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CARBAMYLANTHRAQUINONE COMPOUNDS AND MATERIALS DYED THEREWITH

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6 Claims. (Cl. 260—347.4)

This invention relates to new anthraquinone compounds and their application to the art of dyeing or coloring.

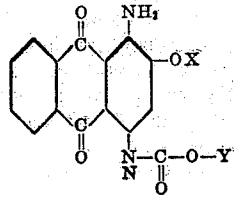
The dyeing of polyester textile materials, such as polyethylene terephthalate, has presented difficulties. While it is known that the familiar disperse dyes, that is water-insoluble dyes, employed for the coloration of cellulose acetate frequently possess affinity for polyester textile materials such as polyethylene terephthalate, by far the majority of the known disperse dyes for cellulose acetate exhibit poor fastness to light when applied to polyester textile materials. The new water-insoluble anthraquinone compounds of our invention possess good affinity for polyester textile materials and give red dyeings thereon having good fastness properties, including good fastness to light. Additionally, they have good affinity for cellulose acetate, for example, and yield dyeings of high quality thereon.

Polyester fabrics are usually heat set, after dyeing, at temperatures which often reach 400° F. If the dye is not fast to sublimation it will be removed in part, at least, from the goods during this operation. Some dyes, otherwise suitable for dyeing polyester fabrics, are unsuitable because they are not fast to sublimation. The new anthraquinone compounds of our invention yield dyeings on the textile materials indicated herein which have excellent fastness to sublimation.

Similarly, dyeings desirably should be fast to solvent rubbing. When a dry cleaner receives a garment he may wish to remove the heavier stains by rubbing the garment with a solvent prior to putting it with other garments. If the dyeing is not resistant to this treatment the spot or spots rubbed with solvent will become lighter in shade. The anthraquinone compounds of our invention yield dyeings on the textile material indicated herein which have satisfactory resistance to solvent rubbing.

It is an object of our invention to provide new anthraquinone compounds. Another object is to provide a satisfactory process for the preparation of our new anthraquinone compounds. A further object is to provide dyed polyester textile materials which have good fastness properties. Another object is to provide cellulose alkyl carboxylic acid ester textile materials which have good fastness properties. A particular object is to provide dyed polyethylene terephthalate textile materials which have good fastness properties. A further particular object is to provide dyed cellulose acetate textile materials which have good fastness properties.

We have discovered that the anthraquinone compounds having the formula:

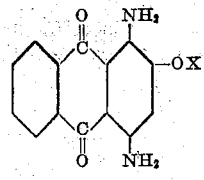


wherein X represents a methyl group, an ethyl group, a β-methoxyethyl group or a β-ethoxyethyl group and Y represents a β-alkoxyethyl group, a β-alkoxy-β-ethoxyethyl group or a tetrahydrofurfuryl group and wherein alkoxy represents an alkoxy group having 1 to 4 carbon atoms are valuable dyes for coloring polyester and cellulose alkyl carboxylic acid ester having 2 to 4 carbon atoms in the acid groups thereof textile materials. These dye compounds when applied to the aforesaid textile materials have good affinity therefor and give red dyeings of high quality. In general the dyeings obtained have excellent fastness, for example, to light, gas, washing and sublimation.

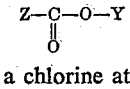
By cellulose alkyl carboxylic acid esters having two to four carbon atoms in the acid groups thereof, we mean to include, for example, both hydrolyzed and unhydrolyzed cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate-propionate and cellulose acetate-butyrate.

The polyester textile materials that can be dyed with the new anthraquinone compounds of our invention include polyethylene terephthalate textile materials obtained for example as described in U.S. Patent 2,465,319, patented March 22, 1949, or other polyester textile materials formed from analogous fiber-forming linear polyesters, such as polyesters derived from p-bis-(sulfonyl)-dibenzoic acid and various aliphatic acids and glycols as described in U.S. Patent 2,744,088, patented May 1, 1956, and polyesters derived from various acids, such as terephthalic acid, and 1,4-cyclohexanedimethanol as described in Kibler, Bell, and Smith U.S. Application Serial No. 554,639, filed December 22, 1955. Dacron (polyethylene terephthalate) and cellulose acetate are specific illustrations of the textile materials that can be dyed with our new anthraquinone compounds.

The new anthraquinone compounds of our invention can be prepared by condensing a 1,4-diaminoanthraquinone compound having the formula:



wherein X represents a methyl group, an ethyl group, a β-methoxyethyl group or a β-ethoxyethyl group with a haloformic acid ester having the formula:



wherein Z represents a chlorine atom or a bromine atom and Y represents a β-alkoxyethyl group, a β-alkoxy-β-ethoxyethyl group or a tetrahydrofurfuryl group and wherein alkoxy represents an alkoxy group having 1 to 4 carbon atoms. We prefer to use chloroformic acid esters because these esters are readily prepared from simple starting materials; namely, phosgene and the requisite alcohol.

We prefer to carry out the condensation reaction between the 1,4-diaminoanthraquinone and the haloformic acid ester compound in a neutral, organic solvent for the reactants employed which is inert under the reaction conditions employed. While solvents other than those specifically disclosed herein can be used we prefer to use, for example, ethers of ethylene glycol such as ethylene glycol monomethyl ether and ethylene glycol monoethyl ether, for example, ethers of diethylene glycol such as the monoethyl ether of diethylene glycol and the monoethyl ether of diethylene glycol, for example, nitrobenzene, dichlorobenzene and trichlorobenzene because suitable reaction temperatures can be obtained and the solubility

characteristics of the starting materials and the reaction products are well suited to these solvents. Other suitable solvents are hydrocarbons such as "Solvesso 100," predominately aromatic, boiling at about 160°–190° C. As a practical matter we prefer to use temperatures in excess of 100° C. Temperatures of about 110° C. to about 145° C. appear to be very practical. Temperatures lower than 100° C. can be used but are not practical because of the increased reaction time required. Similarly, temperatures higher than 145° C. can be employed if desired.

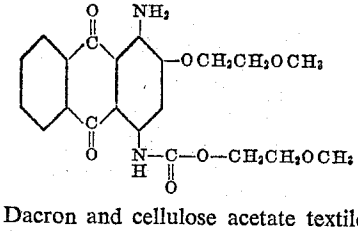
The use of the solvents indicated hereinbefore permits the reaction to be carried out readily at a suitable temperature. The boiling points of the solvents named are such that by maintaining the reaction mixture under reflux a satisfactory reaction temperature results.

1,4 - diamino - 2 - methoxyanthraquinone, 1,4 - diamino - 2 - ethoxyanthraquinone, 1,4 - diamino - 2 - β-methoxyethoxyanthraquinone and 1,4-diamino-2-β-ethoxyethoxyanthraquinone are used in the preparation of the new anthraquinone compounds of our invention when prepared in accordance with the process described herein. β-methoxyethyl chloroformate, β-ethoxyethyl chloroformate, β-n-propoxyethyl chloroformate, β-n-butoxyethyl chloroformate, β - methoxy - β - ethoxyethyl chloroformate, β-ethoxy-β-ethoxyethyl chloroformate, β-n-propoxy-β-ethoxyethyl chloroformate, β-n-butoxy-β-ethoxyethyl chloroformate and tetrahydrofurfuryl chloroformate are illustrative of the haloformic acid ester compounds used in the preparation of the anthraquinone compounds of our invention.

The following examples illustrate the anthraquinone compounds and the process of our invention.

Example 1

1 gram of 1,4-diamino-2-β-methoxyethoxyanthraquinone, 1 gram of β-methoxyethyl chloroformate and 5 cc. of ethylene glycol monomethyl ether were refluxed together with stirring until no further color change took place. The reaction mixture was cooled below the boiling point of methanol and then diluted with 10 cc. of methanol and cooled to 0° C. The reaction product (1 - amino - 2 - β - methoxyethoxy - 4 - β - methoxyethoxycarbamylanthraquinone) which precipitated was recovered by filtration, washed, in turn, with methanol and hexane and dried. It has the formula:



and dyes Dacron and cellulose acetate textile materials, for example, bright red shades having excellent fastness to light.

Example 2

1 gram of 1,4-diamino-2-ethoxyanthraquinone, 1 gram of tetrahydrofurfuryl chloroformate and 10 cc. of ethylene glycol monoethyl ether were heated together, with stirring, at 125–130° C. until evolution of HCl ceased. The reaction mixture was then cooled to 0° C. and kept at this temperature for 2 hours. The reaction product (1 - amino - 2 - ethoxy - 4 - tetrahydrofurfuryloxycarbamylanthraquinone) which precipitated was recovered by filtration, washed well with cold methanol and dried. It dyes Dacron and cellulose acetate textile materials, for example, bright red shades having excellent fastness to light. The yield was 1.2 gram.

Example 3

10 grams of 1,4-diamino-2-methoxyanthraquinone, 20 grams of tetrahydrofurfuryl chloroformate and 100 cc. of ethylene glycol monomethyl ether were refluxed together with stirring until evolution of HCl ceased. The reaction mixture was diluted with methanol to incipient crystallization and then cooled to 0° C. The reaction product (1 - amino - 2 - methoxy - 4 - tetrahydrofurfuryloxycarbamylanthraquinone) which precipitated was recovered by filtration, washed well with cold methanol and dried. It dyes cellulose acetate and Dacron textile materials, for example, bright red shades having excellent fastness to light.

Example 4

10 grams of 1,4-diamino-2-methoxyanthraquinone, 20 grams of β-n-butoxy-β-ethoxyethyl chloroformate and 100 cc. of ethylene glycol monomethyl ether were refluxed together with stirring until evolution of HCl ceased. The reaction mixture was diluted with methanol to incipient crystallization and then cooled to 0° C. The reaction product (1 - amino - 2 - methoxy - 4 - β - n-butoxy - β - ethoxyethoxycarbamylanthraquinone) which precipitated was recovered by filtration, washed well with cold methanol and dried. It dyes cellulose acetate and Dacron textile materials, for example, bright red shades having excellent fastness to light.

Example 5

1.34 grams of 1,4-diamino-2-methoxyanthraquinone, 1.5 grams of β-methoxyethyl chloroformate and 10 cc. of ethylene glycol monomethyl ether were refluxed together with stirring until no further color change was observed. The reaction mixture was then cooled to 0° C. and the reaction product (1-amino-2-methoxy-4-β-methoxyethoxycarbamylanthraquinone) which precipitated was recovered by filtration, washed well with methanol and dried. It dyes Dacron and cellulose acetate textile materials, for example, bright red shades having excellent fastness to light. The yield was 1.3 grams.

Example 6

By the use of 2 grams of β-ethoxyethyl chloroformate in place of β-methoxyethyl chloroformate in Example 5, 1 - amino - 2 - methoxy - 4 - β - n - propoxyethoxyanthraquinone was obtained. It dyes Dacron and cellulose acetate textile materials, for example, bright red shades having excellent fastness to light.

Example 7

1 gram of 1,4-diamino-2-β-ethoxyethoxyanthraquinone, 10 cc. of ethylene glycol monomethyl ether and 2 grams of tetrahydrofurfuryl chloroformate were refluxed together with stirring until no further color change took place. The reaction mixture was cooled to 90° C., diluted with 10 cc. of hot water and cooled to 0° C. The reaction product (1-amino-2-β-ethoxyethoxy-4-tetrahydrofurfuryloxycarbamylanthraquinone) which precipitated was recovered by precipitation, washed well with methanol and dried. It dyes Dacron and cellulose acetate textile materials, for example, bright red shades having excellent fastness to light.

Example 8

By the use of 2.5 grams of β-ethoxy-β-ethoxyethyl chloroformate in place of β-methoxyethyl chloroformate in Example 5, 1.6 grams of 1-amino-2-methoxy-4-β-ethoxy-β-ethoxyethoxycarbamylanthraquinone was obtained. It dyes Dacron and cellulose acetate textile materials, for example, bright red shades having excellent fastness to light.

Following the procedures described hereinbefore 1 - amino - 2 - methoxy - 4 - β - n - propoxyethoxycarbamylanthraquinone, 1 - amino - 2 - methoxy - 4 - β - n - butoxyethoxycarbamylanthraquinone, 1 - amino - 2 - ethoxy - 4 - β - methoxyethoxycarbamylanthraquinone, 1 - amino - 2 - ethoxy - 4 - β - ethoxyethoxycarbamylanthraquinone, 1 - amino - 2 - ethoxy - 4 - β - methoxy-β - ethoxyethoxycarbamylanthraquinone, 1 - amino - 2-β - methoxyethoxy - 4 - β - ethoxyethoxycarbamylanthra-

quinone, 1 - amino - 2 - β - methoxyethoxy - 4 - tetrahydrofurfuryloxycarbamylanthraquinone, 1 - amino - 2-β - ethoxyethoxy - 4 - β - methoxyethoxycarbamylanthraquinone, 1 - amino - 2 - β - ethoxyethoxy - 4 - β - ethoxyethoxycarbamylanthraquinone and 1-amino-2-β-ethoxyethoxy - 4 - β - ethoxy - β - ethoxyethoxycarbamylanthraquinone, for example, are readily prepared. All these compounds yield red dyeings on the textile materials disclosed herein which have fastness properties of the character set forth hereinbefore.

Many of the intermediates used in the preparation of the new anthraquinone dye compounds of the invention are old. However, certain of the intermediates appear to be new and, accordingly, examples illustrating the preparation of the intermediate compounds are given hereinafter, even though the manner in which they are prepared is believed to be clear from the prior art.

Example 9.—Preparation of 1,4-diamino-2-β-methoxyethoxyanthraquinone

5 grams of 1-amino-4-p-toluenesulfonamidoanthraquinone-2-sulfonic acid were added portionwise, with stirring, at 80° C. over a period of about 1 hour to a melt prepared from 15 grams of KOH in 30 cc. of methyl Cellosolve and the reaction mixture resulting was stirred 2 hours longer at 80–85° C. The reaction mixture was then cooled to 40° C. and run into 500 cc. of cold water. The product which precipitated was recovered by filtration, washed with hot water and then dried.

The product obtained as described above was dissolved by stirring in 50 grams of 96% H_2SO_4 and after complete solution held at 45–50° C. for 1½ hours. The solution thus obtained was then drowned in 1000 cc. of water while keeping the temperature below 20° C. 1,4-diamino-2-β-methoxyethoxyanthraquinone precipitated and was recovered by filtration, washed with cold water until neutral to Congo red and then dried.

Example 10.—Preparation of 1,4-diamino-2-β-ethoxyethoxyanthraquinone

Example 9 is repeated except that 30 cc. of ethyl Cellosolve are used in place of methyl Cellosolve.

Example 11.—Preparation of β-methoxyethyl chloroformate

Into a 3-neck flask fitted with a stirrer, gas-inlet tube and Dry Ice trap, cooled in an ice-HCl bath, phosgene was run from a tank until 76 cc. of phosgene had collected in the flask. The stirrer was started and 76 cc. of ethylene glycol monomethyl ether were added dropwise. After complete addition of the ethylene glycol monomethyl ether, the Dry Ice trap was removed and the excess phosgene was distilled off by allowing the temperature to rise to room temperature. The residue in the flask was washed with ice water, dried over $CaCl_2$ and distilled under vacuum. The fraction boiling at 98–99° C./118 mm. was collected and consisted essentially of β-methoxyethyl chloroformate. A yield of 98.4 grams was obtained.

Example 12.—Preparation of β-ethoxyethyl chloroformate

Example 11 was repeated except that 74 grams of ethylene glycol monoethyl ether were used in place of ethylene glycol monomethyl ether. 71 grams of β-ethoxyethyl chloroformate boiling at 103° C./100 mm. were obtained.

Example 13.—Preparation of β-n-butoxy-β-ethoxyethyl chloroformate

Example 11 was repeated except that 40 grams of the monobutyl ether of diethylene glycol were used in place of ethylene glycol monomethyl ether and 45 cc. of phosgene were used instead of 76 cc. 37.8 grams of 2-β-n-butoxy-β-ethoxyethyl chloroformate boiling at 121–125° C./11–12 mm. were obtained.

Example 14.—Preparation of tetrahydrofurfuryl chloroformate

Example 11 was repeated except that 102 grams of tetrahydrofurfuryl alcohol were used in place of ethylene glycol monomethyl ether and 108 cc. of phosgene were used in place of 76 cc. of phosgene. 90.3 grams of tetrahydrofurfuryl chloroformate boiling at 60–64° C./1.0–1.2 mm. were obtained.

The new anthraquinone compounds of our invention can be used to color the polyester and the cellulose alkyl carboxylic acid ester textile materials mentioned hereinbefore by methods well known to those skilled in the art to which this invention is directed. They may be directly applied to the material undergoing coloration in the form of an aqueous suspension which can be prepared by grinding them to a paste in the presence of a sulfonated oil, soap, sodium lignin sulfonate, or other suitable dispersing agent and dispersing the resulting paste in water.

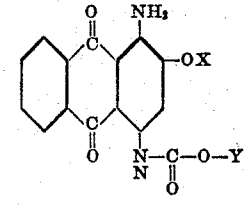
In the case of cellulose alkyl carboxylic acid ester textile materials direct dyeing operations can, with advantage, be conducted at temperatures of about 70°–90° C., but any suitable temperature can be used. Thus, the textile materials such as cellulose acetate, for example, to be dyed or colored is ordinarily added to the dye bath at a temperature lower than that at which the main portion of the dyeing is to be effected, a temperature approximating 45° C.–55° C., for example, following which the temperature is raised to that selected for carrying out the dyeing operation.

While the temperatures given in the dyeing procedure just set forth apply primarily to cellulose alkyl carboxylic acid ester textile materials, with the modifications indicated hereinafter, this dyeing procedure also applies to the dyeing of polyester textile materials. As understood by those skilled in the dyeing art somewhat higher temperatures than those set forth in the preceding paragraph are ordinarily employed when polyester textile materials, such as Dacron, are being dyed. These latter materials are ordinarily dyed at the boil and usually an assistant, commonly known as a "carrier" is employed. The "carriers" have various active ingredients, such as chlorinated benzenes and o-phenylphenol, for example, in emulsion. Dacronyx is the tradename of an illustrative suitable "carrier."

As is understood by those skilled in the dyeing art, the intensity of dyeing can be varied by varying the proportion of dye to material undergoing coloration. The amount of dye used can be, for example, ⅓% to 3% (by weight) of that of the textile material, although lesser or greater amounts of dye can be used.

We claim:

1. The anthraquinone compounds having the formula:



wherein X represents a member selected from the group consisting of methyl, ethyl, β-methoxyethyl and β-ethoxyethyl and Y represents a member selected from the group consisting of an unsubstituted β-alkoxyethyl radical, an unsubstituted β-alkoxy-β-ethoxyethyl radical and an unsubstituted tetrahydrofurfuryl radical and wherein alkoxy represents an unsubstituted alkoxy radical having 1 to 4 carbon atoms.

2. 1 - amino - 2 - methoxy - 4 - β - n - butoxy - β - ethoxyethoxycarbamylanthraquinone.

3. 1 - amino - 2 - methoxy - 4 - tetrahydrofurfuryloxy-carbamylanthraquinone.

4. 1 - amino - 2 - ethoxy - 4 - tetrahydrofurfuryloxy-carbamylanthraquinone.

5. 1 - amino - 2 - β - methoxyethoxy - 4 β - methoxy-ethoxycarbamylanthraquinone.

6. 1 - amino - 2 - methoxy - 4 - β - methoxyethoxy-carbamylanthraquinone.

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UNITED STATES PATENT OFFICE

Certificate of Correction

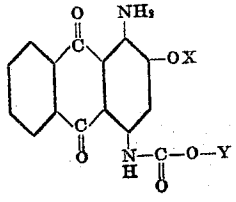
May 17, 1960

Patent No. 2,937,190

James M. Straley et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, lines 57 to 65, claim 1, the formula should appear as shown below instead of as in the patent:



Signed and sealed this 29th day of November 1960.

[SEAL]

Attest:
KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.