

UNITED STATES PATENT OFFICE

2,195,067

WOOL DYESTUFFS OF THE ANTHRA- QUINONE SERIES

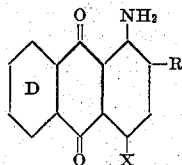
Klaus Weinand, Leverkusen-I. G. Werk, and Kurt Bamberger, Cologne-Mulheim, Germany, assignors to General Aniline & Film Corporation, a corporation of Delaware

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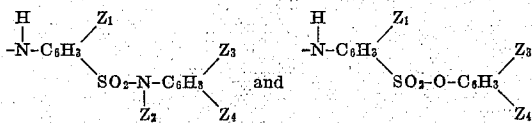
4 Claims. (Cl. 260—371)

Our present invention relates to new and valuable wool dyestuffs and to a process of making the same.

Our new dyestuffs correspond to the general formula



wherein X stands for a member of the group consisting of the radicals



Z₁ standing for a member of the group consisting of hydrogen, halogen and an alkyl radical, Z₂ standing for a member of the group consisting of hydrogen and an alkyl radical, Z₃ standing for a member of the group consisting of hydrogen, halogen, an alkyl radical and a carbalkoxy radical, Z₄ standing for a member of the group consisting of hydrogen and the SO₃H-group, and R stands for a member of the group consisting of hydrogen, halogen, an alkyl radical or the SO₃H-group.

It is to be understood that also those compounds fall into the scope of our present invention in which the carbon atoms 1,9 of the anthraquinone in the above formula form part of the pyridone or pyrimidone ring and also those compounds in which the benzene nucleus of the anthraquinone indicated in the above formula with the letter D is substituted.

Our new dyestuffs are obtained by causing aminoanthraquinones, pyridone anthrones or pyrimidone anthrones containing substituents which can be replaced by amino groups to react with monoamino-benzene sulfonic acid-arylesters or monoamino-benzene sulfonic acid-arylamides and subjecting the compounds thus obtained to a treatment with sulfonation agents or by causing 1-amino-4-halogenanthraquinone-2-sulfonic acids to react with monoamino-benzene sulfonic acid-arylesters or monoamino-benzene sulfonic acid-arylamides respectively.

As suitable sulfonation agents there may be mentioned concentrated sulfuric acid or chlorosulfonic acid.

The reaction is preferably carried out in the presence of a copper salt, such as copper acetate

or cuprous chloride, and in the presence of an acid-binding agent. Such acid-binding agents are, for instance, the alkali and earth alkali metal salts of weak acids, such as sodium acetate, sodium carbonate or sodium bicarbonate. The presence of an indifferent solvent may be advantageous. The corresponding aminoaryl sulfonic acid derivative itself employed in an excess may also act as solvent.

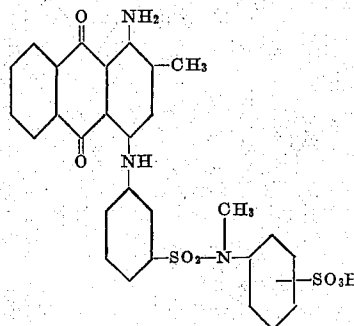
The new dyestuffs dye wool already from a neutral bath. In this respect they are superior to the hitherto known wool dyestuffs of the anthraquinone series. The dyes are also distinguished by an excellent fastness to washing and fulling.

In order to further illustrate our invention the following examples are given, but we wish it however to be understood that our invention is not limited to the particular products or the reaction conditions stated therein.

The following examples illustrate the invention without, however, restricting it thereto, the parts being by weight:

Example 1

A mixture of 52 parts of 1-amino-2-methyl-4-bromoanthraquinone, 250 parts of m-sulfanilic acid methylanilide (obtainable by condensing m-nitrobenzene-sulfochloride with methylaniline and reducing the nitro group), 50 parts of anhydrous sodium acetate and 5 parts of copper acetate are heated to 130-140° C. for 16 hours. The reaction product obtained by working up the melt in the usual manner with dilute hydrochloric acid is suitably purified by recrystallizing it from aniline; then the product is sulfonated by means of fuming sulfuric acid containing 5-10% of SO₃. The dyestuff thus obtained which corresponds to the following formula



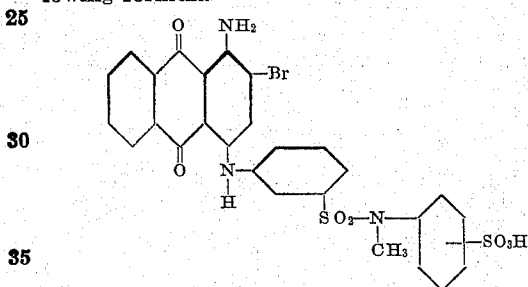
yields on wool from a neutral or weakly acid bath bright violet shades.

By using *m*-sulfanilic acid anilide or *p*-toluidide instead of *m*-sulfanilic acid methylanilide, dyestuffs of similar properties are obtained.

5 When the 1-amino-2-methyl-4-bromoanthraquinone is substituted by the equivalent quantity of 1-amino-2-methyl-4-chloroanthraquinone, dyestuffs are obtained which are identical to those as described above.

10 **Example 2**

6 parts of 1-amino-2,4-dibromoanthraquinone and 6 parts of anhydrous sodium acetate are added to 32 parts of melted *m*-sulfanilic acid methylaniline. The mixture thus obtained is heated to 120° C. for 6 hours after having been added 0.3 part of copper acetate and 0.1 part of cuprous chloride. The melt is worked up in the usual manner by adding ethyl alcohol. The reaction product obtained can be purified by recrystallizing it from organic solvents. By sulfonating it in oleum of a low percentage at room temperature, a dyestuff is obtained corresponding to the following formula

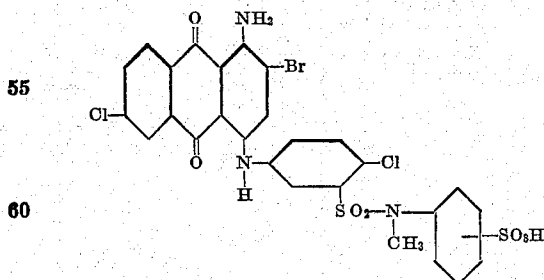


and yielding on wool from a neutral or weakly acid bath bright reddish blue shades.

40 **Example 3**

A mixture consisting of 10 parts of 1-amino-2,4-dibromo-6-chloroanthraquinone, 10 parts of anhydrous sodium acetate, 40 parts of 1-amino-4-chlorobenzene-3-sulfomethylanilide, 1 part of copper acetate and 0.1 part of copper powder is heated to 155° C. for 3 hours. The melt is worked up in the usual manner by adding ethyl alcohol.

When sulfonated the product thus obtained in oleum of a low percentage a dyestuff is obtained corresponding to the following formula



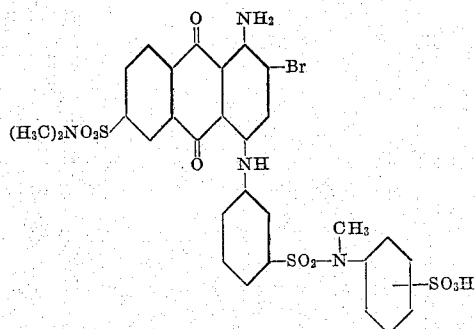
yielding on wool from a neutral or weakly acid bath bright blue shades.

By using 1-amino-4-methyl-3-sulfomethylanilide instead of 1-amino-4-chlorobenzene-3-sulfomethylanilide a similar dyestuff is obtained.

70 **Example 4**

A mixture consisting of 12 parts of 1-amino-2,4-dibromo-6-sulfdimethylamido anthraquinone, 12 parts of anhydrous sodium acetate, 60 parts of *m*-sulfanilic acid methylanilide, 0.6 part of copper acetate and 0.2 part of cuprous chloride is

heated to 140–150° C. for 4–5 hours and the melt obtained worked up in the usual manner by diluting it with hot ethyl alcohol. By dissolving the product thus obtained in sulfuric acid monohydrate and adding fuming sulfuric acid containing 20% of SO₃ a dyestuff is obtained corresponding to the following formula

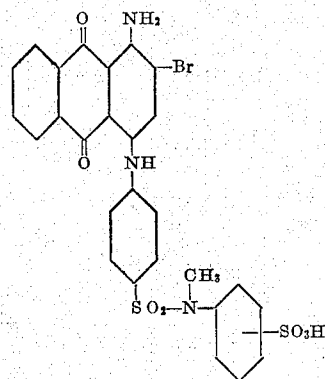


and yielding on wool from a neutral or weakly acid bath bright greenish blue shades.

A similar dyestuff is obtained by using 1-amino-2,4-dibromo-6-sulfdimethylamido anthraquinone instead of 1-amino-2,4-dibromo-6-sulfdimethylamide anthraquinone.

Example 5

A mixture consisting of 25 parts of 1-amino-2,4-dibromoanthraquinone, 25 parts of anhydrous sodium acetate, 40 parts of *p*-sulfanilic acid methylanilide (obtainable from *N*-acetyl-*p*-sulfanilic acid chloride and methylaniline and saponifying the acetyl group), 40 parts of amyl alcohol, 2.5 parts of copper acetate and 1 part of cuprous chloride is heated to 115–120° C. for about 40 hours while stirring. The melt thus obtained is worked up in the usual manner by diluting it with hot ethyl alcohol. The reaction product can be purified by recrystallizing it from 5 parts of pyridine. When sulfonated it by means of fuming sulfuric acid having a low SO₃-content a dyestuff is obtained being similar to that of Example 2 and corresponding to the following formula

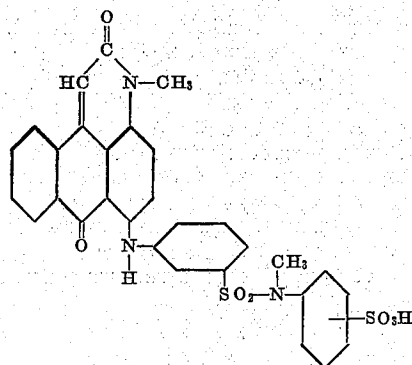


but yielding dyes of somewhat more blue shades.

Example 6

A mixture consisting of 12 parts of 4-bromo-*N*-methylanthrapyridone, 12 parts of anhydrous sodium acetate, 1.2 parts of copper acetate and 60 parts of *m*-sulfanilic acid methylanilide is heated to 180° C. for 2 hours. The reaction product is separated in form of red needles by diluting the melt cooled down to a temperature of 80° C. with hot ethyl alcohol. It can be recrystallized from a mixture of glacial acetic acid and chlorobenzene. When sulfonated in oleum of 10% at

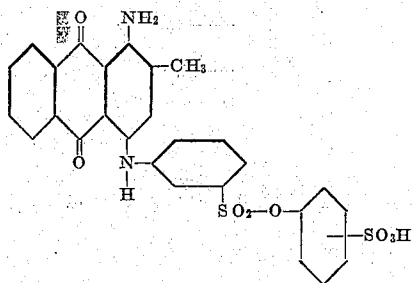
room temperature a dyestuff is obtained corresponding to the following formula



which dyes wool from a neutral or weakly acid bath clear red shades.

Example 7

A mixture consisting of 12 parts of 1-amino-2-methyl-4-bromoanthraquinone, 48 parts of m-sulfanilic acid phenylester (obtainable by condensing m-nitrobenzene-sulfochloride with phenol and reducing the nitro group), 12 parts of anhydrous sodium acetate and 1 part of copper acetate is heated to 180° C. for 2 hours while stirring. The melt is cooled down to a temperature of 80° C. and diluted with 50 parts of hot ethyl alcohol, whereby the reaction product obtained separates. It can be purified by recrystallizing it from pyridine. When sulfonated it in fuming sulfuric acid containing less than 5% of SO₃ while cooling, a dyestuff is obtained which corresponds to the following formula



and yields on wool from a neutral or weakly acid bath bright violet shades.

Dyestuffs of similar properties are obtained by using instead of m-sulfanilic acid phenylester the corresponding p-cresylester or p-chlorophenylester.

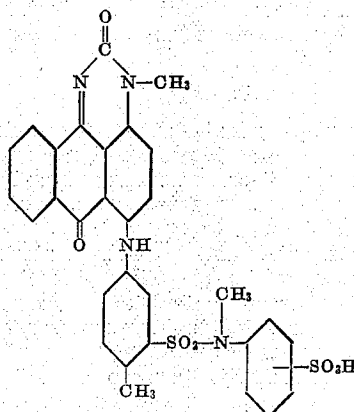
Example 8

A mixture consisting of 60 parts of melted 1-amino-4-methylbenzene-3-sulfomethylanilide, 15 parts of 1-methylamino-4-bromoanthraquinone, 6 parts of anhydrous sodium acetate and 1.5 parts of copper acetate is heated to 132° C. for 5 hours. The melt is worked up in the usual manner by diluting it with ethyl alcohol. The reaction product is purified by recrystallizing it from organic solvents.

A mixture of 5 parts of the product thus obtained, 3.2 parts of ammonium chloride and 3.2 parts of urea is heated to 184° C. for 6 hours in 45 parts of phenol, whereby pyrimidone ring formation is effected. The phenol melt is worked up in the usual manner. The reaction product thus obtained is purified by recrystallizing it from organic solvents.

By sulfonating the reaction product in weak

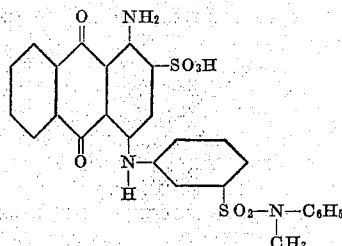
oleum a dyestuff is obtained which corresponds to the following formula



and dyes wool from a neutral or weak acid bath bright violet shades.

Example 9

10 parts of 1-amino-4-bromoanthraquinone-2-sulfonic acid sodium, 10 parts of m-sulfanilic acid-methylanilide, 10 parts of sodium bicarbonate, and 1 part of cuprous chloride is heated to boiling in a mixture of 150 parts of water and 50 parts of ethyl alcohol for 8 hours. On cooling the dyestuff obtained separates; it is filtered with suction and purified by repeatedly dissolving it in water and separating it with sodium chloride. The dyestuff crystallizes in form of needles which are soluble in water with a blue color. It corresponds to the following formula

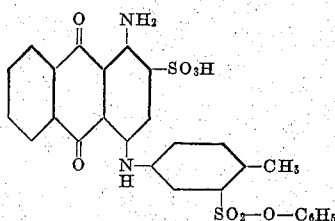


and yields on wool from an acid or neutral bath with an addition of Glauber's salt reddish blue shades.

A dyestuff of similar properties is obtained by using m-sulfanilic acid phenylester instead of m-sulfanilic acid methylanilide.

Example 10

10 parts of 1-amino-4-bromoanthraquinone-2-sulfonic acid sodium, 15 parts of 4-methylaniline-3-sulfophenylester, 10 parts of sodium bicarbonate and 1 part of cuprous bromide are heated to boiling in a mixture of 150 parts of water and 50 parts of alcohol with reflux, until the color of the solution has become brightly blue. The dyestuff which separates on cooling is worked up and purified in the usual manner. It corresponds to the following formula

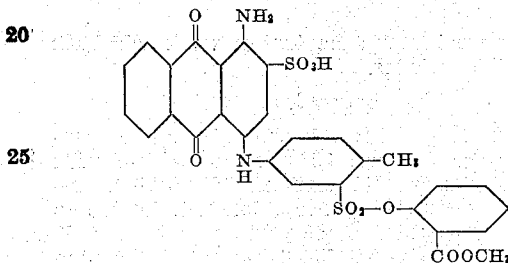


and dyes wool from an acid or neutral bath reddish blue shades.

Dyestuffs of similar properties are obtained by using instead of the 4-methylaniline-3-sulfo-phenylester the corresponding 4-methylaniline-3-p'-chlorophenylester or the 4-methylaniline-3-sulfomethylanilide.

Example 11

10 parts of 1-amino-4-bromoanthraquinone-2-sulfonic acid sodium, 15 parts of 4-methylaniline-3-sulfonic acid-2'-carbomethoxy-phenylester, 10 parts of sodium bicarbonate and 1 part of cuprous chloride are heated to boiling in a mixture of 150 parts of water and 50 parts of alcohol with reflux for several hours. The dyestuff obtained which separates on cooling is filtered with suction and purified by dissolving it in water and precipitating it with sodium chloride. It corresponds to the following formula



It crystallizes in form of blue needles which dissolve in water with a blue color and dyes wool from a weakly acid or neutral bath with an addition of Glauber's salt bright reddish blue shades.

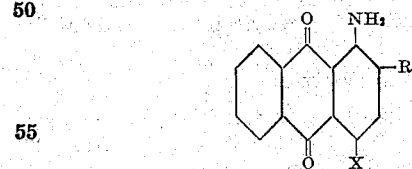
A similar dyestuff is obtained by using instead of 4-methylaniline-3-sulfonic acid-carbomethoxyphenylester the corresponding carboethoxyphenylester.

The same dyestuff may be made by reacting 1-amino-4-bromoanthraquinone-2-sulfonic acid upon 4-methylaniline-3-sulfo-o'-carboxyphenylester and subsequently esterifying the carboxyl group, for instance with dimethyl- or diethyl-sulfate in an alkaline solution.

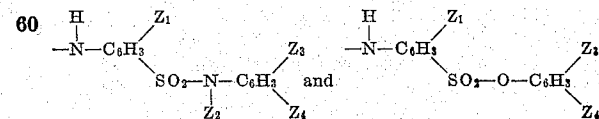
Instead of the above carboxy-phenylester derivatives also the corresponding carboxymethylanilide derivatives may be employed.

We claim:

1. Wool dyestuffs of the following general formula

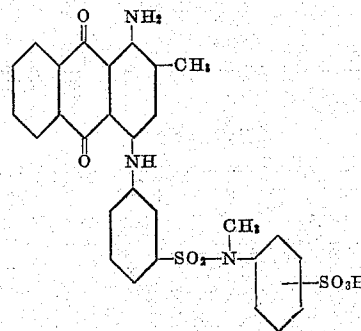


wherein X stands for a member of the group consisting of the radicals

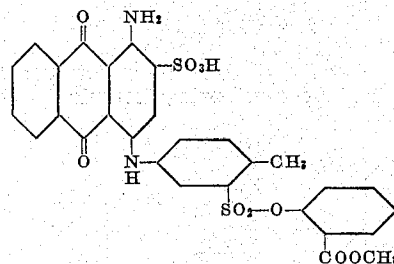


Z₁ standing for a member of the group consisting of hydrogen, halogen, and an alkyl radical, Z₂ standing for a member of the group consisting of hydrogen and an alkyl radical, Z₃ standing for a member of the group consisting of hydrogen, halogen, an alkyl radical and a carbalkoxy radical, Z₄ standing for a member of the group consisting of hydrogen and the SO₃H-group, and R stands for a member of the group consisting of hydrogen, halogen, an alkyl radical and the SO₃H-group the substituents for Z₄ and R being chosen in such a way that the compounds contain at least one sulfonic acid group.

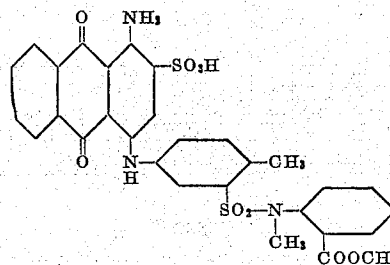
2. The compound of the following formula



3. The compound of the following formula



4. The compound of the following formula



KLAUS WEINAND.
KURT BAMBERGER.