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2,737,517

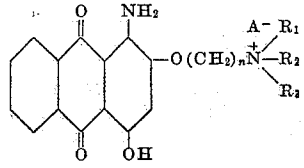
QUATERNARY AMMONIUM ANTHRAQUINONE SALTS

Samuel Neil Boyd, Jr., Salem, N. J., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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4 Claims. (Cl. 260—379)

This invention relates to the preparation of anthraquinone dyes, and more particularly to cationic anthraquinone dyes which are alkylammonium salts of 1-amino-4-hydroxy - 2 - dialkylaminoalkoxyanthraquinones of the general formula:



in which R_1 and R_2 are alkyl groups containing from 1 to 4 carbon atoms; R_3 is a member of the group consisting of alkyl containing from 1 to 4 carbon atoms and aralkyl of the benzene series; A is an anion of a quaternizing agent which does not confer insolubility to the dye molecule; and n is an integer of from 2 to 4, inclusive.

The invention has for its object to produce new cationic anthraquinone dyes particularly useful for the dyeing of polyacrylonitrile fibers in pink to red shades of good fastness properties.

In the dyeing of the new polyacrylonitrile fibers presently sold on the market under the du Pont trade name "Orlon," no dye has been found which would dye this new fiber in pink to red shades having the fastness properties that are desirable for textiles made therefrom. Dyes of the "Rhodamine" type, such as those listed in Rowe's Colour Index under numbers 749 to 752, while capable of being applied to the new polyacrylonitrile fiber, show light fastness of only 1 to 3 on the AATCC scale of 1 to 8. Various other classes of dyes have been suggested for use on this new fiber, such as the dispersed dyes commonly used on cellulose acetate, as well as water soluble sulfonic acid compounds, but none have been found to give the light fastness which characterizes the dyes of the present invention.

The quaternized ammonium salts of the compounds of the following examples all show good affinity for polyacrylonitrile fibers and dye such fibers in desirable pink to red shades which exhibit excellent light fastness (6 to 7 on the AATCC scale of 1 to 8), sublimation and wash fastness. These novel dyes also show good fastness to carbonizing treatments, which is an important property of a dye used in dyeing union fabrics of wool and polyacrylonitrile fibers.

The dyes of this invention are water soluble and are applied to the polyacrylonitrile fibers in water solutions, preferably at or near the boil. No additions to the dye bath are necessary although the cationic surface active agents may be employed when desired.

The new quaternized ammonium salts of this invention may be applied to the textiles from neutral, acid or alkaline solutions, and preferably from solutions having a pH of from 5 to 8, although a pH range of from 3 to 10 has been found to be satisfactory. This characteristic permits the dyeing of these colors on mixed goods containing cellulosic fibers or wool in conjunction with the polyacrylonitrile fibers. On dyeing such mixed goods containing wool, the polyacrylonitrile fiber is dyed without any significant staining of the wool when the dyeing is carried out in a slightly acid bath. The water soluble aliphatic acids may be employed in such dye baths together with anionic surface active agents. Union fabrics of viscose and polyacrylonitrile fibers may be dyed from acid, neutral or alkaline baths, preferably at a pH of from 5 to 8, in which case the viscose is not significantly stained.

The dyes of this application may be applied to polyacrylonitrile fibers made from either the homopolymers or the copolymers which are produced predominantly from acrylonitrile as more particularly described in U. S. Patent 2,436,926.

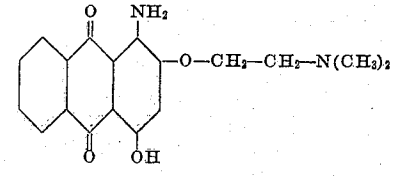
The compounds of the present invention may be prepared by reacting 1-amino-4-hydroxy-2-phenoxyanthraquinone with dialkylaminoalkanols in the presence of caustic hydroxide such as potassium hydroxide, as more particularly illustrated in Examples 1 and 2, or by carrying out the reaction in the presence of metallic sodium as more particularly illustrated in Examples 3 and 4.

The 1-amino - 4 - hydroxy - 2 - (dialkylaminoalkoxy)-anthraquinones are converted to the quaternary ammonium salts in the usual manner by reaction with short chain alkyl chlorides, bromides or sulfates, or with alkyl esters of organic sulfonic acids such as the methyl, ethyl, propyl or butyl ester of paratoluene sulfonic acid.

The following examples are given to more fully illustrate the invention. The parts used are by weight.

Example 1

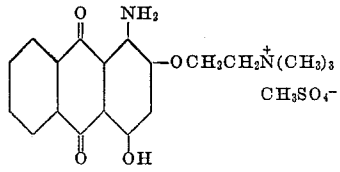
(*a*) 1-amino-2-(2-dimethylaminoethoxy)-4-hydroxyanthraquinone.



A mixture of 20.6 parts of 2-dimethylaminoethanol and 1 part of potassium hydroxide is heated at reflux for one hour and cooled to 100° C.; 5.3 parts of 1-amino-4-hydroxy-2-phenoxyanthraquinone is added and the mixture is refluxed for from 16 to 24 hours. The cooled reaction mixture is filtered and the filter cake is combined with the solid isolated from the filtrate by distillation of the excess amino-alcohol. The combined solid material is mixed with 29 parts of water plus 4.4 parts of glacial acetic acid and heated to 85° C. The mixture is filtered while hot and the filtrate, cooled to from 0° to 10° C., is rendered slightly alkaline with sodium hydroxide or aqueous ammonia solution. The precipitate is isolated by filtration, washed with water and dried. The product, 1-amino-2-(2-dimethylaminoethoxy)-4-hydroxyanthraquinone is a red solid which dissolves in aqueous acid solution with a red coloration.

(*b*) To a solution of 2.14 parts of 1-amino-2-(2-dimethylaminoethoxy)-4-hydroxyanthraquinone in approximately 19 parts of isopropanol is added 1.0 part of dimethyl sulfate. The mixture is refluxed for two hours and allowed to stand overnight. The reaction mixture is heated to from 70° to 80° C., filtered and the solid material is washed twice with approximately 20 part portions of warm isopropanol, acetone and finally petroleum ether. The dry product, methyl[2-(1-amino-4-hydroxy-2-anthraquinonyloxy) - ethyl]trimethylammonium sulfate

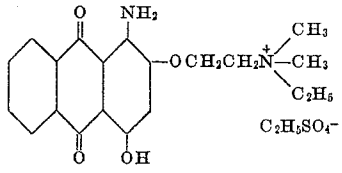
is a red powder which dissolves readily in water to yield a red solution. It has the formula:



(*c*) In a similar manner, [2-(1-amino-4-hydroxy-2-anthraquinonyloxy)ethyl]benzyldimethylammonium chloride is prepared by replacing the dimethylsulfate in (*b*) with 1.27 parts of benzyl chloride.

(*d*) In a similar manner, [2-(1-amino-4-hydroxy-2-anthraquinonyloxy)ethyl]trimethylammonium p-toluenesulfonate is prepared by replacing the dimethyl sulfate in (*b*) with 2.29 parts of methyl p-toluene sulfonate.

(*e*) In a similar manner, ethyl[2-(1-amino-4-hydroxy-2-anthraquinonyloxy)ethyl]dimethylethylammonium sulfate of the formula:



is prepared by replacing the dimethyl sulfate in (*b*) with 1.78 parts of diethyl sulfate.

(*f*) [2-(1-amino - 4 - hydroxy-2-anthraquinonyloxy)-ethyl]-dimethylethylammonium bromide is prepared by allowing a mixture of 31.8 parts of isopropanol, 1.64 parts of ethyl bromide and 1 part of 1-amino-2-(2-dimethylaminoethoxy)-4-hydroxyanthraquinone to stand at room temperature for from 48 to 72 hours. The red product, isolated by filtration of the reaction mixture, washed with petroleum ether and dried, is soluble in water with a red coloration.

Example 2

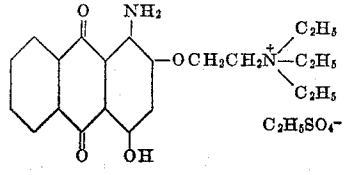
(*a*) 1-amino - 2 - (2 - diethylaminoethoxy)-4-hydroxyanthraquinone.

The procedure of Example 1–*a* for the preparation of 1-amino-2-(2-dimethylaminoethoxy) - 4 - hydroxyanthraquinone is followed, using 21.6 parts of 2-diethylaminoethanol, 5.3 parts of 1-amino-4-hydroxy-2-phenoxyanthraquinone and 1 part of potassium hydroxide. The product, 1-amino-2-(2-diethylaminoethoxy)-4-hydroxyanthraquinone, is a red solid which dissolves in aqueous acid solutions with a red coloration.

(*a*–1) In a similar manner, 1-amino-2-(2-diethylaminoethoxy)-4-hydroxyanthraquinone is prepared by replacing the potassium hydroxide in (*a*) with 0.8 part of sodium metal.

Calculated for $C_{20}H_{22}N_2O_4$: C, 67.8%; H, 6.26%; N, 7.94%. Found: C, 67.5, 67.6, 68.2%; H, 6.30, 6.44, 6.46%; N, 7.85, 7.99%.

(*b*) To a solution of 2.13 parts of 1-amino-2-(2-diethylaminoethoxy)-4-hydroxyanthraquinone in 58 parts of "Cellosolve" (2-ethoxyethanol-1) or 100 parts of isopropanol is added 1 part of diethyl sulfate. The mixture is refluxed for two hours and is then allowed to stand at room temperature for from 12 to 24 hours. The mixture is concentrated by boiling off 20% to 75% of the solvent, and the product, ethyl[2-(1-amino-4-hydroxy-2-anthraquinonyloxy)ethyl]triethylammonium sulfate of the formula:



is precipitated by cooling and/or addition of petroleum ether (normal boiling range, 30°–60° C.). This material, isolated by filtration, is readily soluble in water to give a red coloration.

(*c*) In a similar manner, methyl[2 - (1 - amino-4-hydroxy - 2 - anthraquinonyloxy)ethyl]diethylmethylammonium sulfate is prepared by replacing the diethyl sulfate in (*b*) with 0.82 part of dimethyl sulfate.

(*d*) In a similar manner, [2-(1-amino-4-hydroxy-2-anthraquinonyloxy)ethyl]diethylmethylammonium p-toluenesulfonate is prepared by replacing the diethyl sulfate in (*b*) with 1.2 parts of methyl p-toluenesulfonate.

Example 3

(*a*) 1-amino-2-(3-diethylaminopropoxy) - 4 - hydroxyanthraquinone.

A mixture of 69.2 parts of dry 3-diethylamino-1-propanol and 1 part of metallic sodium is heated to 120° C. to effect solution; 7.7 parts of 1-amino - 4 - hydroxy-2-phenoxyanthraquinone is then added and the mixture heated at a temperature of 135° to 140° C. for a period of from 16 to 20 hours. The reaction product, 1-amino-2-(3-diethylaminopropoxy) - 4 - hydroxyanthraquinone, is obtained according to the isolation procedure used for 1-amino-2-(2-dimethylaminoethoxy) - 4 - hydroxyanthraquinone in Example 1–*a*. The red product is soluble in dilute acid solutions with red coloration.

(*b*) A solution of 1 part of 1-amino-2-(3-diethylaminopropoxy)-4-hydroxyanthraquinone in 12 parts of isopropanol is treated with 2.7 parts of dimethyl sulfate. The mixture is allowed to stand at the room temperature for 48 hours and is filtered. The solid material is washed with acetone and dried. The product methyl[3-(1-amino - 4 - hydroxy-2-anthraquinonyloxy)propyl]diethylmethylammonium sulfate, is a red powder soluble in water with a red coloration.

Example 4

(*a*) 1 - amino-2-(2-di-n-butylaminoethoxy)-4-hydroxyanthraquinone is prepared from 69 parts of dry 2-di-n-butylaminoethanol, 1 part of metallic sodium and 7.7 parts of 1-amino-4-hydroxy-2-phenoxyanthraquinone according to the procedure for the synthesis of 1-amino-4-hydroxy-2-(3-diethylaminopropoxy)anthraquinone in Example 3–*a*. The product dissolves in dilute acid solutions with blue-red coloration.

(*b*) 1-amino-2-(4-dimethylamino-n-butoxy)-4-hydroxyanthraquinone is prepared from 70 parts of dry 4-dimethylamino-1-butanol, 1 part of metallic sodium and 7.7 parts of 1-amino-4-hydroxy-2-phenoxyanthraquinone according to the process described in Example 3–*a*. The product obtained dissolves in dilute acid in which it exhibits a red color.

(*c*) A solution containing 1.8 parts of 1-amino-2-(2-di - n - butylaminoethoxy) - 4-hydroxyanthraquinone, 55 parts of isopropanol and 1 part of dimethyl sulfate is allowed to stand at the room temperature for three days. The reaction product, methyl[2-(1-amino-4-hydroxy-2-anthraquinonyloxy)ethyl]di - n - butylmethylammonium sulfate, which is isolated by evaporation of the isopropanol solvent, dissolves readily in water to yield a blue-red solution.

(*d*) When the butoxy derivative obtained in Example 4–*b* is quaternized with dimethyl sulfate according to the process described in the previous paragraph, one obtains the methyl[4-(1-amino-4-hydroxy-2-anthraquinonyloxy)n-butyl]trimethylammonium sulfate which dissolves in water to give a red colored solution.

The specific examples given above disclose as anions chloride, bromide, methyl sulfate, ethyl sulfate and p-toluene sulfonate. From numerous tests it appears that the dyeing of polyacrylonitrile fibers with these quaternized compounds occurs by an ion exchange mechanism. The dye cation displaces a sodium ion or hydrogen ion associated with a sulfonate or sulfate anion present as

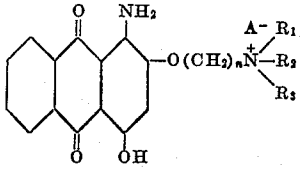
a polymer end-group in the fiber. Thus the anion associated with the cationic dye plays no important role in the dyeing process. Any anion therefore may be used as long as it does not render the cationic dye insoluble in the dye bath. The nature of the anion associated with the dye cation may be altered by the known metathetical or "double decomposition" reactions, according to the law of mass action.

As illustrative of compounds that may be used to produce the quaternary ammonium salts may be mentioned aryl- or aralkyl substituted aliphatic halides such as p—CH_3—C_6H_4—CH_2Cl or C_6H_5—CH_2—CH_2Cl, or benzyl chloride or their Br analogs. Diethyl sulfate, dipropyl sulfate, dibutyl sulfate or short chain chlorides or bromides may also be employed in the above examples.

Various organic solvents may be used in the quaternization reaction, such as acetone, monochlorobenzene, nitrobenzene, isopropanol, n-butanol, etc.

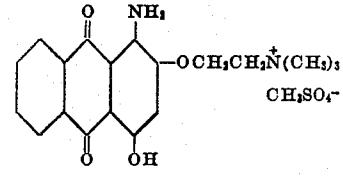
I claim:

1. Compounds of the general formula:

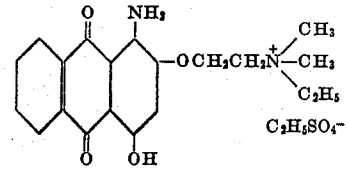


wherein R_1 and R_2 are alkyl groups containing from 1 to 4 carbon atoms; R_3 is a member of the group consisting of alkyl containing from 1 to 4 carbon atoms and aralkyl of the benzene series; A is an anion of a quaternizing agent which does not confer insolubility to the dye molecules and *n* is an integer from 2 to 4, inclusive.

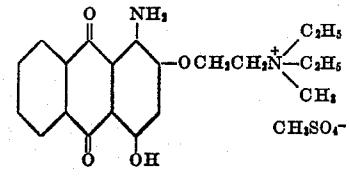
2. Compound having the formula:



3. Compound having the formula:



4. Compound having the formula:



No references cited.