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2,957,010

QUATERNARY AMMONIUM SALTS OF ANTHRAQUINONE DYE COMPOUNDS

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No Drawing. Filed Aug. 28, 1958, Ser. No. 757,679

8 Claims. (Cl. 260—377)

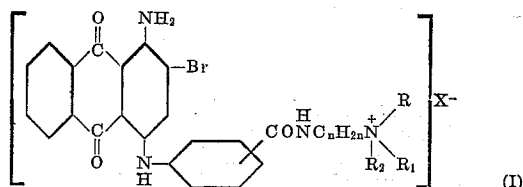
This invention relates to new anthraquinone compounds and their application to the art of dyeing or coloring.

It is well known that polyacrylonitrile fibers are difficult to dye in deep, fast shades without the use of special dyeing techniques, such as, for example, the use of pressure, "carriers" or the so-called "cuprous ion" technique involving the use of acid wool dyes. Each of these methods involves one or more disadvantages. The use of pressure involves the use of pressure equipment which is more expensive than the equipment used where no pressure is involved. The use of "carriers" involves the expense of providing the carriers. Also, when "carriers" are employed operations for the recovery of the "carrier" for reuse are involved and these recovery operations add to the expense of the dyeing operation.

While many variations in the "cuprous ion" technique have been proposed all suffer some disadvantage. One of the chief disadvantages of this method is the fact that it is almost impossible to restrict the amount of copper absorbed to such a low degree that serious browning of the dyed fabric upon exposure to light does not occur.

It is an object of the present invention to provide blue anthraquinone dyes which yield dyeings on polyacrylonitrile textile materials which have excellent fastness to light and washing. A further object is to provide water-soluble anthraquinone dye compounds which can be applied to polyacrylonitrile textile materials in water solutions. Another object is to provide new quaternary anthraquinone dye compounds capable of dyeing polyacrylonitrile textile materials deep blue shades.

The new anthraquinone compounds of the present invention by means of which the objects of the invention can be accomplished are the quaternary anthraquinone compounds having the formula:



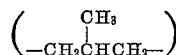
wherein R and R₁ each represents an alkyl group having 1 to 4 carbon atoms, a hydroxyalkyl group having 1 to 4 carbon atoms, a β-methoxyethyl group or a β-ethoxyethyl group, R₂ represents an alkyl group, n represents 2, 3 or 4, X⁻ is an anion and wherein



taken together also represent a morpholinyl group or a piperidyl group.

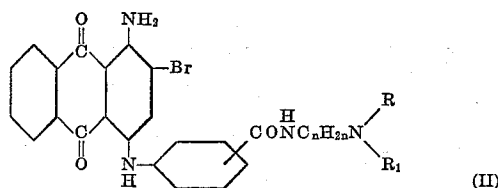
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Ethylene, trimethylene, propylene, tetramethylene and 2-methyl trimethylene:



for example, are illustrative of the alkylene radicals represented by C_nH_{2n}.

The new quaternary anthraquinone compounds of the present invention are prepared by quaternizing the anthraquinone compounds having the general formula:

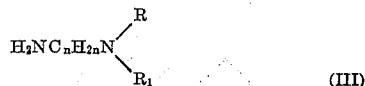


wherein n, R, R₁ and



have the meaning previously assigned to them. These compounds which are valuable dyes for polyacrylonitrile fibers, especially modified polyacrylonitrile fibers, are new compounds and are described and claimed in our copending application Serial No. 757,680, filed August 28, 1958.

The anthraquinone compounds having the formula designated II are conveniently prepared by condensing the acid chloride of the appropriate 1-amino-2-bromo-4-carboxyanilinoanthraquinone with a primary amine having the formula:



wherein n, R, R₁ and



have the meaning previously assigned to them. The acid chloride of the 1-amino-2-bromo-4-carboxyanilinoanthraquinone compound is prepared by known methods.

Quaternization of the anthraquinone compounds having the formula designated II may be carried out in an inert solvent using the known quaternizing agents. A dialkyl sulfate, an alkyl chloride, an alkyl bromide, an alkyl iodide, an aralkyl chloride, an aralkyl bromide or an alkyl ester of para-toluene sulfonic acid, for example, can be employed. Specific quaternizing agents include, for example, dimethyl sulfate, diethyl sulfate, dipropyl sulfate, dibutyl sulfate, ethyl bromide, ethyl chloride, methyl iodide, ethyl iodide, n-butyl iodide, lauryl iodide, benzyl chloride, benzyl bromide, methyl p-toluene sulfonate, ethyl p-toluene sulfonate, n-propyl p-toluene sulfonate and n-butyl p-toluene sulfonate.

Inert solvents that can be employed in the quaternization reaction include, for example, dimethyl formamide, acetone, ethylene glycol monoethyl ether, isopropanol, n-butanol, chlorobenzene and nitrobenzene.

Inasmuch as the new quaternary anthraquinone compounds of the present invention are water soluble they are applied to the polyacrylonitrile textile material from their solution in water, preferably at the boil. The property of water solubility is of real practical importance because dyes are almost exclusively applied from an

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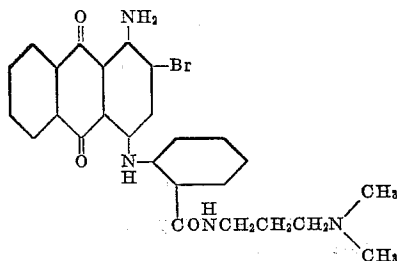
aqueous dyebath. Because the dyes are water soluble the manufacturer thereof is relieved from the costly process of preparing mixes or dispersions that will form suspensions of finely divided solids and the dyer is relieved from the necessity of adding other substances, for example, in order to prevent the suspension or emulsion from breaking. If the dye suspension or emulsion breaks, uneven dyeing of the goods results and the dye fails to deliver the full money value of which it is capable. It is interesting to note that no significant differences appear to depend upon the character of the quaternizing agent used.

The following examples illustrate the compounds of our invention and their manner of preparation.

Example 1

One gram of 1-amino-2-bromo-4-o-carboxyanilinoanthraquinone was suspended in 20 cc. of dry chlorobenzene. Two cc. of thionyl chloride were added and the reaction mixture obtained was heated on a steam bath, with stirring, until a clear solution was obtained and no further color change toward the red occurred. The solution thus obtained was cooled to 80° C., diluted with an equal volume of n-hexane and cooled to 20° C. The acid chloride thus prepared was recovered by filtration, washed with n-hexane and sucked dried. The acid chloride product thus obtained was added to 3.5 cc. of 3-dimethylaminopropylamine and the resulting mixture was warmed on a steam bath to complete solution. The reaction mixture was then poured into five times its volume of water and the reaction product which precipitated was recovered by filtration and dried at 110° C. 0.95 gram

of 1-amino-2-bromo-4-o-N-(3-dimethylaminopropyl)carboxamido]anilinoanthraquinone having the formula:



was obtained as a blue solid which dissolved readily in warm dilute HCl. It dyes polyacrylonitrile fibers blue shades having excellent fastness to light and wet processing.

Example 2

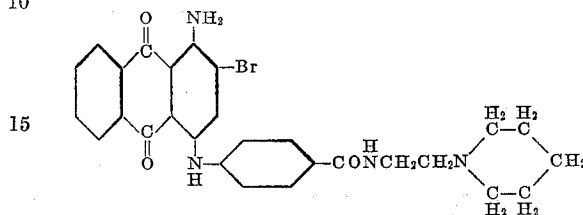
Ten grams of 1-amino-2-bromo-4-o-carboxyanilinoanthraquinone were suspended in 100 cc. of dry o-dichlorobenzene. 3.4 cc. of thionyl chloride were added and the temperature of the reaction mixture was gradually raised to 80° C. over a period of about 1.5 hours and held at this temperature for one hour while stirring. Excess thionyl chloride was removed by passing a stream of dry air through the reaction mixture at 65° C.-70° C. After cooling the reaction mixture to room temperature 2.8 grams of 3-dimethylaminopropylamine and 2.26 grams of anhydrous sodium acetate were added and the reaction mixture was stirred at 70° C.-75° C. for one hour. The reaction mixture was cooled and the product which precipitated was recovered by filtration, washed with n-hexane

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and then with hot water and dried at 110° C. 11.3 grams of product identical with that prepared in Example 1 were obtained.

Example 3

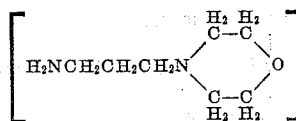
Example 1 was repeated using 1 gram of 1-amino-2-bromo-4-p-carboxyanilinoanthraquinone and 4 grams of N-(2-aminoethyl)piperidine. 1-amino-2-bromo-4-p-[N-(2-piperidylethyl)carboxamido]anilinoanthraquinone having the formula:



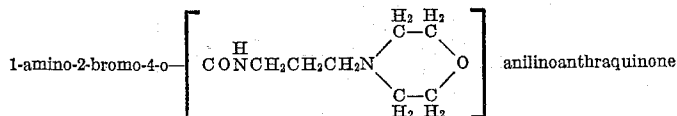
was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 4

Example 2 was repeated using 3.3 grams of 3-(4'-morpholino)propylamine



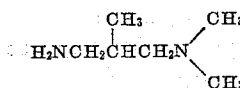
in place of 3-dimethylaminopropylamine.



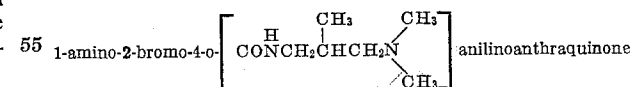
was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

Example 5

Example 2 was repeated using 3 grams of

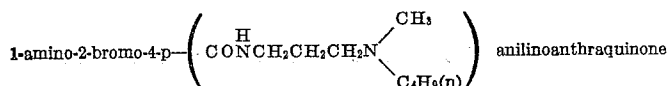


in place of 3-dimethylaminopropylamine.



was obtained as a blue solid. It dyes polyacrylonitrile textile materials blue shades which have excellent fastness to light and wet processing.

By the use of the appropriate dialkylaminoalkylamine and by following the procedure described hereinbefore, such as that described in Example 1, 1-amino-2-bromo-4-o-[N-(2-dimethylaminoethyl)carboxamido]anilinoanthraquinone, 1-amino-2-bromo-4-m-[N-(3-dimethylaminopropyl)carboxamido]anilinoanthraquinone, 1-amino-2-bromo-4-p-[N-(3-dimethylaminopropyl)carboxamido]anilinoanthraquinone, 1-amino-2-bromo-4-o-[N-(3-diethylaminopropyl)carboxamido]anilinoanthraquinone, 1-amino-2-bromo-4-m-[N-(2-diethylaminoethyl)carboxamido]anilinoanthraquinone



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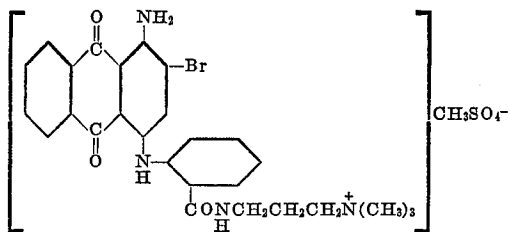
1 - amino - 2 - bromo - 4 - o - [N - (3 - di - β - hydroxyethylaminopropyl)carboxamido]anilinoanthraquinone, 1 - amino - 2 - bromo - 4 - m - [N - (4 - diethylamino - n - butyl)carboxamido]anilinoanthraquinone, 1 - amino - 2 - bromo - 4 - m - [N - (4 - dimethylamino - n - butyl)carboxamido]anilinoanthraquinone, 1-amino-2-bromo-4-o-[N - (3 - di - β - methoxyethylamino - n - propyl)carboxamido]anilinoanthraquinone and 1-amino-2-bromo-4-o-[N - (3 - di - β - ethoxyethylamino - n - propyl)carboxamido]anilinoanthraquinone were prepared.

Other primary amines having the Formula III that can be used to prepare the anthraquinone compounds having the formula II include, for example, 2-di-n-propylaminoethylamine, 2-diiso-propylaminoethylamine, 2-di-n-butylaminoethylamine, 2-(di- β -hydroxyethylamino)ethylamine, 2-(di- β -ethoxyethylamino)ethylamine, 3-(di- δ -hydroxybutylamino)propylamine, 4-(di- β -hydroxyethylamino)-butylamine and 4-(4'-morpholino)propylamine.

The anthraquinone compounds having the Formula II can be applied to polyacrylonitrile textile materials from an aqueous dyebath in the same manner that water-insoluble cellulose acetate dyestuffs are commonly applied to cellulose acetate textile materials. Thus they may be directly applied to the polyacrylonitrile textile 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 this method of dyeing the dye in finely divided condition is intimately dispersed in water and applied directly to the fiber.

Example 6

1.5 gram of the product obtained in accordance with the procedure described in Example 1 was dissolved in 15 cc. of dimethylformamide. One cc. of dimethyl sulfate was added and the reaction mixture resulting was heated at 75° C.-80° C. for 45 minutes. Upon cooling, the reaction mixture was diluted with three times its volume of hexane and the liquid was decanted from the sticky solid. The solid was dissolved in 25 cc. of water, heated to boiling and 1.5 to 2 grams of sodium chloride were added. On cooling to room temperature the solid present in the reaction mixture was recovered by filtration, washed well with a 5% aqueous solution of sodium chloride and then dried at 60° C. in vacuo. The dye product obtained is believed to have the following structure:



Example 7

0.4 gram of the dye product obtained in accordance with the procedure described in Example 1 and 3 cc. of dimethyl sulfate were warmed together on a steam bath. The resulting solution obtained was dull brown in color. After cooling, the solution was diluted with four times its volume of ether resulting in the precipitation of a sticky solid. The sticky solid was washed with ether and the ether was removed by decantation. The residue remaining after the ether decantation was boiled in 10 cc.

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of water, 1 gram of salt was added and after cooling, the product was recovered by filtration, washed well with an aqueous salt solution and dried. The product obtained is identical to that of Example 6. It dyes Verel and Orlon textile materials beautiful blue shades having excellent fastness to light and washing.

Example 8

Example 6 was repeated using 1.5 cc. of methyl-p-toluene sulfonate instead of dimethyl sulfate. Upon working up the reaction mixture in accordance with the procedure described in Example 6, a dyestuff which dyes Verel and Orlon beautiful blue shades having excellent resistance to light and washing was obtained. The dyeings obtained are indistinguishable from the dyeings obtained with the dyestuffs of Examples 6 and 7. The dyeing was carried out in accordance with the dyeing procedure described hereinafter.

Example 9

Example 6 was repeated using 1 gram of benzyl chloride as the quaternizing agent in place of dimethyl sulfate. The dyeings obtained on Verel textile materials are identical to those obtained with the dyestuffs of Examples 6, 7 and 8.

Example 10

Example 6 was repeated using 1.8 grams of butyl iodide as the quaternizing agent instead of dimethyl sulfate. The dyeing properties of the dyestuff obtained in accordance with this example are indistinguishable from those of the dyestuffs of Examples 6, 7, 8 and 9.

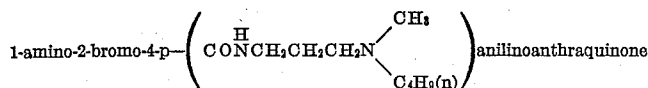
Example 11

One gram of 1-amino-2-bromo-4-m-[N-(2-diethylaminoethyl)carboxamido]anilinoanthraquinone was dissolved in 20 cc. of acetone, 1 cc. of dimethyl sulfate was added and the acetone was removed by heating on a steam bath. The sticky product obtained was ground with hexane following which the hexane was removed by decantation and the residue remaining was allowed to air-dry. The solid thus obtained was dissolved in 10 cc. of boiling water and precipitated by the addition of 1 gram of sodium chloride. The reaction product was recovered by filtration, washed well with an aqueous salt solution and dried. The dyestuff obtained in accordance with this example yields blue dyeings on Verel and Orlon textile materials which have good fastness to light and washing.

Example 12

1 - amino - 2 - bromo - 4 - p - [N - (2 - piperidylethyl)-carboxamido]-anilinoanthraquinone was quaternized with dimethyl sulfate using the procedure described in Example 6. The quaternized dye compound obtained dyes polyacrylonitrile textile materials, such as Verel and Orlon, blue shades having good fastness to light and washing.

Example 13



was quaternized with dimethyl sulfate using the procedure described in Example 6. The quaternized dye compound obtained dyes polyacrylonitrile textile materials, such as Verel and Orlon, blue shades having good fastness to light and washing.

Example 14

Example 6 was repeated using 1-amino-2-bromo-4-o-[N-(3 - di - β - hydroxyethylaminopropyl)carboxamido]anilinoanthraquinone instead of the dye product of Example 1. The quaternized dye compound obtained dyes

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polyacrylonitrile textile materials, such as Verel and Orlon, blue shades having good fastness to light and washing.

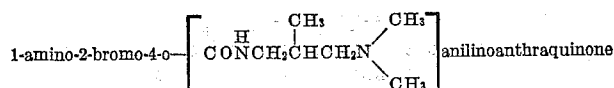
Example 15

Example 6 was repeated using the dye compound of Example 4, 1-amino-2-bromo-4-o-[N-(3-4'-morpholino-propyl)-carboxamido]-anilinoanthraquinone, instead of the dye product of Example 1. The quaternized dye compound obtained dyes polyacrylonitrile textile materials, such as Verel and Orlon, blue shades having good fastness to light and washing.

Example 16

1-amino-2-bromo-4-m-[N-(4-diethylamino-butyl)carboxamido]-anilinoanthraquinone was quaternized with dimethyl sulfate using the procedure described in Example 6. The quaternized dye compound obtained dyes polyacrylonitrile textile materials, such as Verel and Orlon, blue shades having good fastness to light and washing.

Example 17



was quaternized with dimethyl sulfate using the procedure described in Example 6. The quaternized dye compound obtained dyes polyacrylonitrile textile materials, such as Verel and Orlon, blue shades having good fastness to light and washing.

Example 18

1-amino-2-bromo-4-o-[N-(3-diethylamino-propyl)carboxamido]-anilinoanthraquinone was quaternized with dimethyl sulfate using the procedure described in Example 6. The quaternized dye compound obtained dyes polyacrylonitrile textile materials, such as Verel and Orlon, blue shades having good fastness to light and washing.

The following example illustrates how the quaternized anthraquinone compounds of the invention can be applied to polyacrylonitrile textile materials. These compounds are particularly useful in connection with the dyeing of modified polyacrylonitrile textile materials, such as Verel.

Example 19

16.7 milligrams of the dye product of Example 6 were dissolved in 200 cc. of water and 5 grams of Verel polyacrylonitrile textile material in fabric form were added. The temperature was raised to 90° C.-95° C. and 5 cc. of a 5% aqueous solution of formic or acetic acid were added. The temperature was maintained at 90° C.-95° C. for 1 hour. The goods were then removed from the dye bath, rinsed in hot water and allowed to dry. The Verel polyacrylonitrile textile material was dyed a blue color which was fast, for example, to light and washing. The blue dyeing showed no break upon 20 hours exposure in a fadeometer. Further, in a standard AATCC No. 3 wash test for synthetic materials no loss in color occurred and no staining of the undyed multifiber (nylon, cellulose acetate, cotton, silk, viscose and wool) fabric took place. Similar results are obtained when an Orlon 42 polyacrylonitrile textile material is dyed. This procedure is applicable to polyacrylonitrile textile materials generally. The textile material can be, for example, in fabric, yarn, filament or fiber form.

The primary amine compounds having the Formula III used in preparing the new anthraquinone compounds having the Formula II appear to include new as well as old compounds. Many of these amines are specifically disclosed in the prior art. Those not specifically disclosed can be prepared by the methods used to prepare the known compounds. The preferred amine 3-dimethylaminopropylamine is an article of commerce.

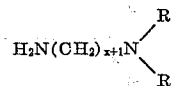
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Three general processes by which primary amines having the Formula III can be prepared are set forth hereinafter:

(1) An amine having the formula:

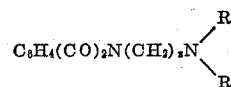


is condensed with a chloroalkylnitrile having the formula: $\text{Cl}(\text{CH}_2)_x\text{CN}$, and the product obtained is reduced by sodium-alcohol or with hydrogen over Raney nickel to give the desired product:

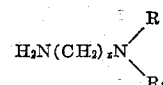


(2) Potassium phthalimide is condensed with a di-bromoalkyl compound having the formula: $\text{Br}(\text{CH}_2)_z\text{Br}$

to obtain $\text{C}_6\text{H}_4(\text{CO})_2\text{N}(\text{CH}_2)_z\text{Br}$ which is treated with IV to give

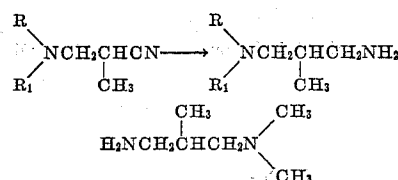


which is hydrolyzed with dilute mineral acid to give

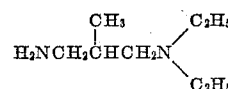


the desired product. Method 2 is the well-known Gabriel synthesis.

(3) A secondary amine is added to an unsaturated nitrile, e.g. methacrylonitrile, and the product hydrogenated to the primary amine:



and



for example, can be readily prepared by method 3 by reacting dimethylamine and diethylamine, respectively, with methacrylonitrile and then hydrogenating the products obtained to their primary amine form.

R, R₁ and



as used herein have the meaning previously assigned to them, while x is 1, 2 or 3 and z is 2, 3 or 4.

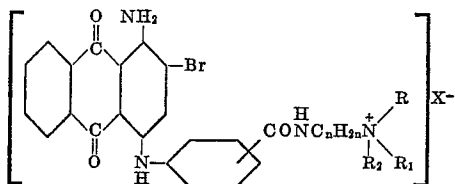
The 1-amino-2-bromo-4-carboxyanilinoanthraquinone compounds used in the preparation of the new anthraquinone compounds having the Formula II can be prepared by the procedure described in Berichte, vol. 49,

page 2167 (1916), wherein the preparation of 1-amino-2-bromo-4-o-carboxyanilinoanthraquinone is described.

As previously indicated, there appears to be no significant difference in the dyeing properties of the new quaternized anthraquinone compounds of the invention regardless of the quaternizing agent used. However, from the standpoint of ease of manipulation and economy we prefer to use dimethyl sulfate.

We claim:

1. The anthraquinone compounds having the formula:

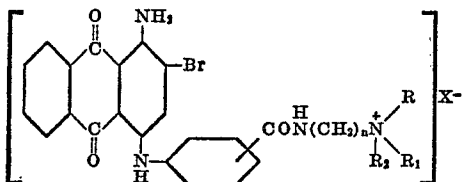


wherein R and R₁ each represents a member selected from the group consisting of an alkyl group having 1 to 4 carbon atoms, a hydroxyalkyl group having 1 to 4 carbon atoms, a β-methoxyethyl group and a β-ethoxyethyl group, R₂ represents an alkyl group, n represents a small whole number from 2 to 4, X⁻ is an anion and wherein



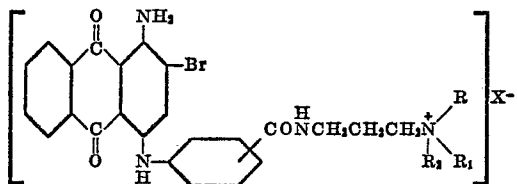
taken together represent a member selected from the group consisting of a morpholinyl group and a piperidyl group.

2. The anthraquinone compounds having the formula:



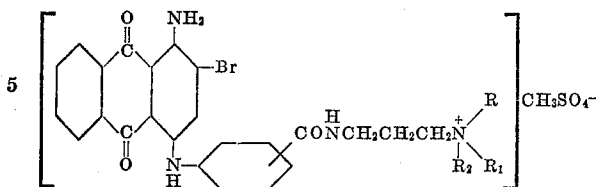
wherein R, R₁ and R₂ each represents an alkyl group having 1 to 4 carbon atoms, X⁻ is an anion and n represents a small whole number from 2 to 4.

3. The anthraquinone compounds having the formula:



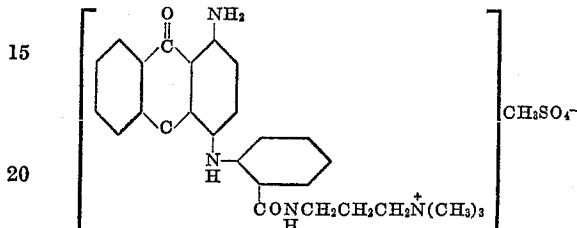
wherein R, R₁ and R₂ each represents an alkyl group having 1 to 4 carbon atoms and X⁻ is an anion.

4. The anthraquinone compounds having the formula:

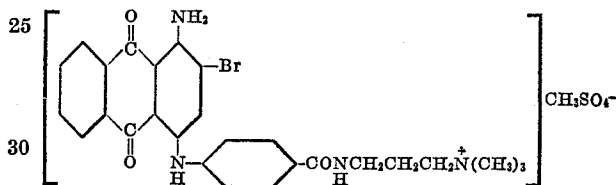


wherein R, R₁ and R₂ each represents an alkyl group having 1 to 4 carbon atoms.

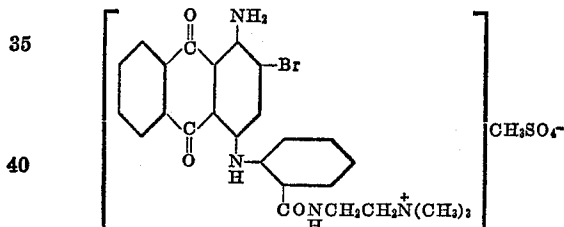
5. The anthraquinone compound having the formula:



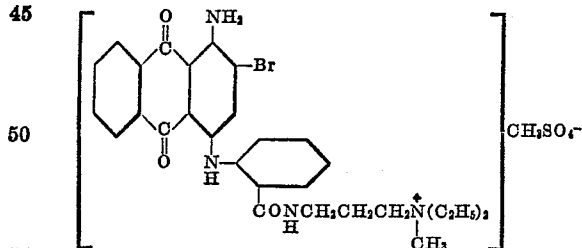
6. The anthraquinone compound having the formula:



7. The anthraquinone compound having the formula:



8. The anthraquinone compound having the formula:



References Cited in the file of this patent

UNITED STATES PATENTS

2,716,655 Boyd Aug. 30, 1955

FOREIGN PATENTS

855,541 Germany Nov. 13, 1952

UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 2,957,010

October 18, 1960

James M. Straley et al.

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

Column 1, line 27, for "the carriers," Also, " read
-- the "carriers." Also, --; column 3, line 40, for "4-o-N"
read -- 4-o-[N --; column 7, line 65, for "polyacrylontrile"
read -- polyacrylonitrile --; column 8, line 2, for "perpared"
read -- prepared --; column 9, line 10, for "anhraquinone"
read -- anthraquinone --.

Signed and sealed this 25th day of April 1961.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents