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Continuation-in-part of application Ser. No.
386,735, July 31, 1964, now abandoned.

[54] **2-BENZOYLANTHRAQUINONE DYES FOR
POLYESTER FIBERS**
3 Claims, No Drawings

- [52] U.S. Cl. **8/39,**
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372, 377; 8/39, 179

[56] **References Cited**

UNITED STATES PATENTS

- 2,937,190 5/1960 Straley et al. 260/377 X
3,211,755 10/1965 Fitzpatrick et al. 260/376

FOREIGN PATENTS

- 661,045 11/1961 Great Britain 260/376

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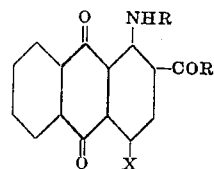
H. A. Lubs, Chemistry of Synthetic Dyes and Pigments (1955) pp. 417-419. Copy in 260-377

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ABSTRACT: Dyeings and printings are produced on fibrous materials of aromatic polyesters, especially polyethylene terephthalate, by using as dyestuff a 2-benzoylanthraquinone of the formula:



in which R is hydrogen, alkyl, particularly lower alkyl, and sulfonyl, particularly arylsulfonyl, including substituted arylsulfonyl, R' is phenyl, naphthyl, diphenyl and phenyl, naphthyl or diphenyl containing as substituents, halogen, i.e. chlorine, bromine or fluorine, lower alkyl or alkoxy substituents, and X is anilino, toluidino, acylamino, alkylsulfonamido, or benzenesulfonamide where the benzene nucleus is devoid of a water solubilizing group.

2-BENZOYLANTHRAQUINONE DYES FOR POLYESTER FIBERS

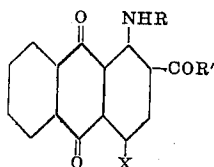
This application is a continuation-in-part of our application Ser. No. 386,735, filed on July 31, 1964, now abandoned.

BACKGROUND OF THE INVENTION

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.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been discovered that valuable dyeings and printings are produced on fibrous materials of aromatic polyesters, especially polyethylene terephthalate, by using as dyestuff a 2-benzoylanthraquinone of the formula:



in which R is hydrogen, alkyl, particularly lower alkyl, and sulfonyl, particularly arylsulfonyl, including substituted arylsulfonyl, R' is phenyl, naphthyl, diphenyl and phenyl, naphthyl or diphenyl containing as substituents, halogen, i.e. chlorine, bromine or fluorine, lower alkyl or alkoxy substituents, and X is anilino, toluidino, acylamino, alkylsulfonamido, or benzenesulfonamide where the benzene nucleus is devoid of a water solubilizing group.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Many of the 2-benzoylanthraquinones employed in the practice of the present invention are known compounds and can be prepared according to known procedures, as for example, the processes of U.S. Pat. No. 2,499,003 and Berichte 51, 1233 (1918). Others of the 2-benzoylanthraquinones employed are novel compounds and the preparation and utilization of these novel compounds are specifically disclosed herein.

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 sulfite 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 percent 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 percent 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 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 nonionic detergent.

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 of attractive shade and good color buildup having excellent fastness properties, especially a good fastness to sublimation and to light. 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. Pat. No. 2,901,466 and British Pat. Nos. 578,079; 579,462; 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 unless otherwise specified.

Example 1

16 g. of 1-amino-2-benzoyl-4-bromoanthraquinone is added to 230 g. by volume of amyl alcohol, and 30 g. of p-toluenesulfonamide, 20 g. of sodium acetate and 0.12 g. of copper acetate are then added. The mixture is heated with stirring to reflux (134° C.) and held at reflux temperature for a period of 12 hours, the color very quickly changing from a reddish-orange to a very deep violet. The reaction mixture is cooled to room temperature, then suction-filtered and washed twice with 50 g. by volume portions of amyl alcohol. Residual solvent is removed by steam distillation and the product again filtered and dried. The dye, 1-amino-2-benzoyl-4-p-toluenesulfonamidoanthraquinone, is obtained in a yield of 18 g. and in the form of dark violet platelike crystals.

Example 2

Ten g. of the dyestuff of example 1 are brought to a state of fine dispersion by milling in a ball mill with 3.0 g. of the condensation product of naphthalene-2-sulfonic acid with formaldehyde, and 37 g. of water.

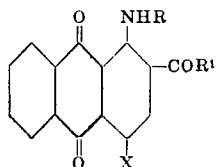
Amounts of this preparation, sufficient to provide a concentration of 1.5, 3.0 and 6.0 grams of dyestuff per liter of dye bath, are finely dispersed in water containing 10.0 g. of sodium alginate per liter and the resultant pad liquor is brought to a temperature of 25° C.

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

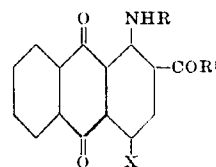
Among other known 2-benzoylanthraquinones which can be employed according to the present invention, there can be mentioned 1-p-toluenesulfonamido-2-benzoylanthraquinone, 1-amino-4-p-chloro-benzamido-2-benzoylanthraquinone, the anthraquinone vat dyes of the formula 1,2,4-H₂N (ROC) (R'OCNH) C₁₄H₉O₂ where R is an aryl group having six-12 C atoms and R' is an aryl or alkaryl group with not more than 12 C atoms as disclosed in British Pat. No. 663,383, the anthraquinone vat dyes of U.S. Pat. No. 2,567,821 corresponding to British Pat. No. 663,383, particular examples comprising those instances wherein R is naphthyl, and particularly phenyl and substituted phenyl, such as tolyl, halophenyl and alkoxyphenyl, and the COR' moiety represents the radical of an aromatic or aliphatic-aromatic carboxylic acid containing at most 13 carbon atoms and which may contain substituents in the aromatic nucleus such as the residue of benzoic acid.

When the above dyestuffs are employed in the procedure of example 2 in lieu of the specific dyestuff recited in example 2, dyeings of desirable shade ranging from orange to blue-violet are obtained having good to excellent light and sublimation fastness and penetration characteristics.

In addition to the known dyestuffs referred to in the preceding paragraph and the foregoing example, the novel 2-benzoylanthraquinone hereinafter discussed can also be employed. In general, the novel dyestuffs of the present invention have the formulas



where R is lower alkyl, R' is phenyl, naphthyl, diphenyl, halo-phenyl, halo-naphthyl, halo-diphenyl, alkyl-phenyl, henyl alkyl-naphthyl, and alkyl-diphenyl, alkoxy-phenyl, alkyl-naphthyl and alkoxy-diphenyl; and X is anilino, toluidino, lower alkylsulfonamido, benzenesulfonamido, lower alkyl-benzenesulfonamido, halobenzenesulfonamido, or lower alkoxybenzenesulfonamido; and



where R is the same as above, but also hydrogen; R' is the same as above; and X is anilino, toluidino, lower alkylsulfonamido, benzenesulfonamido, halobenzenesulfonamido or lower alkoxy-benzenesulfonamido.

Examples 3-6

The procedure of example 1 is repeated except that the sulfonamide reactant listed in the table below under the column entitled "Sulfonamide" is used in place of the p-toluene-sulfonamide employed in example 1 in the amount given under the column entitled "Grams" to give the 2-benzoylanthraquinone dyestuff listed under the column entitled "Dyestuff."

Dyestuff	Sulfonamide	Grams
1-amino-2-benzoyl-4-p-chloro benzenesulfonamidoanthraquinone	p-chlorobenzenesulfonamide	33.5
1-amino-2-benzoyl-4-benzenesulfonamidoanthraquinone	benzenesulfonamide	27.5
1-amino-2-benzoyl-4-p-methoxy-benzenesulfonamidoanthraquinone	p-methoxybenzenesulfonamide	33.0
1-amino-2-benzoyl-4-methanesulfonamidoanthraquinone	methanesulfonamide	16.8

When dispersed in the conventional manner described in example 2 and applied to polyethylene terephthalate fibers, these dyestuffs gave dyeings of bright violet shades characterized by excellent sublimation and light fastness and by good penetration properties.

Example 7

1-amino-2-benzoyl-4-p-toluidinoanthraquinone

Ten g. of 1-amino-2-benzoyl-4-bromoanthraquinone, 20.0 g. anhydrous sodium acetate, 11.7 g. p-toluidine, 0.12 g. copper acetate and 150 g. by volume of amyl alcohol are heated with stirring at reflux (135°) for 12 hours, the color changing to a dark blue.

At the end of the above time period, the reaction mixture is cooled to room temperature, filtered, washed with ethyl alcohol and then water, and then dried.

The product, 1-amino-2-benzoyl-4-p-toluidinoanthraquinone, is obtained in yield of 8 g.

When dispersed and applied to polyethylene terephthalate by the procedure of example 2, 1-amino-2-benzoyl-4-p-toluidinoanthraquinone gave dyeings of a bluish-grey shade having good light and sublimation fastness and good penetration characteristics.

Example 8

The procedure of example 7 is repeated except that 10.4 g. of aniline is employed in place of p-toluidine. The product, 1-amino-2-benzoyl-4-anilinoanthraquinone is obtained in a yield of 7 g.

When dispersed and applied to polyethylene terephthalate by the procedure of example 2, 1-amino-2-benzoyl-

4anilinoanthraquinone gave dyeings of a blue shade having good light and sublimation fastness and good penetration characteristics

Examples 9-14

The procedure of example 1 is repeated except that the reactants listed in the pertinent columns in the Table below are employed in the indicated quantities to provide the dyestuffs listed in column 5.

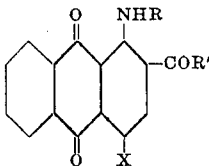
TABLE

Example	Sulfonamide	Grams	Reactant	Grams	Dyestuff
9.....	p-Toluenesulfonamide.	29.0	1-methylamino-2-benzoyl-4-bromoanthraquinone.	16.0	1-methylamino-2-benzoyl-4-p-toluenesulfonamidoanthraquinone.
10.....	Benzenesulfonamide.	27.0	do.....	16.0	1-methylamino-2-benzoyl-4-benzenesulfonamidoanthraquinone.
11.....	p-Chlorobenzene-sulfonamide.	33.0	1-methylamino-2-benzoyl-4-bromoanthraquinone.	16.0	1-methylamino-2-benzoyl-4-p-chlorobenzenesulfonamidoanthraquinone.
12.....	p-Methoxybenzenesulfonamide.	32.0	do.....	16.0	1-methylamino-2-benzoyl-4-p-methoxybenzenesulfonamidoanthraquinone.
13.....	p-Toluenesulfonamide.	28.0	1-amino-2-(p-chlorobenzoyl)-4-bromoanthraquinone.	16.0	1-amino-2-(p-chlorobenzoyl)-4-p-toluenesulfonamidoanthraquinone.
14.....	p-Toluenesulfonamide.	26.0	1-amino-2-(3',4'-dichlorobenzoyl)-4-bromoanthraquinone.	16.0	1-amino-2-(3',4'-dichlorobenzoyl)-4-p-toluenesulfonamidoanthraquinone.

When dispersed and applied to polyethylene terephthalate by the procedure of example 2, the 2-benzoylanthraquinone dyestuffs of column 6 gave blue-violet dyeings having excellent light and sublimation fastness.

We claim:

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



in which R is a member selected from the group consisting of hydrogen, lower alkyl, and sulfonyl, R' is a member selected from a group consisting of phenyl, naphthyl, diphenyl, halo-phenyl, halo-naphthyl, halo-dipheynl, alkyl-phenyl, lower alkyl-naphthyl, lower alkyl-diphenyl, alkoxy-phenyl, lower alkoxy-naphthyl and lower alkoxy-diphenyl, and X is a member selected from a group consisting of anilino, toluidino, lower alkylsulfonamido, benzenesulfonamido, lower alkylbenzenesulfonamido, loweralkoxybenzenesulfonamido,

halo-benzenesulfonamido, benzamido and halo-benzamido.
2. Polyester fiber according to claim 1, wherein the polyester fiber is polyethylene terephthalate.
3. Polyester fiber dyed with 1-amino-2-benzoyl-4-p-toluenesulfonamidoanthraquinone.

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