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METHOD FOR DYEING HIGH-TEMPERATURE-RESISTANT POLYAMIDES AND POLYIMIDES

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ABSTRACT OF THE DISCLOSURE

Filaments of aromatic polyamides and aromatic polyimides that structurally withstand temperatures of over 150° C. are difficult to dye by conventional techniques, but are readily dyed at temperatures over 100° C., preferably 120 to 160° C., in a solution of a dye in a polar organic solvent that contains oxygen in the molecule, preferably N,N-dialkylcarboxylic acid amides such as N,N-dimethylformamide. The filaments can be led through a narrow conduit in which the dye solution is held. The filaments can be mixed with other filaments and fibers that are not materially damaged by the dye solution, and such mixtures subjected to the dyeing treatment.

The present invention relates to the dyeing of aromatic polyamides and polyimides such as polypyromellitic acid imides of phenylene diamines and polyisophthalic acid amide of 1,3-phenylene diamine. These and similar aromatic acid polyamides and polyimides of aromatic diamines have a peculiar structure which causes them to withstand temperatures of over 150° C. and even as high as 500° C. without softening. They are also extremely inert to just about every organic solvent. Prolonged contact with boiling water greatly weakens them, and they are most vulnerable to attack by aqueous caustic. However attempts to dye these polymers with aqueous dye formulations have not been satisfactory, even at boiling temperatures for extended periods.

As pointed out above the present invention provides a technique for satisfactorily dyeing such materials. To this end the dyeing is effected at temperatures above 100° C. by a solution of a dye in a polar organic solvent that contains oxygen in the molecule, like N,N-dialkylcarboxylic acid amides such as N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, unsubstituted formamide, dimethyl sulfoxide, dimethyl sulfone, butyrolactone, tetramethylene sulfone, glycol carbonate, isophronediacetamide, and o-, m- and p-cresols as well as mixtures thereof. The preferred solvents are compounds that can be heated up to and maintained at dyeing temperatures under atmospheric pressure without decomposing, and N,N-dimethylformamide is particularly desirable. The preferred dyeing temperatures are from about 120 to about 160° C. so that the solvents should have boiling points at least as high at atmospheric pressure. In this preferred range dyeing can be completed in two minutes or less. If desired the foregoing polar solvents can be mixed with up to about 25% by weight of other solvents like xylene, toluene, dioxane and acetonitrile.

The following examples illustrate the present invention and show how effectively and rapidly it dyes the foregoing difficultly dyed filaments.

EXAMPLE 1

Two hundred fifty grams of a fabric woven entirely of 23 denier filament polyisophthalic acid amide of m-phenylene diamine, is without prior cleaning completely

immersed in 2.5 liters of a 10 weight percent solution of Color Index Reactive Red No. 45 in dimethyl formamide heated to 150° C. After one minute of immersion the fabric is removed, washed in a 2% soap solution in water, rinsed with water, and dried. The fabric is dyed a very uniform red that is extremely resistant to washing and to sublimation.

Similar results are obtained with the following dye solutions in place of the solution of Example 1:

0.05% solution of Supranolcyanine G (C.I. 42655)
0.08% solution of Procions yellow M 4 RS (Color Index Reactive Orange 14)

The dyes named in the examples are fully described in the Colour Index, 2nd ed., 1956, and the additions and amendments thereto, Society of Dyers and Colourists, Bradford, Yorkshire, England, The American Association of Textile Chemists and Colorists, Lowell Technological Institute, Lowell, Mass.

EXAMPLE 2

A fabric woven of 65% aromatic polyamide Nomex fibers and 35% Egyptian cotton fibers, both 16 denier, is dipped in a boiling 0.5% solution of C.I. Acid Blue No. 78 (C.I. 62105) in dimethylformamide for 50 seconds, removed, rinsed with dimethyl-formamide and dried. A highly satisfactorily dyed product results, both types of fibers being very attractively dyed.

Similarly satisfactory results are obtained when silk, polyester or polyacrylate filaments are substituted for the cotton in this example.

EXAMPLE 3

A core-yarn of 70% of a polymer of polyisophthalic acid and m-phenylene diamine and 30% polyethylene glycol terephthalate, Nm 70/2, is dyed by threading them through an electrically heated, U-shaped tubular conduit, containing the saturated, boiling dye-solution Supranol Fast Bordeaux B (C.I. 24810) during 30 sec. After this the thread passes through a perchloroethylene rinsing bath and is dried. The dyed core yarn resulting from this procedure is extremely resistant to washing and sublimation.

The process of the present invention is particularly suited for dyeing filaments made of linear condensations between benzene polycarboxylic acids or their anhydrides and diamino benzenes, including those described for instance in U.S. Pats. 3,179,631; 3,179,632; 3,179,633; and 3,179,634. Although those filaments can be handled very much like other thermoplastic filaments, they do not soften readily at elevated temperature and some will even char without much softening. Naphthalene compounds can be used in place of the corresponding benzene compounds and up to about 10% of the acid or amide being condensed can be replaced by other condensing ingredients. Mono-, tri-, or penta-carboxy benzenes, or aliphatic mono-, di-, tri-, tetra-, or penta-carboxylic acids can thus be used to take the place of some of the acid or anhydride, and similar mono- or tri-amino benzenes or mono-, di- or tri-amino aliphatic amines can replace some of the phenylene diamine. Di- and tetracarboxyl diphenyls, di- and tetracarboxy naphthalenes, benzene di- and tetra-acetic acids and corresponding diamines can also be used as such replacements.

The unusually high temperature resistance of the foregoing polymers seems to be associated with a resistance to dyeing. While prolonged immersion in boiling water will cause these polymers to lose appreciable strength, the dyeing process of the present invention will have only a slight effect, generally involving not more than a 10% loss in strength.

The filaments or mixed filaments of the present invention are conveniently dyed by threading them through a narrow tubular conduit, e.g. ½ inch in inside diameter, which conduit can be U-shaped and contain the dye solution. The lower run of the U can be heated to dyeing temperature and the total quantity of dye solution thus reduced to a very small amount. As the filaments leave the conduit they can be passed through a solvent recovery where excess solvent is evaporated from them and collected and additional dye then dissolved in it to make fresh dyeing solution to add to the conduit.

In general the dye content of the dye solutions used pursuant to the present invention can vary from saturation down to 0.005%. Different concentrations of the same dye can produce different dyeing effects. The dyeing of the present invention can also be carried out at superatmospheric or subatmospheric pressures.

What is claimed:

1. A method of dyeing aromatic filaments selected from the group consisting of polyisophthalic acid amide of m-phenylene diamine and polypyromellitic acid imide of phenylene diamine that structurally withstand temperature of over 150° C., which method consists essentially of contacting the fibers at a temperature higher than 100° C. with a solution consisting essentially of a dye in a polar organic solvent that includes oxygen in its molecule and ha a boiling point at atmospheric pressure at least as high as the dyeing temperature.

2. The method of claim 1 in which the solvent is N,N-dimethyl formamide.

3. The method of claim 1 in which the contacting is at a temperature of from about 120 to 160° C.

4. The method of claim 1 in which the filaments are mixed with other filaments that are not materially damaged by the dye solution, and the mixed filaments are together contacted with the dye solution.

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