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MORDANT DYEING PROCESS

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13 Claims. (Cl. 8—29)

This invention relates to a dyeing process wherein as dyestuffs heavy metal containing condensated imino-pyrrolenines are used. More particularly it relates to a pretreatment of the fibers used in such a process.

It is known that heavy metal-containing condensated imino-pyrrolenines such as are obtainable according to the process of German patent specification Nos. 839,939 and 914,250 (cf. also F. Baumann, B. Bienert, G. Rösch, H. Vollmann and Walther Wolf, "Angewandte Chemie," volume 68, 1956, pages 141 seq. "Isoindolenines as intermediate products in the phthalocyanine synthesis") may be used for the production of phthalocyanine dyeings (cf. also German patent specifications Nos. 861,300 and 888,837). These processes are generally carried out in such a manner that the heavy metal-containing condensated imino-pyrrolenines are mechanically applied to the fiber in a solution or suspension by a padding process or appropriate process. The fiber is then dried and the dyestuff subsequently developed by steaming in the presence of mild reducing agents or by dry heating. In practice, however, these processes suffer from disadvantages. The dry process, for example, involves the risk that the heavy metal-containing condensated imino-pyrrolenines migrate on the dyed material. Whilst with piece goods the migration may be completely avoided by a smooth conveyance of the goods and an even heat circulation in the drier, a satisfactory level dyeing cannot be achieved with yarn. On account of their small substantivity, the heavy metal-containing condensated imino-pyrrolenines cannot be dyed satisfactorily onto piece goods on the jig or reel or onto yarns in dyeing apparatus. In general in these cases only light shades are obtained even with concentrated dye-liquors. The dyeings are moreover uneven and not sufficiently through.

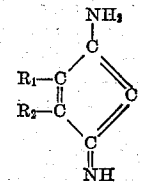
It has now been found that the above-mentioned disadvantages can be obviated by subjecting the materials to be dyed, preferably cellulose, regenerated cellulose and natural silk to a preliminary mordant with organic compounds containing acid groups. When the heavy metal-containing condensated imino-pyrrolenines are applied to the fiber thus mordanted by a conventional dyeing process, they are so strongly fixed on the fiber that even and through dyeings are obtained.

Organic compounds containing acid groups which are suitable for the process of the invention are for example compounds containing sulfonic acid, sulfinic acid or carboxylic acid groups—especially compounds of aromatic character—or phenolic groups. These compounds can belong to the most different types of compounds, a great variety of which is disclosed in the examples. There may be mentioned especially sulfurated chlorophenols or thiophenols which can be prepared according to the process described in German patent specification 572,361 and which are on the market under the designation "Katanol" or there can be used a tannin tartar emetic mordant. Furthermore there are suited 1,3,5-triazines and stilbenes which can be substituted by the most various radicals as can be seen from the examples. A large number of such compounds is enumerated in British patent specification 495,479. Compounds of the benzidine-, diphenylamine-, diaminodiphenylurea- and of

the flavonic acid series are suitable. Furthermore there can be used all substantive organic dyestuffs.

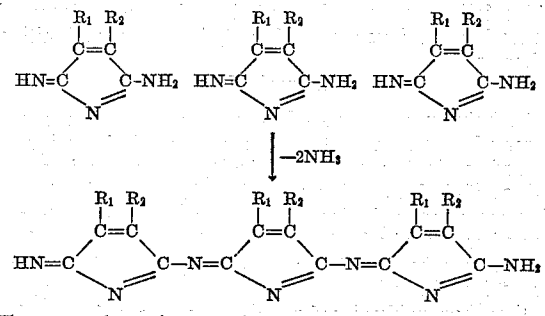
The treatment of the fibers with the compounds used as mordant can be carried out in such a manner that the materials are treated for some time with an aqueous solution of the compounds used as mordant, preferably at room temperature or somewhat elevated temperatures, for example at temperatures of 40–90° C. If desired, higher temperatures can be used as well. In most cases it is sufficient if a concentration of 2–10% of these compounds is used. Subsequently the treated materials are rinsed and then dyed with the metal-containing condensated imino-pyrrolenines.

The heavy metal-containing condensated imino-pyrrolenines which are suitable for the new process can be prepared from compounds which can be described in one of the tautomeric formulae by the formula



wherein R_1 and R_2 represent hydrogen, alkyl-, cycloalkyl-, aryl- or aralkyl radicals and where R_1+R_2 can be part of an carbocyclic or heterocyclic ring system, the heterocyclic ring system containing for example nitrogen atoms, wherein said radicals can be substituted for example by alkoxy-, aryl- or alkylmercapto groups etc.

The condensation products can be obtained therefrom by a process which can be illustrated in the case of the condensation of 3 molecules as follows:



These condensation products can contain metals if the condensation is carried out in the presence of such metal compounds. Preferably there are used condensation products obtained from 4–6 imino-pyrrolenine molecules which can form chains or ring systems.

Extremely well suited for the process of the invention are the heavy metal-containing condensated imino-isoindolenines which can be designated as well as benzo-imino-pyrrolenines and which can be obtained e.g. from 4–6 1-amino-3-imino-isoindolenine molecules under development of ammonia. These compounds have been described for example by F. Baumann, B. Bienert, G. Rösch, H. Vollmann and W. Wolf in "Angewandte Chemie," volume 68, 1956, page 141. Very well suited are also the heavy metal-containing condensation products of 2-amino-5-imino-pyrrolenines which are substituted in the 3- and/or 4-position by alkyl or aryl radicals etc. and which can be obtained by a heat treatment of the 2-amino-5-imino-pyrrolenines at temperatures up to about 65° C. in an organic solvent. Heavy metals which can be incorporated into the condensated imino-pyrrolenines are especially copper, nickel and cobalt. These condensated imino-pyrrolenines can be obtained as well from such compounds which contain instead of the above-mentioned amino group another exchangeable group, for example

an alkoxy group. They can be obtained for example by the methods described in German patent specifications Nos. 914,250; 839,939; 855,710; 852,588; 940,164; U.S.A. patent specification No. 2,683,643; or French patent specification No. 1,023,765. To produce the dyeings, the heavy-metal-containing condensated imino-pyrrolenines are dissolved in a suitable solvent, for example glycol, diethylene- or poly-ethyleneglycol or their monoethers, with the addition of an acid such as glacial acetic acid.

After the application of the heavy metal-containing condensated imino-pyrrolenines to the fiber pretreated as described above, the fibers are advantageously subjected to an intermediate rinsing and the dyestuff is then developed on the fiber. The development may be carried out either by conventional methods, for example with steam or dry heat, or with special advantage by a wet process, i.e. by treating for some time, for example half an hour, at elevated temperature in a dyebath which, depending on the dyestuff intermediate used, is rendered neutral or basic or acid, in order to attain a maximum depth of the dyeing. The dyed fiber is then subjected to a usual after-treatment by acid and subsequent alkaline soaping. In some cases a reducing treatment prior to soaping may have advantages.

The process according to this invention has the advantage that the heavy metal-containing condensated imino-pyrrolenines may be dyed onto yarns without impairing the fastness properties, thus enabling the manufacture of very fast colored fabrics. It is moreover also possible by the process of the invention to dye on the jig and especially on the reel. This is of great importance for the dyeing of goods which are sensitive to squeezing on the foulard, such as velvet. Furthermore the new process enables fibers of regenerated cellulose to be dyed and also to be printed. When using materials made of viscose (rayon), the prior methods with unmordanted fibers did not yield satisfactory results.

The following examples are given for the purpose of illustrating the invention, without, in any way, limiting it thereto.

Example 1

Preliminary mordant.—Cotton yarn or viscose rayon is treated with 5 percent aqueous tannin solution (liquor-to-goods ratio 20:1) by introducing the goods into the bath at 60–70° C. and leaving them in the cooling liquor with occasional agitating for 2–4 hours. The goods are then after-treated with 2.5 percent of antimony potassium tartrate in a bath having a liquor-to-goods ratio of 20:1 for half an hour in order to fix the tannin. The goods are then thoroughly rinsed and advantageously dyed moist. As dyestuffs there can be used for example one of the following dyestuffs:

(*a*) 2.5 grams of the condensated copper-containing imino-isoindolenine obtained according to the process described in Example 18 of German patent specification No. 914,250 by heating phthalodinitrile with alcoholic sodium methylate solution in the presence of benzene for some time to about 35° C., adding subsequently at a temperature of 20° C. copper acetate and stirring then the reaction mixture for some time at the same temperature are pasted with 7.5 grams of diethyleneglycol and carefully dissolved in 12.5 grams of glacial acetic acid. After 15 minutes the solution is made up with cold water to one liter. A pre-mordanted cotton skein (10 grams) is dyed in 200 milliliters of this bath at room temperature for 30 minutes. The skein is then rinsed, introduced into boiling water, which contains 3 grams of sodium carbonate and 0.5 gram of sodium bisulfite per liter, and the dyeing is developed on a boiling water bath within a half hour. The skein is then treated in a bath containing 3 grams of concentrated hydrochloric acid per liter at 60–70° C. for 10 minutes and, after a short intermediate rinsing, boiled and soaped with Marseilles soap and a sodium carbonate solution containing 2 grams per liter for half an hour.

(*b*) 1.5 grams of the condensated cobalt-containing pyrrolenine obtained according to Example 1 of German patent specification No. 940,164 by heating a mixture consisting of 50 parts of phthalic acid anhydride, 60 parts of urea, 12 parts of anhydrous cobalt chloride, 8.2 parts of ammonium nitrate and 0.1 part of ammonium molybdate in 120 parts of nitrobenzene for 1 hour at 140° C. while stirring and thereafter at 160–170° C. until besides the blue needles of cobalt phthalocyanine, brownish yellow crystals of a complex cobalt compound is obtained and subsequently 4–5 hours at a temperature within the range of 170–205° C. until the blue crystals of the cobalt phthalocyanine have disappeared and then heating the compound obtained with an equivalent amount of ethylene diamine in methanolic solution for about 20 minutes are pasted with 4.5 parts of diglycolmonoethylether and dissolved with 7.5 grams of glacial acetic acid with good stirring. After 15 minutes this solution is diluted with cold water to 1 liter. A pre-mordanted cotton yarn is treated in this bath at a liquor-to-goods ratio of 20:1 at room temperature for 30 minutes. After short rinsing, the material is left in boiling water which contains 1 milliliter of concentrated formic acid and 0.5 gram of zinc sulfoxylate per liter for 30 minutes and then treated in an acid bath containing 3 grams of concentrated hydrochloric acid per liter at 60–70° C. for 5 minutes. Subsequently the yarn is first boiled in a bath containing 1 gram per liter of sodium carbonate and 0.5 gram per liter of hydrosulfite and then soaped in usual manner in a soda alkaline medium.

(*c*) 1 gram of the condensated copper containing imino-isoindolenine obtained according to Example 19 of German patent specification No. 914,250 by heating phthalodinitrile with sodium methylate in the presence of pyridine for about 1 hour at 60° C. and thereafter adding at 20° C. copper acetate, keeping the solution at the same temperature for 1 hour and thereafter precipitating a copper complex compound with water is pasted with 3 grams of diglycolmonoethylether and dissolved by the addition of 5 grams of glacial acetic acid with good stirring. After 15 minutes the solution is made up with cold water to 1 liter. A pre-mordanted skein of viscose rayon is treated in this solution at a liquor-to-goods ratio of 20:1 at room temperature for 45 minutes. The skein is then rinsed and the dyeing is developed on a boiling water-bath in a bath containing 3 grams per liter of sodium carbonate during 30 minutes. The skein is then after-treated as described in Example 1.

(*d*) Instead of the pyrrolenine mentioned under (*a*) there can be used as well the pyrrolenine obtained as follows:

A solution of 5.2 mols of 1,3-diimino-isoindolenine in a solution of anhydrous methanol is reacted with 1 mol of copper acetate and the reaction mixture is heated under reflux and stirring slowly up to the boiling point until the development of ammonia is finished. Thereby crystallizes a copper complex compound which is—according to the analysis—a copper-penta-imino-isoindolenine. This compound is filtered off, washed with methanol and dried. An olive colored powder is obtained which is soluble in pyridine with brownish-yellow color.

(*e*) Instead of the pyrrolenine mentioned under (*a*) there can be used as well the pyrrolenine obtained as follows:

To a solution of 25 grams of methoxy-phthalodinitrile in 116 milliliters of methanol gaseous ammonia is added at 20° C. until the solution is saturated. Thereafter there are added 8 milliliters of sodium methylate, containing 3.8% of sodium, and the reaction mixture is heated slowly to about 55° C. while introducing gaseous ammonia until a sample is soluble in 5% acetic acid. Thereafter there are added 130 milliliters of methanol and the methanol is subsequently distilled off to remove the ammonia. Then there is added the same amount of methanol, and 4.2 grams of anhydrous copper chloride

dissolved in 50 milliliters of methanol are added. After addition of 25 milliliters of sodium methylate solution (containing 6% of sodium) the reaction mixture is kept for 2 hours at 20° C., then 3 hours at 35° C. and then 10 hours again at room temperature while stirring. Upon removing the solvent 24 grams of a yellowish-olive colored copper-containing pyrrolenine is obtained.

(*f*) Instead of the pyrrolenine mentioned under (*a*) there can be used as well the pyrrolenine obtained as follows:

520 grams of 4-aza-1,3-diimino-isoindolenine nitrate are dispersed in 1.5 liters of methanol and then there are added 125 grams of sodium hydroxide as a 10% methanolic solution. Subsequently 91 grams of copper acetate are introduced and the temperature of the reaction mixture is slowly raised within 3 hours up to about 65° C. Then the reaction mixture is heated for another 3 hours while slowly boiling. The mixture is then introduced into 6 liters of water and the precipitate is washed with water and dried. The copper complex obtained is a yellowish-olive colored powder which dissolves in formamide at room temperature to about 90%. By heating this formamide solution a dark-brown tetra-azo-copperphthalocyanine precipitates from the solution.

(*g*) Instead of the pyrrolenine mentioned under (*a*) there can be used as well the pyrrolenine obtained as follows:

40 grams of 2-amino-5-imino-3,4-dimethyl-pyrrolenine nitrate are dissolved in 400 milliliters of methanol by adding 1–2 milliliters of concentrated aqueous ammonia. Thereafter there are added 9 grams of nickel chloride ($NiCl_2.6H_2O$) and the mixture is heated for half an hour to the boil, then it is filtered and from the filtrate the solvent is evaporated at room temperature. The residue is digerated with 200–300 milliliters of water and the remaining red-brown nickel complex compound isolated.

Example 2

5 percent of a sulfur-treated chlorophenol compound known under the trademark "Katanol ON" (see also German patent specification 572,361) are dissolved in hot water with an addition of 3 percent of anhydrous sodium carbonate. After diluting this solution to a liquor-to-goods ratio of 12:1, 40 percent of common salt are slowly added. Viscose (rayon) is introduced into this bath at 60–70° C. and treated at this temperature for an hour. It is thoroughly rinsed and may then be dyed e.g. as follows:

The dyeing is carried out with the condensated nickel-containing imino-isoindolenine obtainable according to Example 20 of German patent specification No. 914,250 by treating phthalodinitrile with alcoholic sodium methylate solution in the presence of pyridine at a temperature of 20–30° C. and subsequently for 1 hour at 60° C.; thereafter at 20° C. nickel chloride is introduced into the reaction mixture and the reaction mixture is stirred at the same temperature for another hour, in the same manner as described in Example 1. To obtain a full brilliancy and the desired final shade, the dyeing is after-treated in a hot bath containing per liter 1 gram of sodium carbonate and 0.5 gram of hydrosulfite for 5 minutes and then thoroughly rinsed.

Example 3

500 grams of cotton cross-wound bobbins are treated with an aqueous solution of 300 grams of sodium chloride and 5 grams of the condensation product obtained from 2 mols of cyanuric chloride with 1 mol of the sodium salt of 4,4'-diamino-diphenyl-3,3'-disulfonic acid in 10 liters of water at 20–25° C. for about 15 minutes. Thereafter there are added 50 grams of sodium carbonate to the solution and the cotton yarn is moved in this solution for another 45 minutes. Thereafter the cotton is rinsed and then soaped at the boil for 15 minutes in a bath containing 30 grams of soap and 20 grams of sodium carbonate in 10 liters of water.

20 grams of the condensated copper-containing imino-isoindolenine described in Example 1(*a*) are pasted with 60 grams of diethylene glycol and dissolved with 100 milliliters of glacial acetic acid. After 15 minutes the solution is made up with cold water to 10 liters. The cotton cross-wound bobbins treated as described in the one paragraph of this example are dyed in this dye bath for about 30 minutes at a temperature of 20–25° C. Thereafter the dyeing is rinsed and subsequently treated in a bath containing 50 milliliters of sodium hydroxide solution (38° Bé.) and 20 grams of sodium hydrosulfite in 10 liters of water for about 20 minutes at 50–60° C. After the rinsing the dyed material is soaped at the boil in a bath containing 30 grams of soap and 20 grams of sodium carbonate in 10 liters of water. The yarn is then dyed in a blue shade.

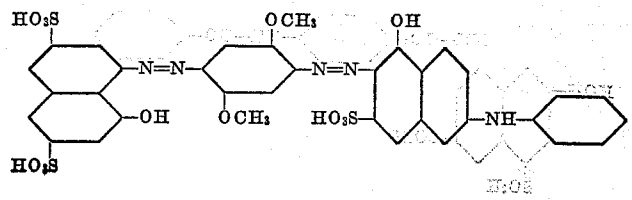
Instead of the condensated copper-containing imino-isoindolenine used as described before there can be used as well the condensation product obtained according to Example 1(*e*) from methoxy-phthalodinitrile. In this case a blueish-green dyeing is obtained.

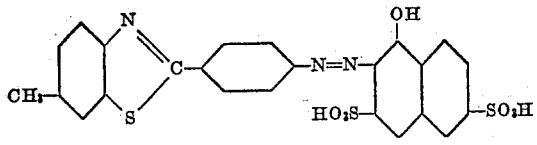
As mordant there can be used instead of the condensation product of cyanuric chloride with the sodium salt of 4,4'-diamino-diphenyl-3,3'-disulfonic acid, for example the condensation products from cyanuric chloride with the alkali salt of 4,4'-diamino-diphenyl-urea-3,3'-disulfonic acid or the alkali salt of 4,4'-diamino-diphenyl-amino-3,3'-disulfonic acid or corresponding condensation products from cyanuric chloride and substituted aromatic mono- or diamino compounds, containing sulfonic acid groups. Condensation products of this kind can be obtained, for example by dissolving cyanuric chloride in acetone and adding to this solution an equivalent amount of an aqueous solution of such an amine at temperatures of about 0° C. During this addition the reaction mixture is kept slightly acid to neutral by adding alkaline agents. As soon as the diazotation and the coupling show that the solution does not contain free amino groups the condensation product is precipitated by acidifying the reaction mixture or by salting out.

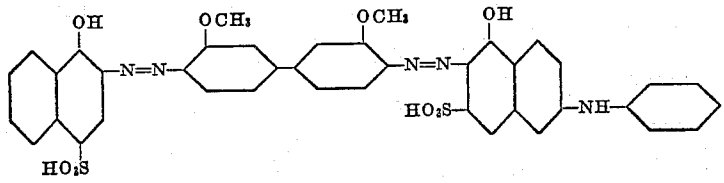
Example 4

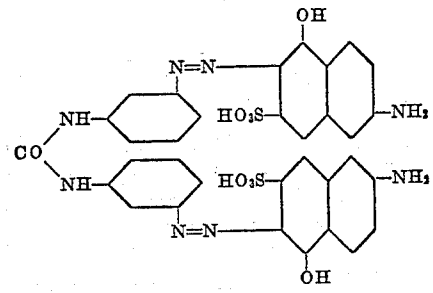
Yarns of cotton, regenerated cellulose or natural silk are treated with a 1 percent aqueous solution of 4,4'-diamidobenzoyl-diphenylurea-3,3'-disulfonic acid (liquor-to-goods ratio 20:1) at room temperature for 30 minutes. After removal of the water the dyeing is effected as described in Example 1.

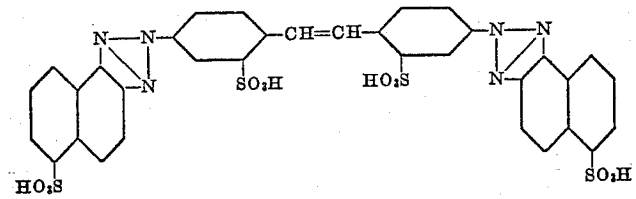
Instead of 4,4'-diamidobenzoyl-diphenylurea-3,3'-disulfonic acid it is also possible to use 4,4'-diamidotoluyl-diphenylurea-3,3'-dimethyl-diphenyl, N,N'-dibenzoyl-benzidine-3,3'-disulfonic acid or the 1,3,5-triazines known from the British patent specification No. 495,479 or the compounds described in German patent specification No. 640,908 on pages 1 and 2 as Nos. 1–19, or for example the following compounds:

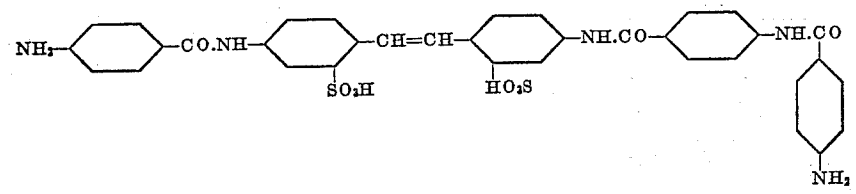


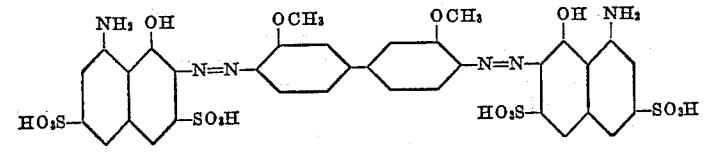


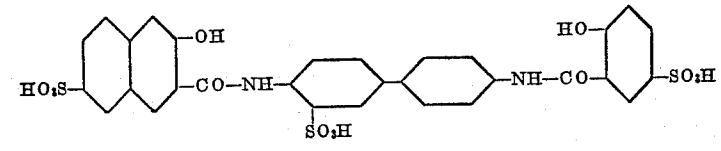


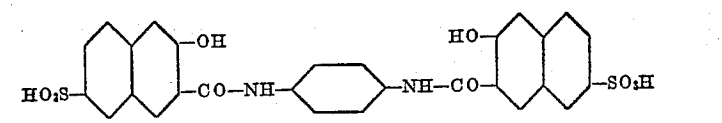


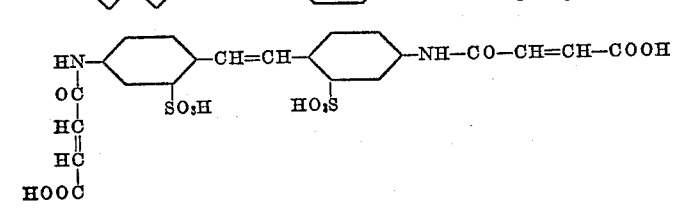


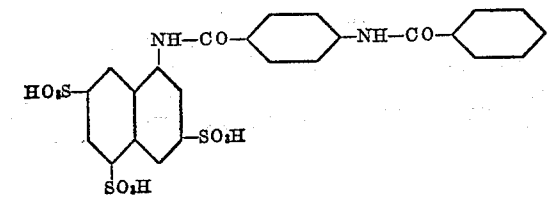


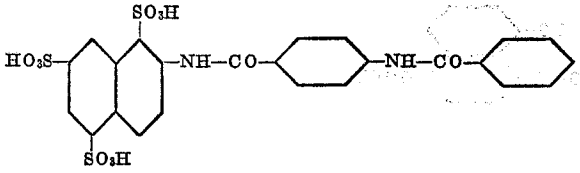


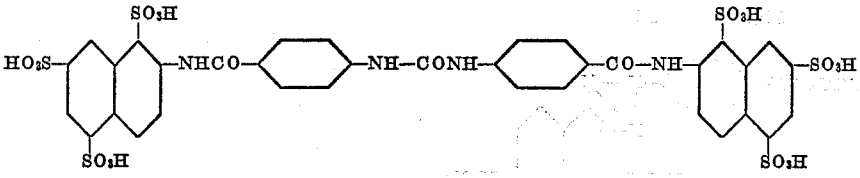


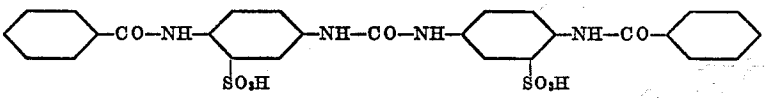


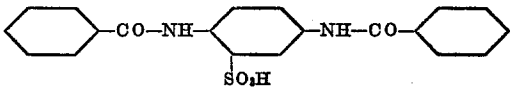


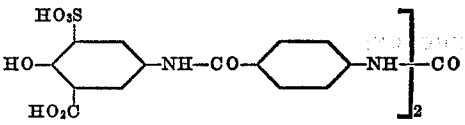


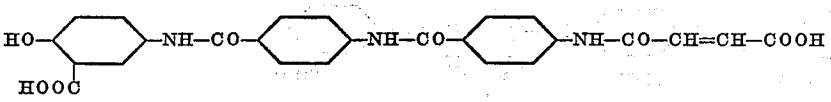


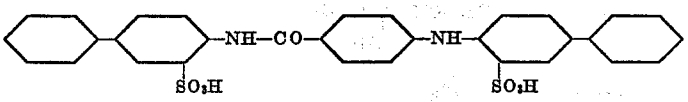


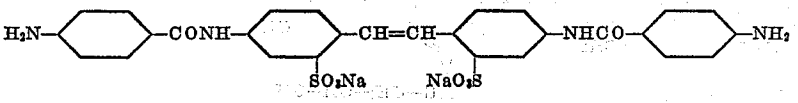


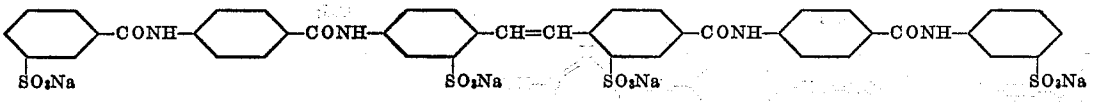


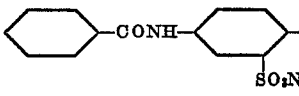


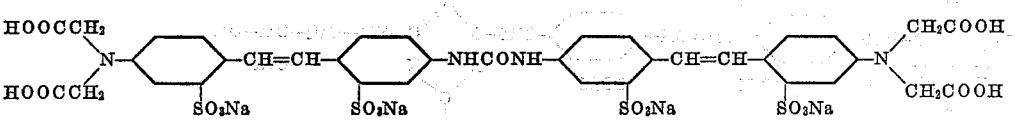


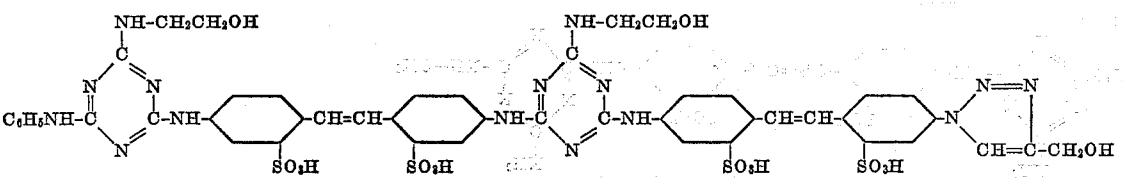


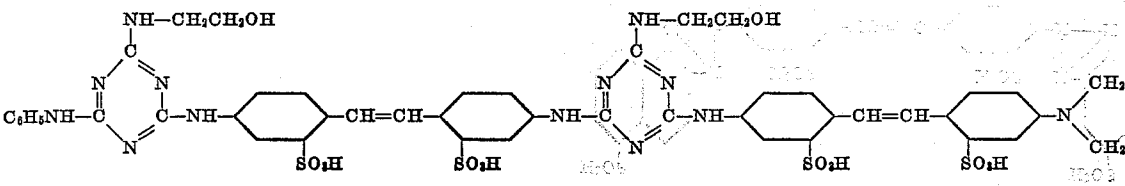


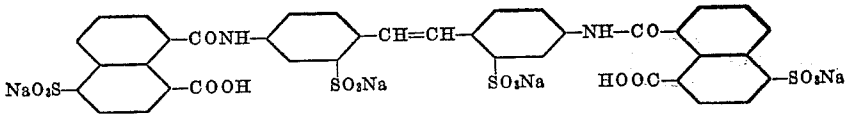


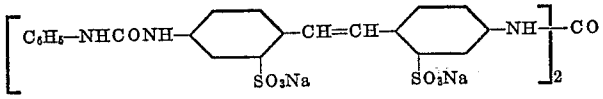


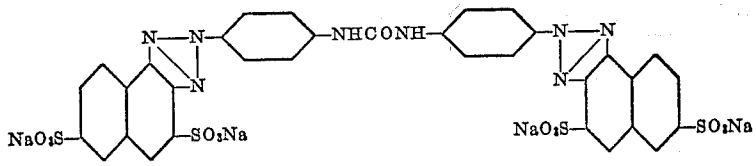


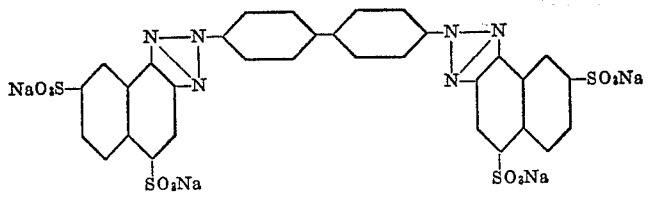


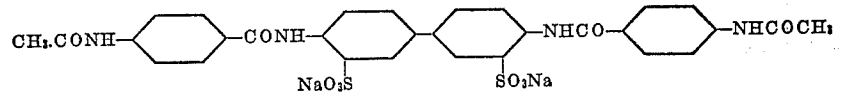


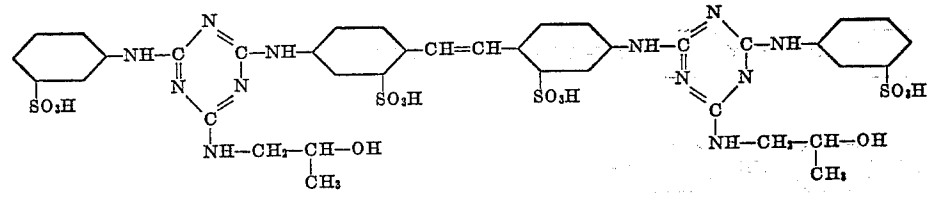


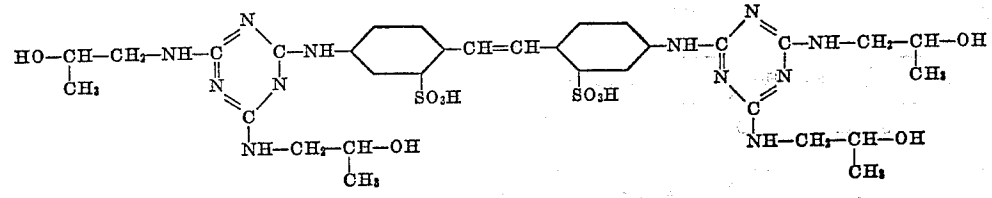


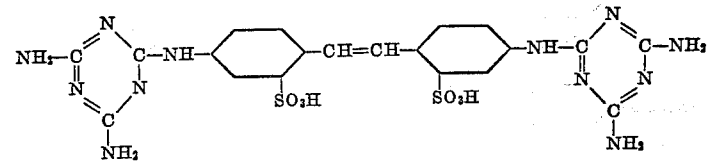


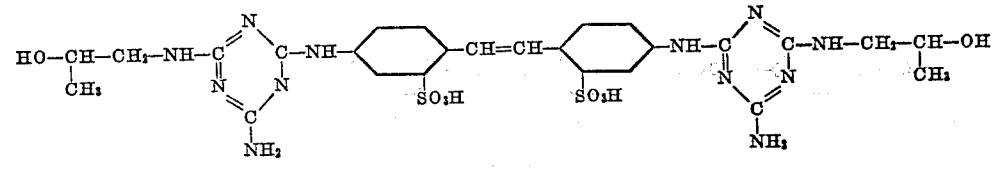


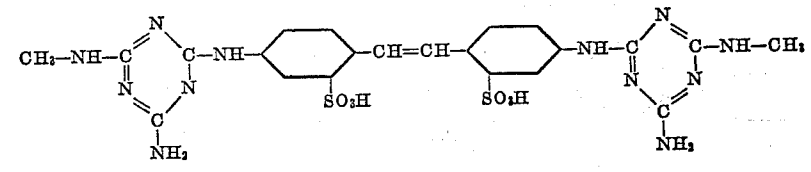


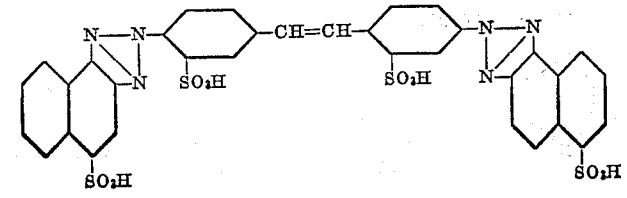


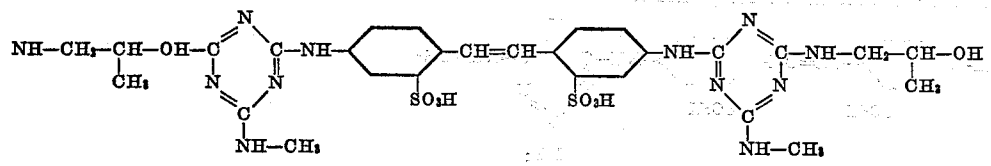


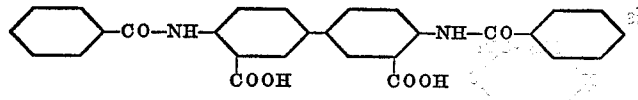


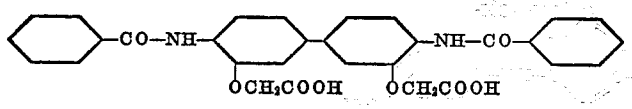


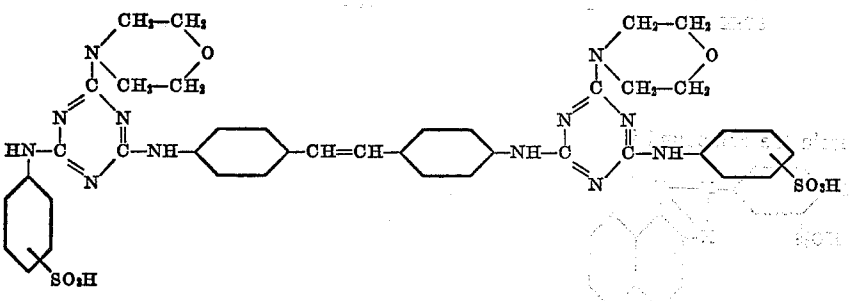


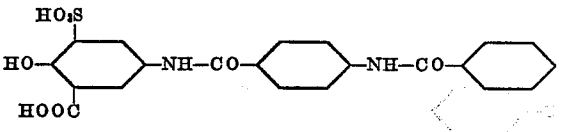


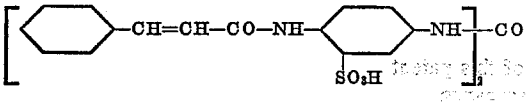


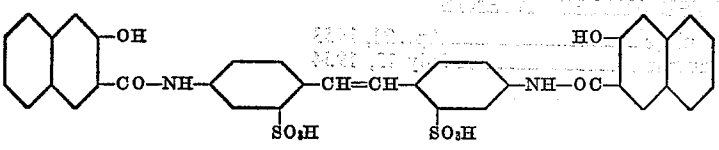


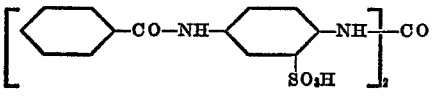


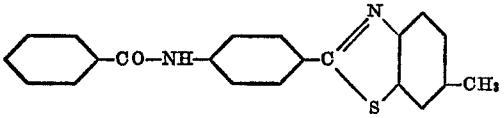


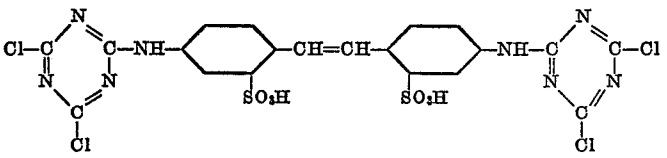












I claim:

1. In a process for dyeing and printing a textile material with heavy metal-containing condensated iminopyrrolenines, the improvement which comprises pretreating the textile material with a compound selected from the group consisting of a sulfurated chlorophenol, a sulfurated thiophenol, a tannin tartar emetic mordant, a sulfonated member of the benzidine series, a sulfonated member of the diphenylamine series, a sulfonated member of the diamino-diphenylurea series, a sulfonated member of the stilbene series, and a sulfonated substantive azo dyestuff.

2. A method of claim 1 wherein the process is the slop-padding process.

3. A method of claim 1 wherein the process is a dyeing process from a dye bath.

4. A method of claim 1 wherein the process is a printing process.

5. A process according to claim 1 wherein the compound is a sulfonated member of the diamino-diphenylamine series.

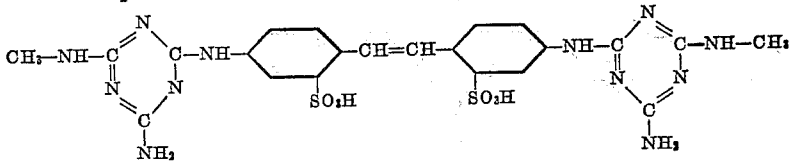
6. A process according to claim 1 wherein the compound is a sulfonated member of the benzidine series.

7. A process according to claim 1 wherein the compound is a sulfonated member of the stilbene series.

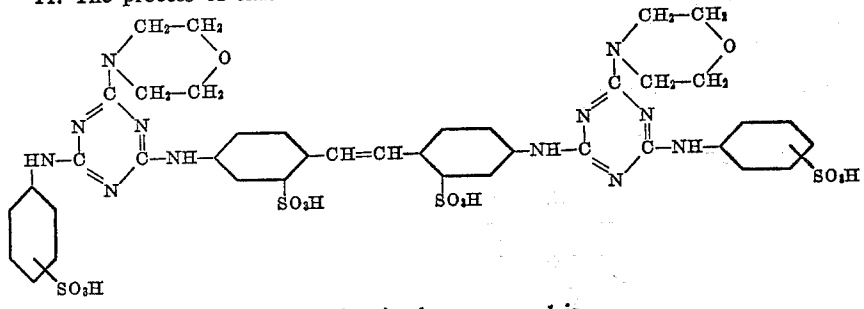
8. A process according to claim 1 wherein the compound is a sulfonated substantive azo dyestuff.

9. The process of claim 1 wherein the compound is N,N'-dibenzoyl-benzidine-3,3'-disulfonic acid.

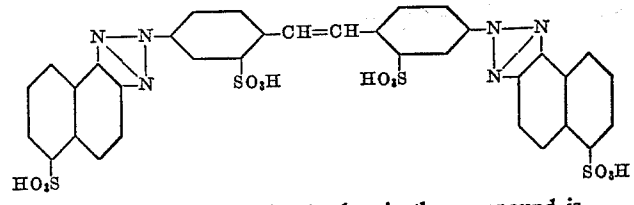
10. The process of claim 1 wherein the compound is



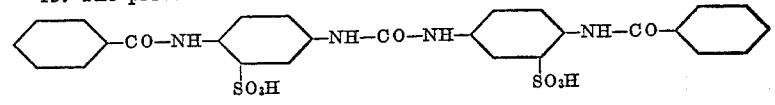
11. The process of claim 1 wherein the compound is



12. The process of claim 1 wherein the compound is



13. The process of claim 1 wherein the compound is



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