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PROCESS OF DYEING POLYESTER FIBERS WITH DIAMINO - ANTHRAQUINONE - CARBONITRILE DYESTUFFS

John David Hildreth, Beachwood, N.J., assignor to Toms River Chemical Corporation, Toms River, N.J., a corporation of Delaware

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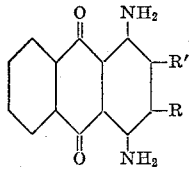
9 Claims. (Cl. 8—39)

This invention relates to the production of valuable dyeings on fibrous materials of aromatic polyesters, and more particularly to dyed polyethylene terephthalate fibers of excellent color strength and good fastness properties.

Polyester fibers present particular dyeing problems, arising at least in part out of the hydrophobic nature of such fibers. In the dyeing of polyester fibers, the class of dyes known as disperse dyestuffs has come to have the widest application. These dyestuffs are essentially water-insoluble products applied in a finely divided condition from a dispersion. In the application of such dyestuffs, the dyeing difficulties associated with polyester fibers have been met by the development of special methods for the application of disperse dyes to the fibers. Of these methods, the one known as the Pad/Thermofix method has become of increasing importance since it is particularly adapted for high-speed, continuous dyeing operations. In this method, a fabric is padded by passing it through an aqueous suspension of the dyestuff and squeezing the fabric between closely-set rollers in order to remove excess dye liquor. The dyestuff is only loosely attached to the fiber at this point. The dyestuff is then fixed on the fiber by subjecting the material to a short, intensive heat-treatment at elevated temperatures of the order of about 120–220° C. It is evident that a dyestuff, in order to be suitable for application by this method, must be fast to sublimation or else it will wholly or partially volatilize from the fiber during the heat-treatment step. The result of such sublimation will be a loss of color value on the polyester fiber and, if a union dyeing operation is being carried out, the staining of the other fibers, such as cotton, which may be present in the blend.

In accordance with the present invention, it has been discovered that valuable dyeings and prints are produced on fibrous materials of aromatic polyesters, especially polyethylene terephthalate, by using as dyestuff a 1,4-diaminoanthraquinonecarbonitrile of the formula



in which R is cyano and R' is hydrogen or cyano.

The 1,4-diaminoanthraquinonecarbonitriles employed in the practice of the present invention can be obtained in known manner by heating the appropriate 1,4-diaminoanthraquinonesulfonic acid in water with an alkali metal cyanide. Instead of the single dyestuffs there can be used a mixture of the two dyestuffs or a mixture of such dyestuff with a dyestuff of similar structure.

For dyeing, the said dyestuffs are preferably used in a finely divided form and the dyeing is carried out in the presence of a dispersing agent, such as sulphite cellulose waste liquor or a synthetic detergent, or a combination of different wetting and dispersing agents. Before dyeing, it is generally of advantage to convert the dyestuff or dyestuffs to be used into a dyestuff preparation which contains a dispersing agent and the finely divided dyestuff(s) in such a form as to yield a fine dispersion when the preparation is diluted with water. Dyestuff preparations of this kind can be made by known methods, for example, by grinding the dyestuff(s) either in dry or wet form with or without the addition of a dispersing agent.

The dyestuffs used in the invention are especially suitable for dyeing by the so-called thermofixation or Pad/Thermofix method, in which the fabric to be dyed is impregnated advantageously at a temperature not exceeding 60° C. with an aqueous dispersion of the dyestuff, which may contain 1 to 50% of urea and a thickening agent, especially sodium alginate, and the fabric is squeezed in the usual manner. The squeezing is preferably carried out so that the goods retain 50 to 100% of their weight of dye liquor.

The dyestuff is fixed by subjecting the impregnated fabric to a heat treatment at temperatures above 100° C., for example, at a temperature ranging from 120–220° C., it being of advantage to dry the fabric prior to this treatment, for example, in a current of warm air.

The thermofixation mentioned above is of special interest for the dyeing of mixed fabrics of polyester fibers and cellulose fibers, especially cotton. In this case, in addition to the dyestuff to be used in the process of the invention, the padding liquor contains a dyestuff suitable for dyeing cotton, for example, a direct dyestuff or vat dyestuff, or more especially a so-called reactive dyestuff, i.e. a dyestuff capable of being fixed on cellulose fibers with the formation of a chemical bond, for example, a dyestuff containing a chlorotriazine or chlorodiazine residue. In the latter case it is of advantage to add to the padding liquor an agent capable of binding acid, for example, an alkali carbonate, alkali phosphate, alkali borate or alkali perborate, or a mixture of two or more of these agents. When vat dyestuffs are used, the padded fabric must be treated, after the heat treatment, with an aqueous alkaline solution of a reducing agent of the kind used in vat dyeing.

The dyeings produced on polyester fibers by the process of the invention are advantageously given an after-treatment, for example, by heating them with an aqueous solution of a non-ionic detergent.

The process is also suitable for dyeing mixed fabrics of polyester fibers and wool and the wool portion which remains reserved, may be subsequently dyed with a wool dyestuff.

Instead of applying the dyestuffs in the process by impregnation, they may be applied by printing. For this purpose, a printing color is used which, in addition to the usual printing assistants, such as wetting and thickening agents, contains the finely dispersed dyestuff, if desired, in admixture with one of the aforesaid cotton dyestuffs, and, if desired, in the presence of urea and/or an agent capable of binding acid.

There are obtained by the practice of the present invention strong dyeings or prints having excellent fastness properties, especially a good fastness to sublimation and to light. Furthermore, the shade and color build-up of the applied dye are outstanding. Another advantage resides in the fact that the dyestuffs employed in the present invention are produced more economically than available commercial blue dyestuffs of similar fastness properties.

The term polyester defines synthetic polymeric polyesters, such as the highly polymeric linear polyesters, the molecules of which have recurring monomeric units connected by ester linkages. Dibasic acids, for example, aromatic acids, such as terephthalic acid, diphenyl-4,4'-dicarboxylic acid and/or diphenylsulfone-4,4'-dicarboxylic acid and dihydroxy compounds, for example, glycols, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol and/or butylene glycol, as well as other diols, such as 1,4-cyclohexyldiol can be used as the monomers to form the polymeric polyesters. Typical commercial examples of such fibers are Dacron, Terylene, Fortrel, Trevira, Terlanca, Kodel, Vycron, etc. They are disclosed, for example, in U.S. Patent No. 2,901,466 and British Patents Nos. 578,079; 579,462; 588,411; 588,497 and 596,688.

The present invention is, of course, equally applicable to the dyeing of blends of polyester fibers and cellulosic fibers. The latter term includes native cellulose, such as linen or, more particularly, cotton, as well as regenerated cellulose, such as viscose or cuprammonium rayon.

The following examples illustrate the invention, the parts and percentages being by weight.

Example 1

366 parts of 1,4-diamino-2,3-anthraquinonedisulfonic acid, sodium salt is added to 14,500 parts of water, stirred and adjusted to a pH of 10.6 at 75° C. by the addition of 30% sodium hydroxide solution. 226.5 parts of sodium cyanide is then added and the mixture stirred for 6 hours at 75–80° C. At the end of this period, the reaction mixture is filtered hot at 60° C., washed with 1,500 parts hot (60° C.) water and dried. The product is obtained in a yield of 170 parts.

The product gives a reddish-orange vat with caustic soda and hydrosulfite, a pale greenish solution in concentrated sulfuric acid, turning yellower on addition of formaldehyde and has a melting point above 330° C.

The product comprises 1,4-diamino-2,3-anthraquinonedicarbonitrile in admixture with other carbonitrile derivatives of 1,4-diaminoanthraquinone, principally 1,4-diamino-2-anthraquinonecarbonitrile.

Example 2

60 parts 1,4-diamino-2-anthraquinonesulfonic acid (prepared by the hydrolysis of 1-amino-4-p-toluenesulfonamido-anthraquinone-2-sulfonic acid, potassium salt with 96% H_2SO_4) is added to 1,250 parts water. 40 parts of sodium cyanide and 20 parts ammonium bicarbonate are then added and the whole stirred for 5 hours at 95–100° C., the color changing from a bluish-violet to a purple. After cooling, the reaction mixture is filtered and the product, separated by filtration, is washed with hot water and dried. The yield is 40 parts.

The product gives a reddish-orange vat with caustic soda and hydrosulfite, a pale greenish solution in concentrated sulfuric acid, turning yellower on addition of formaldehyde and has a melting point above 330° C.

The product comprises 1,4-diamino-2-anthraquinonecarbonitrile in admixture with other 1,4-diaminoanthraquinonecarbonitrile derivatives, principally the 1,4-diamino-2,3-anthraquinonedicarbonitrile.

Example 3

10 parts of the dyestuff of Example 1 are brought to a state of fine dispersion by milling in a ball mill with

3.0 parts of the condensation product of naphthalene-2-sulfonic acid with formaldehyde, and 37 parts of water.

Amounts of this preparation, sufficient to provide a concentration of 1.5, 3.0 and 6.0 grams of dyestuff per liter of dye bath, is finely dispersed in water containing 10.0 g. of sodium alginate per liter and the resultant pad liquor is brought to a temperature of 25° C.

Polyethylene terephthalate fabric is then padded with the above liquor and mechanically squeezed to a 65% pick up. The padded material is then air dried and developed by dry heat, curing in an electrically-heated, hot-air drier for 1 minute at 200° C. The dyed fabric is scoured for 5 minutes at the boil in a solution containing 3% of sodium di-iso-butylnaphthalene monosulfonate and 5% sodium carbonate and then dried. A bright blue dyeing is obtained, characterized by good penetration and excellent fastness to light and sublimation.

Example 4

The procedure of Example 3 is repeated, except that the dyestuff of Example 2 is used in place of the dyestuff of Example 1. A bright blue dyeing of slightly redder shade is obtained, characterized by good penetration and excellent fastness to light and sublimation.

Example 5

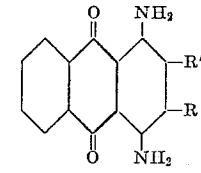
The procedure of Example 3 is repeated, except that 1,4-diamino-2,3-anthraquinonedicarbonitrile is used instead of the dyestuff of Example 1. A bright blue dyeing of excellent light and sublimation fastness and good penetration characteristics is obtained.

Example 6

The procedure of Example 3 is repeated, except that 1,4-diaminoanthraquinone-2-carbonitrile is used instead of the dyestuff of Example 1. A bright blue dyeing of good light and sublimation fastness and good penetration characteristics is obtained.

What is claimed is:

1. Polyester fiber dyed with an anthraquinone compound having the formula



wherein R' is a member selected from the group consisting of hydrogen and cyano and R is cyano.

2. Polyester fiber according to claim 1, wherein R and R' are both cyano, that is, the anthraquinone compound is 1,4-diamino-2,3-anthraquinonedicarbonitrile.

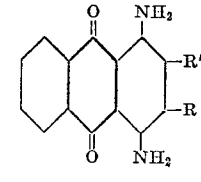
3. Polyester fiber according to claim 1 wherein R is cyano and R' is hydrogen, that is, the anthraquinone compound is 1,4-diamino-2-anthraquinonecarbonitrile.

4. Polyester fiber according to claim 1, in which the polyester fiber is polyethylene terephthalate.

5. Polyester fiber according to claim 2, in which the polyester fiber is polyethylene terephthalate.

6. Polyester fiber according to claim 3, in which the polyester fiber is polyethylene terephthalate.

7. A process of dyeing and printing a polyester material, which comprises applying to fibrous material of synthetic polyester an aqueous dispersion containing a 1,4-diaminoanthraquinonecarbonitrile of the formula



wherein R' is a member selected from the group consisting of hydrogen and cyano and R is cyano, as the essential color imparting substance.

8. A process of dyeing and printing a polyester material, which comprises applying to fibrous material of synthetic polyester an aqueous dispersion containing as the essential color imparting substances a mixture of 1,4-diamino-2,3-anthraquinonedicarbonitrile and 1,4-diamino-2-anthraquinonecarbonitrile.

9. A process according to claim 7, in which the anthraquinone compound is 1,4-diamino-2,3-anthraquinonedicarbonitrile.

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NORMAN G. TORCHIN, *Primary Examiner.*