Flame-resistant polyamide filaments are made by treating drawn polyamide filaments with an aqueous composition of a halogenated compound selected from the class consisting of chloridic, tetrabromophthalic and tetrachlorophthalic acids and the anhydrides thereof.

9 Claims, No Drawings
BACKGROUND OF THE INVENTION

This invention relates to flame-resistant polyamide filaments and to a process for preparing such filaments. It is known to treat polyamides to improve their resistance to burning. For example, agents to reduce flammability can be present in molten polymer prior to shaping the polyamide, see U.S. Pat. No. 3,418,267. Also, it is known to apply fire-resistant coatings to fabrics containing polyamide filaments. These prior art practices are not entirely satisfactory in that they can lead to deleterious chemical activity or change characteristics of fabrics.

SUMMARY OF THE INVENTION

The present invention provides flame-resistant filaments of drawn aliphatic polyamides containing 2 to about 18 percent, preferably 6 to 10 percent, by weight, based on the weight of the filaments, of at least one halogenated compound selected from the class consisting of chloroacetic acid, chloroacetic anhydride, tetrahydrophthalic acid, tetrahydrophthalic anhydride, tetrachloro phthalic acid and tetrachloro phthalic anhydride. This invention also provides a process for producing flame-resistant filaments wherein filaments of a polyamide are treated with aqueous liquids containing these halogenated compounds. Preferably, the treatment with the aqueous liquid is conducted at temperatures of at least 97°C. and at a pH less than about 5.

DESCRIPTION OF PREFERRED EMBODIMENTS

The filaments produced by the present invention contain from 2 to about 18 percent by weight of a halogenated compound of the aforementioned class. The compound is present in the filaments, presumably, in a salt form from combination with amine ends produced by polymer molecules and/or as a coordinated molecule, and can be substantially entirely extracted from the filaments. For example, chloroacetic acid can be extracted with aqueous solutions containing from 1 to about 5 percent, by weight, of a base such as ammonium, sodium carbonate or sodium hydroxide.

The filaments of this invention show a significant reduction in burning propensity in comparison to untreated fibers. A superior rating, as determined by the Vertical Flame Test, is obtained when the halogenated compound content is at least 3 percent, by weight. At contents greater than about 6 percent, by weight, the filaments are rated self-extinguishing or nearly so when the combustion source is removed and filaments containing 6 to about 10 percent of the halogenated compound are a preferred embodiment of this invention. While amounts greater than 10 percent by weight may be incorporated, the resistance of the filament to burning is not increased proportionally.

Because the halogenated compounds used in the practice of this invention are reactive towards the polyamides, degradative discoloration of the treated filaments can occur at elevated temperatures. However, at moderate temperatures, e.g. in the range of about 130°-150°C., or for short thermal exposure times at higher temperatures, e.g. on the order of 200°C., filaments of this invention exhibit very little, if any, change in color. This is, of course, a distinct advantage over the use of the halogenated compounds in conjunction with molten polymer. In addition, since the halogenated compounds are applied to drawn filaments, the disadvantages attendant to the drawing of polyamide filaments containing foreign matter are avoided.

The process of the present invention provides flame-resistant filaments by treatment of drawn polyamide filaments with aqueous liquids containing the halogenated compounds. Thus, aqueous compositions containing the halogenated compound may be padded onto the filaments and the treated filaments subsequently heated to an elevated temperature such as by passing them over heated rolls or through hot-air ovens and the like. Suitable temperatures range from about 97°C. to about 140°C. Elevated temperatures are used to increase the rate of absorption of the halogenated compound by the filaments and to facilitate removal of water. The treating liquid may or may not contain a dye. In a preferred embodiment, the polyamide filaments are treated in an aqueous bath that contains chlorendic acid and is maintained at an elevated temperature, e.g., at least about 97°C. and preferably at 98° to 100°C. At temperatures below 97°C., the solubility of chlorendic acid in water is so low it will not give an even strike on the fabric. Preferably, the pH of the aqueous bath will not exceed 5 and for best results the pH should be between 2 and 4.

The aqueous bath may be made acidic by the use of either organic or mineral acids such as, for example, acetic, formic, oxalic and phosphoric acids. Although the pH may be relatively high during the initial period of the treatment, the pH should be reduced to a value of 2 to 4 prior to completing the treatment. Low pH values promote bath exhaustion and high fiber uptake of halogenated compound.

In a highly preferred embodiment of this invention polyamide filaments are treated with chlorendic acid in the course of their manufacture. Accordingly, the chlorendic acid may be applied to continuous filaments, yarns, tows, and the like following the drawing step and prior to packaging by having the chlorendic acid present in lubricating finishes, post-draw baths or other treating media. If the filaments are to be converted to short fibers, e.g. staple fibers, the fibers may be treated after the cutting operation.

Alternatively, the filaments may be treated after packaging. Package-dyeing techniques such as are known to those skilled in the art may be followed, it being understood, of course, that the high temperatures and low pH values required for this invention are to be incorporated in the treatment. The filaments may also be treated after they have been converted to fabric. The halogenated compound may be added to conventional baths such as dyebaths used in the processing of the fabrics or in a special bath as an addition to standard treatment. The treatment of the filaments may be before, after, during, or instead of, dyeing. The treatment may be applied to filaments in the form of nonwovens, knit or woven fabrics. Also, carpets, upholstery, artificial hair pieces, wig fibers and the like may be made more flame resistant by the practice of this invention.

The amount of halogenated compound of the aforementioned class that is used in the bath may vary from about 1 percent to about 10 percent, by weight. When using the anhydrides in aqueous baths, substantial hy-
3,772,067

drolysis to the acid will occur and both acid and anhydride may be taken up by the filaments.

In addition to the halogenated compound, the acidifying agent and the optional use of a dye, the aqueous treating baths may contain small amounts of one or more of the following: an organic liquid, a wetting agent, a buffering agent, a whitener and a sequestering agent.

The polyamides useful in the practice of this invention are fiber-forming, long-chain, synthetic polymers having recurring amide groups, i.e.,

\[ -C-NH- \]

groups, as an integral part of the polymer chain. Polhexamethylene adipamide (66-nylon) is highly preferred polyamide. Among other useful polyamides there may be mentioned the polymer prepared from caprolactam (6-nylon) and the polymer made from bis(4-aminocyclohexyl)methane and dodecanedioic acid. Copolymers such as those from 66- and 6-nylon may also be used.

In the following examples illustrating the invention, all percentages are by weight based on the weight of the filaments for polymer and on the weight of the solution for liquids. The Vertical Flame Test described in ASTM-D626 is used to measure the flame resistance of filaments prepared in the examples. Relative viscosity (RV) is the ratio of absolute viscosities at 25°C of solution and solvent. The solvent is 90 percent, by weight, formic acid and 10 percent water and the solution is 8.4 percent, by weight, polyamide. The chlorendic acid content of filaments is determined by coulometric analysis of chloride using the method described in Cotlov et al., Journal of Laboratory and Clinical Medicine, 51, 461-468, 1958 and calculated as chlorendic acid. In practice it has been noted that the weight the filaments gain from the treatment with the halogenated compound differs from the halogenated compound content as determined by analysis by no more than 2 percent. Thus, a measurement of weight gain can be taken as a meaningful indication of the halogenated compound content. The significance of this approximation can be augmented by flame performance wherein filaments showing a weight gain of at least 6 percent are flame resistant, i.e., they self-extinguish, frequently in a matter of seconds, e.g., less than 30 seconds.

EXAMPLE I

Polyhexamethylene adipamide containing, by weight, based on the weight of the polymer 3.5 percent of an ethylene oxide condensate and 0.5 percent of 4,4'-butyldiene-bis-(6-t-butyl-m-cresol) is spun into a yarn having 320 filaments and an RV of 56. The yarn is drawn at a draw ratio of 3.0 to a denier per filament of 18.5.

The yarn is knitted into fabric and dyed using the following procedure.

An aqueous dyebath is prepared wherein for each 100 grams of fabric there is used 2 kilograms of water, 25 ml. of a 1 percent solution of tetrasodium ethylene diaminetetrasuccinate, 16 ml. of a 10 percent solution of the disodium salt of disulfonated monoaoyldiphenyl ether, 50 ml. of a 10 percent solution of trisodium phosphate and 100 ml. of a 10 percent solution of monosodium phosphate. The pH of the bath is adjusted to give the value shown in the Table. Fifty milliliters of a solution containing 0.4 percent of C.I. Acid Blue 25 (C.I. 62055) is added to the bath, followed by the fabric. The bath is then raised to the boil in 45-60 minutes and held at the boil for 30 minutes. A boiling solution of 12 grams of chlorendic acid in 200 ml. of water is then added, the pH adjusted, the bath boiled for an additional 30 minutes and the pH measured. The dyed fabric is rinsed for 10 minutes in cold water and air dried. The chlorendic acid content of the filaments is determined and their flame resistance measured. Results are shown in the Table.

<table>
<thead>
<tr>
<th>pH</th>
<th>Prior to chlorendic acid</th>
<th>After chlorendic acid</th>
<th>End of dyeing</th>
<th>WT. gain (percent)</th>
<th>Chlorendic acid (percent)</th>
<th>Ignition</th>
<th>Brun</th>
<th>Time, sec.</th>
<th>Time, sec.</th>
<th>Length, in. (c.m.)</th>
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</thead>
<tbody>
<tr>
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<td>2.5</td>
<td>2.5</td>
<td>2.1</td>
<td>10.5</td>
<td>9.0</td>
<td>3</td>
<td>4</td>
<td>0.25 (0.6)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>3.1</td>
<td>3.2</td>
<td>3.4</td>
<td>10.6</td>
<td>9.6</td>
<td>3</td>
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<td>4.0</td>
<td>4.0</td>
<td>8.4</td>
<td>6.8</td>
<td>3</td>
<td>4</td>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>4.</td>
<td>5.0</td>
<td>5.0</td>
<td>4.9</td>
<td>4.8</td>
<td>3.8</td>
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<td>0.25 (0.6)</td>
<td>0</td>
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<tr>
<td>5.</td>
<td>6.3</td>
<td>6.3</td>
<td>5.9</td>
<td>1.7</td>
<td>0.8</td>
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<td>0</td>
</tr>
<tr>
<td>6.</td>
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<td>6.9</td>
<td>6.8</td>
<td>0.9</td>
<td>0.2</td>
<td>3</td>
<td>140</td>
<td>8.5 (21.6)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

EXAMPLE II

Poly(methylene-di-1,4-cyclohexylene dodecanedio diamide) prepared from dodecanedioic acid and bis-(4aminocyclohexyl)methane wherein the diamine contains 70 percent of the trans-trans stereoisomer is melt spun into a 36-filament yarn and drawn to a total denier of 60. The 60-denier yarn is woven into an 8-shaft satin fabric and dyed in the following manner.

A 100-ml. bath is prepared by adding to water at 60°C. 0.025 gram of the product obtained by condensing 20 molecular proportions of ethylene oxide with one molecular proportion of a monofunctional 18-carbon, aliphatic alcohol, 0.050 gram of Acid Red 151 (C.I. 26900) and sufficient formic acid to give a pH of 3. A 25-gram swatch of the fabric is added, the temperature raised to 71°C in about 20 minutes, and 0.38 gram of a mixture of alpha and beta methylnaphthalenes added. After 10 minutes formic acid is added to return the pH of the bath to 3 and the bath heated to the boil. To the bath is added 0.25 gram of chlorendic acid. This is accomplished by first removing a portion of the bath, dissolving the chlorendic acid in the said portion and returning the same to the bath. The bath is run 2 hours at the boil and the fabric rinsed in water at about 60°C until the rinse is clear. The treated fabric is scoured at 71°C for 30 minutes in a 100 ml. bath containing 0.025 gram of the above-identified ethylene oxide condensate and 0.013 gram of acetic acid. The scoured fabric is rinsed with cold tap water and dried,
free to relax, at 82°C. in a hot-air oven. The fabric is then heat-set, free to relax, at 190°C. for 60 seconds. The filaments are found to contain 6.2 percent chlorenedic acid and, after a 3-second ignition, to self-extinguish in about 1.3 seconds after burning about 2.5 inches (Average of four samples).

EXAMPLE III

A sample of the same fabric used in Example I is treated, at 27°C., with a padding solution containing, per liter, 200 grams of a purified natural gum ether, 10 grams of acetic acid, 30 grams of a mixture of sulfated, long-chain, fatty alcohols and 10 grams of an ethylene oxide condensate of nonyl phenol in a molar ratio of 9:1. The fabric is padded by passing it between two rolls, the lower of which rotates in the treating solution. The padded fabric is heated with steam at 100°C. for 10 minutes, rinsed in cool water and dried. The dried fabric is then repadded with a paste which contains per 100 parts of paste, 7 parts of chlorendic anhydride, 5 parts thioglycolic, 2 parts of a fatty amide, 2 parts of a nonionic surfactant, 55 parts of the purified natural gum ether, 5 parts of benzyl alcohol, 0.5 part of the sodium salt of a sulfonated alkyl benzene and 0.5 part of 2-ethylhexanol. The repadded fabric is steamed 12 minutes at 100°C., scoured 3 minutes at 60°C. in a solution containing 2 grams per liter of the material obtained by condensing one molecular proportion of an 18-carbon, monohydric alkanol with 20 molecular portions of ethylene oxide and 5 grams per liter of lauryltrimethylammonium bromide and then dried at 80°C. The dried fabric showed a weight pickup of 17.7 percent and after 3 seconds ignition self-extinguished in 14 seconds after burning 0.5 inch (1.3 centimeter).

EXAMPLE IV

Following the procedure given in Example III, except that the anhydride used is tetrabromophthalic anhydride, the fabric is found to have a total weight gain of 18 percent. Using a 3-second ignition, the fabric self-extinguished in 13 seconds after burning 1.25 inch (3.2 centimeters).

EXAMPLE V

A sample of the fabric described in Example I is treated in the following manner using a bath to fabric ratio of 50:1. The fabric is added to room-temperature water and for each 100 grams of fabric there is added 0.25 gram of tetradsodium ethylenediaminetetraacetate, 1.5 grams of the sodium salt of a sulfonated aromatic hydrocarbon, 0.5 gram of trisodium phosphate, 0.5 gram of Acid Blue 78 (C.I. 62105) and 2 grams of monosodium phosphate. The bath pH is 6.0 and it is reduced to 5.5 with acetic acid. The temperature is raised to about 99°C. in 45 minutes and a solution of 12 grams of tetrabromophthalic anhydride in 25 grams of benzyl alcohol heated to 160°C. is added. The bath is maintained at the boil for 60 minutes and the pH found to be 4. The treated fabric is then rinsed for 10 minutes at 21°C., excess water removed and the fabric heated to about 150°C. for 10 minutes. The weight gain for the fabric is 8.7 percent and, following a 12-second ignition, it burns only 14 seconds and 1.5 inches (3.8 centimeters).

EXAMPLE VI

A bath is prepared using 3,500 ml. of water, 25 ml. of a 1 percent solution of sodium ethylenediaminetetraacetate, 16 ml. of a solution containing 10 percent of the disodium salt of disulfonated monoalkyl diphenylether, 50 ml. of 10 percent trisodium phosphate, and 100 ml. of 10 percent monosodium phosphate. The pH of the bath is adjusted to 2.5 with 10 percent phosphoric acid. Fifty ml. of a solution containing 1 percent of Acid Blue 78 (C.I. 62105) and 100 grams of the fabric described in Example I is added. The bath is boiled for 30 minutes, a boiling solution of 12 grams of tetrachlorophthalic anhydride in 500 ml. of water added and the bath boiled for an additional 30 minutes. The pH is found to be 2.5. The fabric is rinsed for 10 minutes in cold water, excess water removed and the fabric dried in air. The weight gain for the fabric is 2.75 percent and the flame retardant content, calculated as tetrachlorophthalic acid, is 2.9 percent. Following a 3-second ignition, the fabric burns 3 seconds and the burn length is 0.25 inch (0.6 centimeter).

What is claimed is:

1. A process for imparting flame resistance to drawn polyamide filaments selected from the group consisting of poly(hexamethylene adipamide) and poly(methylene-di-1,4-cyclohexylene dodecanediamide) filaments comprising treating such filaments with an aqueous composition of a halogenated compound of the class consisting of chlorendic, tetrabromophthalic and tetrachlorophthalic acids and their anhydrides, said aqueous composition being at a temperature of at least 97°C. and at a pH of less than about 5, and drying the filaments.

2. The process of claim 1 wherein the halogenated compound is chlorendic anhydride.

3. The process of claim 1 wherein the pH of the aqueous composition is 2 to 4.

4. The process of claim 1 wherein the concentration of halogenated compound in the aqueous composition is from about 1 percent to 10 percent.

5. The process of claim 1 wherein the treated filaments contain from about 2 to 18 percent by weight of halogenated compound.

6. The process of claim 1 wherein the aqueous treating composition contains a dye.

7. The process of claim 1 wherein the polyamide is poly(hexamethylene adipamide).

8. The process of claim 1 wherein the polyamide is poly(methylene-di-1,4-cyclohexylene dodecanediamide).

9. The process of claim 1 wherein the halogenated compound is chlorendic acid.

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