a layer that has been woven, knitted, or otherwise assembled using one or more different types of the yarn of this invention. Preferably fabrics are woven fabrics. Most preferably the fabrics are a twill weave.

[0019] The dyeing of the flame resistant fabrics is known in the prior art. However in the present invention, criticality is present in the use of a cationic dye with a carrier.

[0020] A suitable disclosure of cationic dyes is set forth in U.S. Pat. No. 4,066,395. Cationic dyes customarily include salts, chlorides, sulphates or metal halides, zinc chloride, salts whose cationic character derives for example from a carbonium, oxonium, sulphonium or ammonium group. Examples of chromophoric systems are azo dyes, primarily monoazo or hydrazine dyes, diphenylmethane, triphenylmethane, methylene or azomethine dyes, cumarin, ketone-imine, cyanine, xanthene, azine, oxazine or thiaazine dyes. It is also possible to use dye salts of the phthalocyanine or anthraquinone series with an external onium group, for example an alkylammonium or cyloammonium group and also benzo-1,2-pyrene dye salts which contain cyloammonium groups. Mixtures of such dyes can also be used.

[0021] A necessary component in the present invention is a dye assistant. Suitable dye assistants are disclosed in U.S. Pat. No. 6,547,835. Specifically, these dye assistants are N-cyclohexylpyrrolidinoc, benzyl alcohol, N,N-dibutylformamidine, N,N-diethylbenzamide, hexadecyltrimethyl ammonium salt, N,N-dimethylbenzamide, N,N-diethyl-m-toluidine, N-octylpyrrolidone, aeryl ether, an approximately 50/50 blend of N,N-dimethylcaprylamide and N,N-dimethylcapramide, and mixtures thereof.

[0022] The dyeing with the cationic dye and dye assistant in an aqueous bath may be undertaken in conventional fashion. Typically the dyeing is undertaken in a temperature range from 70 degrees to 100 degrees centigrade.

[0023] However, it is critical in the present invention that the dye assistant is present in a concentration not greater than 15 grams per liter of dye bath. A preferred concentration is not greater than 12 grams per liter and more preferably not greater than 10 grams per liter. Lower concentrations of dye assistant such as below 5 grams per liter will denote a longer dyeing time, assuming all other conditions of the dye process remain the same.

[0024] An excessive amount of dye carrier can result in two undesirable properties. A first property is excessive shrinkage of the yarn and fabric. A second property is undue stiffness of the yarn and fabric.

[0025] In the following examples all parts and percentages are by weight and degrees in Celsius unless otherwise indicated.

[0026] The color and shade depth for the examples were determined by measuring the Hunter ‘L’, ‘a’, and ‘b’ values in the conventional manner. The ‘L’ color component is a measure of the blackness or whiteness of the sample, while the ‘a’ value is a measure of where the color of the sample is in the red to green range and the ‘b’ value is a measure of where the color of the sample is in the blue to yellow range.

EXAMPLES

[0027] Fabrics comprising 70 weight percent modacrylic fiber, 15 weight percent meta-aramid fiber, 5 weight percent para-aramid fiber, and 10 weight percent nylon fiber were dyed using a dye and dye assistant in a one step batch process.

[0028] The following procedure is set forth for a commercial dyeing process. However, as will be additionally explained below, such commercial dyeing process was modified due to smaller dyeing equipment.

[0029] The fabric is loaded into a pressure jet dyeing vessel in which the fabric is circulated through an open venturi in a continuous loop achieved by sewing the ends of the fabric together. The fabric is scoured for 10 minutes at 60 degrees Celsius in an aqueous solution of 0.5 grams per liter Merpol® HCS surfactant. After scouring the dyeing vessel is drained and charged with dye, dye assistant, and water at an initial temperature of 70 degrees Celsius. The fabric is dyed for 10 minutes while the bath temperature is increased at a rate of 1 degree Celsius per minute. The pH of the solution is then adjusted by the addition of acetic acid to a pH of between 3 and 4. The vessel is then charged with additional dye and dye assistant and a constant temperature of 80 degrees Celsius was maintained for 10 minutes. The temperature is then raised as a rate of 1 degree Celsius per minute until the bath temperature is 98 degrees Celsius. The bath is maintained at this 98 degrees Celsius for 60 minutes or until the dye is exhausted. The bath is then cooled to 60 degrees Celsius and drained. The vessel is then charged with a solution of 2 grams per liter sodium hyposulfite, 2 grams per liter sodium carbonate, and water to neutralize the solution. The bath temperature is raised at a rate of 1 degree Celsius per minute to 60 degrees Celsius and allowed to circulate for 10 minutes. The vessel is then drained and recharged with water. The water temperature is then raised at a rate of 1 degree Celsius per minute to a temperature of
60 degrees Celsius and allowed to circulate for 10 minutes. The vessel is then drained and the fabric dried.

[0030] To generate the data below, smaller dye equipment was employed, namely Ahiba Polmat stainless steel canister dye unit (with a heat medium of carbowax).

[0031] The dye employed was:

[0032] Viocryl Blue RLS dye (ci-41) 0.6% of fabric weight
[0033] Viocryl Red AGL dye (ci-29) 0.75% of fabric weight
[0034] Yorocryl Yellow 6GL (ci-21) 0.15% of fabric weight.

[0035] The fabric described above was presoured at 60 deg. C. with Merpol HCS at 0.5% of fabric weight and Cekogen OX (oxidizing agent) at 3% of fabric weight for 20 minutes followed by cooling, draining and rinsing with water.

[0036] The fabric was dyed at a final temperature of 98 degrees Celsius for 60 minutes. The final temperature was reached by an increase in temperature of about 1 degree Celsius per minute. The pH of the dye bath was about 3-4. Aryl ether or benzyl alcohol was used in amounts of 2, 5, 10, 15, 20 and 30 grams per liter. The dye bath was cooled to about 60 degrees Celsius and drained.

[0037] The dyed fabric was post scoured with reducing agent to neutralize the dye solution (Sodium Hydrosulphite and Sodium Carbonate at 2 g/l) at 60 deg. C. for 20 minutes followed by cooling of the solution and draining.

[0038] The dyed fabrics were dried in a moisture teller unit using a hot air blower.

[0039] The data below represents shrinkage in % of fabric area at different amount of dye assistants of aryl ether and benzyl alcohol

<table>
<thead>
<tr>
<th>Dye assistant (g/l)</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>aryl ether</td>
<td>16</td>
<td>19</td>
<td>22</td>
<td>31</td>
<td>44</td>
<td>84</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>17</td>
<td>16</td>
<td>23</td>
<td>25</td>
<td>36</td>
<td>86</td>
</tr>
</tbody>
</table>

[0040] The fabric showed excessive shrinkage when dyed at high percentage of dye assistant.

[0041] When using dye assistant of more than 20 g/l, the fabric also becomes stiff. The dye uptake is also negatively impacted by high percentages of dye assistant as indicated by the following tables of color measurement.

<table>
<thead>
<tr>
<th>aryl ether(g/l)</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>29.049</td>
<td>27.838</td>
<td>28.705</td>
<td>30.312</td>
<td>32.302</td>
<td>33.539</td>
</tr>
<tr>
<td>a*</td>
<td>2.844</td>
<td>1.962</td>
<td>1.61</td>
<td>0.79</td>
<td>-0.354</td>
<td>-1.091</td>
</tr>
</tbody>
</table>

Benzy alcohol (g/l)

<table>
<thead>
<tr>
<th>Bzyl alcohol (g/l)</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
</table>

What is claimed is:

1. A method of dyeing a blend of modacrylic fiber and aramid fiber employing a cationic dye and a dye assistant wherein the modacrylic fiber is present in range of 1 to 99 weight % and the aramid fiber is present in a range from 99 to 1 weight % on the basis of modacrylic fiber and aramid fiber comprising the step of:

   contacting the blend at a temperature in a range from 70 to 100 degrees C. in an aqueous dye bath containing a cationic dye and a dye assistant present in an amount not greater than 15 grams per liter of dye bath, said dye assistant selected from the group consisting of aryl ether, benzyl alcohol, N-cyclohexylpyrrolidone, N,N-dibutylformamide, N,N-diethylbenzamide, hexadecyltrimethyl ammonium salt, N,N-dimethylbenzamide, N,N-diethyl-m-toluamide, N-octylpyrrolidone, blend of N,N-dimethylcaprylamine and N,N-dimethylcapramide and mixtures thereof.

2. The method of claim 1 wherein the fibers are present as a yarn.

3. The method of claim 1 wherein the fibers are present in a fabric.

4. The method of claim 1 with 40 to 70 weight % modacrylic fiber, 5 to 20 weight percent p-aramid fiber and 10 to 40 weight % m-aramid fiber on a basis of the modacrylic and aramid fibers.

5. The method of claim 1 wherein the blend additionally contains an abrasion resistant fiber.

6. The method of claim 5 wherein the abrasion resistant fiber is nylon.

7. The method of claim 1 wherein the blend contains an antistatic component.

8. The method of claim 1 wherein the dye assistant is present in an amount not greater than 12 grams per liter of dye bath.

9. The method of claim 8 wherein the dye assistant is present in an amount not greater than 10 grams per liter of dye bath.

10. The method of claim 1 wherein the dye assistant is aryl ether or benzyl alcohol.

11. A garment which includes a blend of fibers dyed by the method of claim 1.