Patented June 11, 1940 2,204,229

UNITED STATES PATENT OFFICE

2,204,229

AZO DYES

Swanie S. Rossander and Chiles E. Sparks, Wilmington, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application March 29, 1939, Serial No. 264,836

10 Claims. (Cl. 260—145)

This invention relates to azo dyes, to direct dies, to dyes after-treated with formaldehyde, and to metallized dyes.

Direct azo dyes are those which dye the cloth directly from a water bath without subsequent treatment to bring out the color. Many examples of such direct dyes are recorded in the literature of the trade. These direct colors are generally substantive to cotton and other forms of cellulose and regenerated cellulose, giving bright shades, but having only moderate fastness to light. These direct colors show considerable loss in strength and impart an undesirable stain to associated uncolored or differently colored fibers when they are washed. Direct colors with good washing fastness, and which will not stain associated fibers are desired by the trade, because of their low cost and ease of application. In order to provide dyes which do not have poor fastness to washing the art has been forced to use the developed colors, wherein an intermediate, usually a direct dye, is azotized on the fiber and developed with suitable coupling compounds. These, so-called developed or diazo colors are generally faster to washing than the corresponding direct colors, but they are duller, more costly, more costly to apply as such dyeings require much time and labor and the dyeings change shade during development.

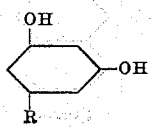
It is an object of this invention to provide a class of colors having the simplicity of application and constant, bright shade of the direct colors, and washing fastness superior to the direct colors. Another object of the invention is to provide methods of applying the colors and of increasing their light fastness.

The objects of the invention are accomplished in general by applying to the material to be dyed, the direct tetrazo dyes represented by the formula

$$A{\leftarrow}X{\rightarrow}Y{\rightarrow}Z{\rightarrow}w$$

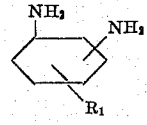
and after-treating the dyed fabric with formaldehyde, formaldehyde and a soluble metal salt, or a soluble metal salt.

The symbol A in the foregoing formula is a meta-dihydroxy benzene represented by the formula



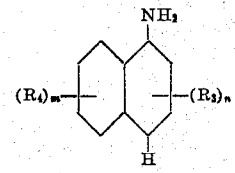
in which R is one of a group consisting of hydrogen, alkyl, alkoxy, hydroxy, amino, halogen, CN, carboxyl and sulfonic acid.

The symbol X is a meta- or para-diamino benzene represented by the formula



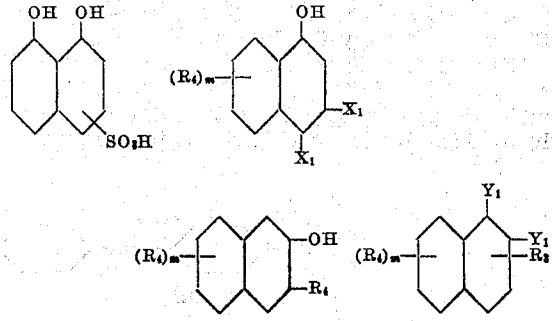
in which R_1 is any one or any combination of the group consisting of hydrogen, alkyl, alkoxy, nitro, nitrile, sulfonic acid and carboxy and is substituted once to four times in any of the unoccupied positions of the benzene nucleus.

The symbols Y and Z are alike or different naphthylamines which are represented by the formula



in which R_3 is any one or any combination of a group consisting of hydrogen, alkyl and alkoxy, n is 1 or 2, R_4 is any one or any combination of a group consisting of hydrogen, alkyl, alkoxy, sulfonic acid and carboxy and m is an integer 1 to 2. The symbol H means that the position occupied thereby is unsubstituted.

The symbol w is one of a class of compounds represented by the formulae



in which R_3, and m have the same significance

and may be substituted once or more than once where they are so indicated as in the compounds Y and Z, R_4, is one or any combination of a group consisting of hydrogen, alkyl, alkoxy, sulfonic acid and carboxy, one X_1 is sulfonic acid and the other is hydrogen and one Y_1 is hydroxy and the other is hydrogen.

In making the tetrakisazo compounds of the invention, one of the amino groups of the compound X is blocked by forming the mono-oxalyl or mono-acyl compound thereof, or by any other satisfactory blocking process, the free amino group of the compound is then diazotized, and the compound is coupled to the compound Y. the product $X \rightarrow Y—NH_2$ having a blocked amino group on the component X is diazotized and then coupled to a compound Z. The product $X \rightarrow Y \rightarrow Z—NH_2$ is diazotized and coupled to the compound *w*. The blocked amino group on the component X of the compound $X \rightarrow Y \rightarrow Z \rightarrow w$ is unblocked as by hydrolizing, diazotized, and then coupled to the compound A.

In this specification the substituents represented by R_1, R_3 and R_4 may be substituted once or more than once in the nucleus depending upon the number of open positions in the nucleus, except when the number of substituents is otherwise limited by the symbols *n* or *m*. For example, when there are four open positions in the nucleus, it can be substituted by three hydrogens and an alkoxy, or two alkyl, a halogen, and a hydrogen, or any other combination of members of the R substituents. In the formulae the symbol H attached to a ring means that the indicated position is unsubstituted.

The following examples are illustrative of the preferred colors and methods of preparing them. The invention is illustrated by, but not limited by the examples.

EXAMPLE I

Slurry 72 parts of 4-oxalylamino-1-amino benzene with 1500 parts of water. Add 6.8 parts of 100% ammonia as a water solution or a sufficient quantity for a complete solution which is slightly alkaline to Brilliant Yellow. Add 28 parts of 100% sodium nitrite as a 30% solution. Ice the solution to 5° C. Diazotize by slowly running this solution into a mixture of 500 parts of water and 51 parts of 100% hydrochloric acid which is iced to 5° C. Maintain a temperature of 5–10° C. during the diazotization and a slight excess nitrite for 20–30 minutes.

Slurry 90 parts of 1-amino-naphthalene-6-sulfonic acid and 2000 parts of water. Add approximately 23 parts of sodium carbonate and stir to complete solution. Add 105 parts of crystalline sodium acetate. Ice to 10° C.

Add the diazo slowly during 10–15 minutes to the 1-amino-naphthalene-6-sulfonic acid. Suspension should be neutral to Congo red paper. Stir approximately five hours.

Dissolve the suspension to a clear solution slightly alkaline to Brilliant Yellow paper by adding approximately 40 parts of 100% sodium hydroxide. Ice to 10° C. and salt to a clear rim on spot with 20% salt. Add 99 parts of 100% hydrochloric acid as a 30% solution. Add 30 parts of 100% sodium nitrite as a 30% solution. Diazotize two hours at 10–15° C. with a strong excess nitrite. Filter the insoluble diazo.

Slurry the filter cake with 1000 parts of water and sufficient ice to maintain a temperature of 0–5° C. A smooth slurry should be obtained.

Slurry 85 parts of 1-amino-naphthalene-6-sulfonic acid and 1600 parts of water. Add 20 parts of sodium carbonate and stir to a complete solution which should be faintly alkaline to Brilliant Yellow paper. Add 85 parts of crystalline sodium acetate. Ice to 10° C.

Add the diazo slurry slowly to the solution of 1-amino-naphthalene-6-sulfonic acid, maintaining the suspension neutral to Congo red paper. Stir 10–12 hours. There should be an excess of 1-amino-naphthalene-6-sulfonic acid.

Make the suspension slightly alkaline to Brilliant Yellow paper with approximately 40 parts of sodium hydroxide. Ice to 5–10° C. and add 10% sodium chloride slowly. Add 102 parts of 100% hydrochloric acid as a 30% solution. Add 31 parts of 100% sodium nitrite as a 30% solution. Diazotize for approximately one hour at 5–10° C. with strong excess nitrite.

Slurry 90 parts of 1-hydroxy-naphthalene-5-sulfonic acid with 1600 parts of water. Add 340 parts of soda ash. Ice to 0° C.

Add the diazo to the solution of 1-hydroxy-naphthalene-5-sulfonic acid during one-half hour. The suspension should be strongly alkaline to Brilliant Yellow paper, and should contain a distinct excess of 1-hydroxy-naphthalene-5-sulfonic acid. Stir approximately one hour after the addition of the diazo. Heat to 80–85° C. and salt 20% with sodium chloride. Stir one hour and filter.

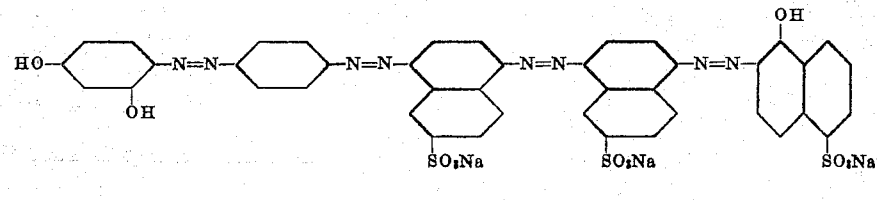
Stir the filter cake with sufficient water to make a total volume of 3300 parts. Heat to 90–95° C. and add 165 parts of 100% sodium hydroxide during five minutes. Stir 15 minutes and ice to 60° C. Add hydrochloric acid as a 30% solution until the suspension is only faintly alkaline to Brilliant Yellow paper. Salt 15% with sodium chloride. Stir one half hour. Filter.

Slurry the filter cake and 3500 parts of water until a smooth slurry is obtained. Ice to 10° C. Salt 10% with sodium chloride. Add 73 parts of 100% hydrochloric acid as a 30% solution. Add 28 parts of 100% sodium nitrite. Diazotize approximately 3 hours at 10–15° C. with a strong excess nitrite.

Stir 55 parts of 1,3-dihydroxy benzene with 2000 parts of water. Ice to 5° C. Add 212 parts of 100% sodium carbonate.

Add the diazo slowly to the alkaline solution of 1,3-dihydroxy-benzene. Maintain a temperature of 0–5° C. The suspension should be alkaline to Brilliant Yellow. Stir one hour. Heat to 80° C. Salt 20% with sodium chloride. Stir one hour after salting. Filter. Dry at 80–85° C. in an oven. The dry powder is blue black in appearance.

The compound is represented by the formula



A dyeing was made with the product and the dyeing was after-treated as follows.

Dissolve 0.4 gram of the product in 100 cc. of water at 190–200° F. and .08 gram of sodium carbonate to assist the solution. Dilute with stirring to a total volume of 500 cc. with water at approximately 160° F. and add 40 cc. of 10% solution of Glauber's salt. Wet out a 10 gram piece of rayon with water and squeeze partially dry and enter this into the dye bath. Raise the temperature of the dye bath to 180–190° F. during a period of fifteen minutes and hold the dye bath at that temperature for one hour. Stir the dyeings at frequent intervals during the dyeing. At the end of one hour remove the dyeing and rinse in cold water.

After-treatment in a fresh bath

Add the rinsed dyeing from the above operation to 500 cc. of water at 130–140° F. and add to the water approximately 10 cc. of 10% formaldehyde (25 cc. of approximately 37% formaldehyde by weight diluted to 250 cc. with water). Hold at this temperature for twenty minutes. Remove the dyeing, rinse and dry.

After-treatment in the dye bath

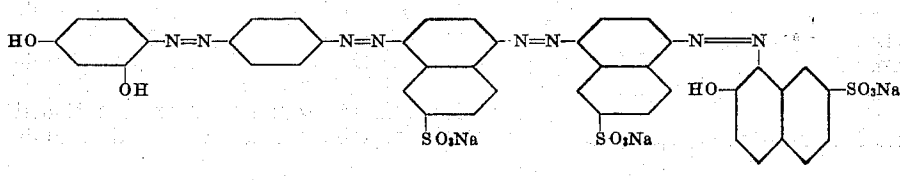
An alternative after-treating process which is the preferred procedure because of its economy and ease of application is carried out as follows.

At the end of the dyeing period add to the dye bath 10 cc. of 10% formaldehyde as in the preceding example at bath temperature. Remove the dyeings after twenty minutes. Rinse and dry.

A dyeing with a navy blue shade was obtained which showed excellent fastness to washing. The fastness to washing was better than the direct dyeing.

EXAMPLE II

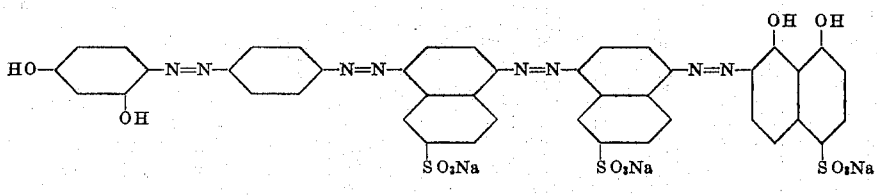
A product having the following formula was prepared by a similar procedure as that of Example I, substituting 90 parts of 2-hydroxy-naphthalene-7-sulfonic acid for 90 parts of 1-hydroxy-naphthalene-5-sulfonic acid.



The product was a blue black powder which when dyed on rayon and after-treated as in Example I, yielded dyeings of a blue shade which had excellent fastness to washing.

EXAMPLE III

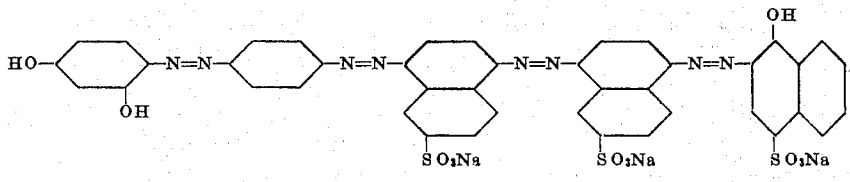
A product having the following formula was prepared by a similar procedure as that of Example I, substituting 105 parts of 1,8-dihydroxy-naphthalene-4-sulfonic acid for 90 parts of 1-hydroxy-naphthalene-5-sulfonic acid.



The product was a blue black powder which when dyed on rayon and after-treated as in Example I, yielded dyeings of a blue shade having washing fastness properties similar to those of Example I.

EXAMPLE IV

A product having the following formula was prepared by a similar procedure as that of Example I, substituting 90 parts of 1-hydroxy-naphthalene-4-sulfonic acid for 90 parts of 1-hydroxy-naphthalene-5-sulphonic acid.



The product was a blue black powder which when dyed on rayon and after-treated as in Example I, yielded dyeings of a blue shade which had excellent fastness to washing.

It is to be understood that modifications of the methods of preparing the tetrakisazo compounds can be used besides those described in the above examples and we do not limit ourselves to the methods particularized in the examples. All the products of the invention can be prepared by the methods particularized and by suitable modifications of the invention which will suggest themselves to those skilled in the art.

The following are additional illustrations of the invention. These products were prepared by methods similar to those recited in the foregoing examples. The most applicable variations in the method of making the compounds may be easily ascertained by those skilled in the art for any specific example wherever a variation is desirable. The direct dyeings with these colors on rayon

and after-treatment with formaldehyde gave bright shades which were comparable in brightness and washing fastness to the dyeings of Example I.

Example	Combination	Shade
V	1,3-dihydroxy-benzene ← 1,4-diamino-2-methyl-5-methoxy-benzene → 1-amino-naphthalene-6-sulfonic acid → 1-amino-naphthalene-6-sulfonic acid → 1-hydroxy-napthalene-5-sulfonic acid.	Blue.
VI	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-6-sulfonic acid → 1-amino-naphthalene-6-sulfonic acid → 2-hydroxy-naphthalene-6-sulfonic acid.	Do.
VII	1,3-dihydroxy-benzene ← 1,4-diamino-2-methyl-5-methoxy-benzene → 1-amino-naphthalene-6-sulfonic acid → 1-amino-naphthalene-6-sulfonic acid → 1,8-dihydroxy-naphthalene-4-sulfonic acid.	Do.
VIII	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene → 1-amino-naphthalene-6-sulfonic-acid → 1-hydroxy-naphthalene-5-sulfonic acid.	Reddish blue.
IX	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-7-sulfonic acid → 1-amino-naphthalene-7-sulfonic acid → 1-hydroxy-naphthalene-5-sulfonic acid.	Blue.
X	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-7-sulfonic acid → 1-amino-naphthalene-7-sulfonic acid → 2-hydroxy-naphthalene-7-sulfonic acid.	Do.
XI	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-7-sulfonic acid → 1-amino-naphthalene-7-sulfonic acid → 2-hydroxy-naphthalene-6-sulfonic acid.	Do.
XII	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-7-sulfonic acid → 1-amino-naphthalene-7-sulphonic acid → 1,8-dihydroxy-naphthalene-4-sulfonic acid.	Do.
XIII	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-7-sulfonic acid → 1-amino-naphthalene → 1-hydroxy-naphthalene-5-sulfonic acid.	Reddish blue.
XIV	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-7-sulfonic acid → 1-amino-naphthalene → 2-hydroxy-naphthalene-7-sulfonic acid.	Blue.
XV	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-7-sulfonic acid → 1-amino-naphthalene → 2-hydroxy-naphthalene-6-sulfonic acid.	Reddish blue.
XVI	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-7-sulfonic acid → 1-amino-naphthalene → 1,8-dihydroxy-naphthalene-4-sulfonic acid.	Do.
XVII	1,3-dihydroxy-5-methyl-benzene → 1,4-diamino-benzene → 1-amino-naphthalene-6-sulfonic acid → 1-amino-naphthalene-6-sulfonic acid → 2-hydroxy-naphthalene-7-sulfonic acid.	Blue.
XVIII	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-6-sulfonic acid → 1-amino-naphthalene-6-sulfonic acid → 2-hydroxy-naphthalene-3,6-disulfonic acid.	Do.
XIX	1,3-dihydroxy-benzene ← 1,3-diamino-benzene → 1-amino-naphthalene-6-sulfonic acid → 1-amino-naphthalene-7-sulfonic acid → 1-hydroxy-naphthalene-5-sulfonic acid.	Brown black.
XX	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene 6-sulfonic acid → 1-amino-naphthalene-6-sulfonic acid → 1-hydroxy-naphthalene 3 sulfonic acid.	Blue.
XXI	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-6-sulfonic acid → 1-amino-naphthalene-6-sulfonic acid → 2-hydroxy-naphthalene.	Do.
XXII	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-napthalene-6-sulfonic acid → 1-amino-naphthalene → 1-hydroxy-naphthalene-5-sulfonic acid.	Reddish blue.
XXIII	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-7-sulfonic acid → 1-amino-naphthalene-6-sulfonic acid → 1-hydroxy-naphthalene-5-sulfonic acid.	Blue.
XXIV	1,3-dihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-6-sulfonic acid → 1-amino-naphthalene-7-sulfonic acid → 1-hydroxy-naphthalene-5-sulfonic acid.	Do.
XXV	1,3,5-trihydroxy-benzene ← 1,4-diamino-benzene → 1-amino-naphthalene-6-sulfonic acid → 1-amino-naphthalene-6-sulfonic acid → 2-hydroxy-naphthalene-7-sulfonic acid.	Do.
XXVI	1,3-dihydroxy-benzene-5-sulfonic acid ← 1,4-diamino-benzene → 1-amino-naphthalene-6-sulfonic acid → 1-amino-naphthalene-6-sulfonic acid → 2-hydroxy-naphthalene-7-sulfonic acid.	Do.

Deeper shades than the direct or formaldehyde treated dyeings and with better light fastness are produced by after-treatment of these colors with water-soluble metal salts, such as water soluble salts of copper, for example copper sulfate. For example, the after-coppering operation may be carried out by either of the procedures outlined in Example I for the after-treatment with formaldehyde, by using a solution containing a 5% solution of hydrated cupric sulfate equal in amount to the formaldehyde used in the preceding step. In both cases the operation is allowed to continue for twenty minutes, or for such other time as is necessary to metallize the dyeing, at the end of which time the treated dyeings are removed, rinsed and dried. The after-coppering may replace the formaldehyde treatment, but both after-treatments are preferred where the best light fastness as well as washing fastness is desired. After-treatment with both formaldehyde and metal salts may be done either in the dye bath or in a fresh bath. When a fresh formaldehyde bath is used and the dyeing is treated for a sufficient time to form the formaldehyde compound, the metal salt may be added and the treatment continued for an interval of time. The dyeings are then removed, rinsed and dried. Similar results are obtained by reversing the order of adding the after-treating reagents, that is, by adding the metal salt solution first, treating for the necessary time, and then adding the formaldehyde solution. After treating the dyeings for about twenty minutes, they are removed, rinsed and dried.

The described method of dyeing is typical but it is to be understood that the invention is not restricted to the precise concentrations, temperatures and intervals of treatment specified in the examples since these details can be variously modified as will be understood by those skilled in the art. For example, the after-treatments with formaldehyde or metal salts may be carried on for longer or shorter periods and at higher or lower temperatures than those specified in the illustrations. Any treatment which will form a formaldehyde complex with the dyeing or one of the described metal complexes with the dyeing, as the case may be, produces the improved results with the dyes described. The exact composition of the described formaldehyde and metal complexes is unknown to us, but from our investigations it is our present belief that formaldehyde and metal complexes are formed.

For the best results the dyes contain at least two sulfonic acid groups but as indicated in the foregoing illustrations more than two sulfonic acid groups may be present.

As examples of other meta dihydroxy benzenes which can be used for the component A are mentioned 3,5-dihydroxy toluene, 3,5-dihydroxy anisole, and 3,5-dihydroxy benzoic acid, 1,3-dihydroxy - 5 - benzo-nitrile, 1,3-dihydroxy-5-chlorobenzene and 1,3-dihydroxy-5-amino-benzene. As other compounds represented by X we can use 1,4-diamino-2-carboxy benzene, 1,4-diamino-2-nitro benzene, 1,4-diamino-benzene-2-sulfonic acid, 2,4-diamino-benzoic acid, 2,4-diamino-benzene sulfonic acid, 2,4-diamino-toluene, 2,4-diamino-anisole, 1,3-diamino-5-benzonitrile, 3,5-(diamino)-diphenyl methane and any of the various similarly substituted meta- and para-diamino benzenes. As illustrations of other compounds represented by Y and Z are mentioned alpha-naphthylamine-6-carboxylic acid, 1-ami-

no- 7 -methoxy-naphthalene, 1 -amino- 2 -methoxy - naphthalene - 6 - sulfonic acid, 1-amino-2-methyl-naphthalene-6-sulfonic acid, 1-amino-naphthalene-5,7-disulfonic acid and 1-amino-2-methoxy-naphthalene-5,7-disulfonic acid, and as many others as indicated by the general formula.

As illustrations of other compounds represented by *w* are mentioned 1-hydroxy-naphthalene-3,7-disulfonic acid, 1-hydroxy-naphthalene-4,7-disulfonic acid, 1-hydroxy-naphthalene-3,6,8-trisulfonic acid, 1 - hydroxy - naphthalene - 8 - methoxy-3,6-disulfonic acid, 2-hydroxy-naphthalene-4-methoxy-7-sulfonic acid, 2-hydroxy-naphthalene-4-methoxy-5,7-disulfonic acid and 1,8-dihydroxy-naphthalene-2- and 3- sulfonic acids.

In the specification and claims alkyl refers to straight and branched chain aliphatic radicals, such as methyl, ethyl, propyl and even longer chain alkyl radicals. Alkoxy refers to the corresponding alkoxy groups. Any of the halogens may be present as substituents where indicated. The sulfonic acid groups in the finished dyes may be the salts of any of the alkali metals and are produced by making the coupling media basic with the corresponding alkalis.

Water-soluble metal salts of various metals can be used for metallizing the dyeings, those having atomic weights between 50 and 65 being the most suitable. As examples of such metals copper, chromium, nickel, cobalt and iron are mentioned. Either water-soluble salts of inorganic or organic acids can be used such as sulfates, halides, formates and acetates, for example copper sulfate, nickel sulfate, chromium chloride, copper formate, copper acetate and many other water-soluble metal salts of inorganic and organic acids.

The compounds of the present invention give dyeings on regenerated cellulose fibers which are equal to and superior in washing fastness to the developed colors. In applying developed colors three baths are necessary, namely a bath containing the azo component, an azotizing bath and a developing bath. In the present process the dyeing may be completed in one bath. The dyeings of the present invention compare favorably in brightness with the direct dyes but they are much faster to washing.

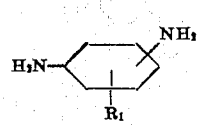
Since from the foregoing description of the invention it will be apparent to those skilled in the art that various other embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the illustrations specifically recited.

We claim:

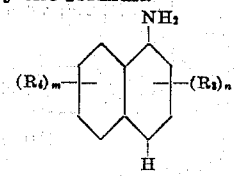
1. A compound represented by the formula

$$A \leftarrow X \rightarrow Y \rightarrow Z \rightarrow w$$

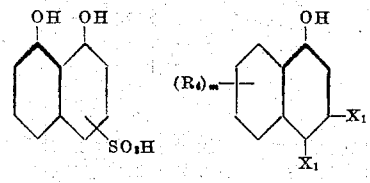
in which X is a meta- or para-diamino benzene represented by the formula

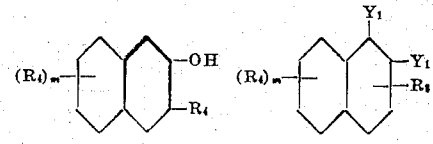


in which R_1 is at least one of a group consisting of hydrogen, alkyl, alkoxy, nitro, nitrile, sulfonic acid and carboxy; Y and Z are each a compound represented by the formula

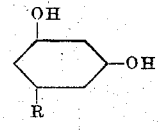


in which R_3 is at least one of a group consisting of hydrogen, alkyl, and alkoxy, R_4 is at least one of a group consisting of hydrogen, alkyl, alkoxy, sulfonic acid and carboxy, *n* is an integer not greater than 2 and *m* is an integer not greater than 2; *w* is one of a group consisting of the naphthols represented by the formulae





in which R_3 is one of a group consisting of hydrogen, alkyl, an alkoxy, R_4 is at least one of a group consisting of hydrogen, alkyl, alkoxy, sulfonic acid and carboxy, *m* is an integer not greater than 2, one X_1 is sulfonic acid and the other is hydrogen and one Y_1 is hydroxy and the other is hydrogen; and A is a meta-dihydroxy benzene represented by the formula



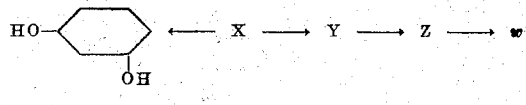
in which R is one of a group consisting of hydrogen, alkyl, alkoxy, hydroxy, amino, halogen, nitrile, carboxyl and sulfonic acid.

2. The formaldehyde complexes of the compounds of claim 1.

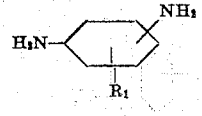
3. The metallic complexes of the compounds of claim 1.

4. The metallic and formaldehyde complexes of the compounds of claim 1.

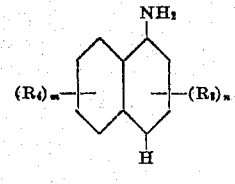
5. A compound represented by the formula



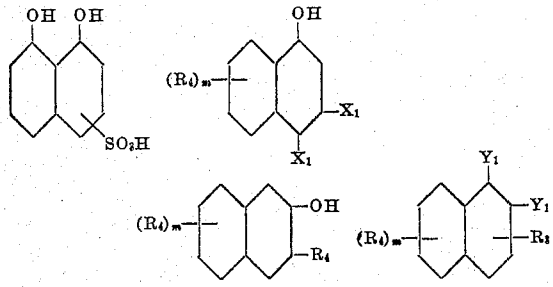
in which X is a meta- or para-diamino benezene represented by the formula



in which R_1 is at least one of a group consisting of hydrogen, alkyl, alkoxy, nitro, nitrile, sulfonic acid and carboxy; Y and Z are each a compound represented by the formula

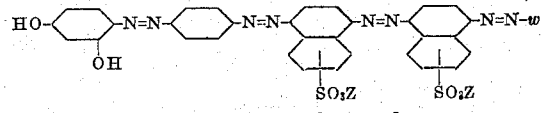


in which R_3 is at least one of a group consisting of hydrogen, alkyl, and alkoxy, R_4 is at least one of a group consisting of hydrogen, alkyl, alkoxy, sulfonic acid and carboxy, n is an integer not greater than 2 and m is an integer not greater than 2; and w is one of a group consisting of naphthols represented by the formulae

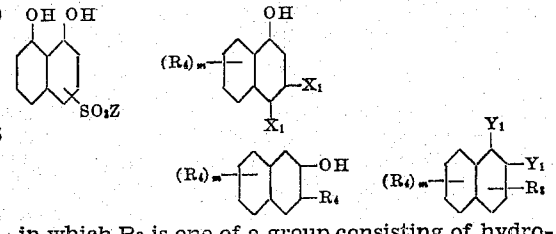


in which R_3 is one of a group consisting of hydrogen, alkyl, and alkoxy, R_4 is at least one of a group consisting of hydrogen, alkyl, alkoxy, sulfonic acid and carboxy, m is an integer not greater than 2, one X_1 is sulfonic acid and the other is hydrogen and one Y_1 is hydroxy and the other is hydrogen.

6. A compound represented by the formula

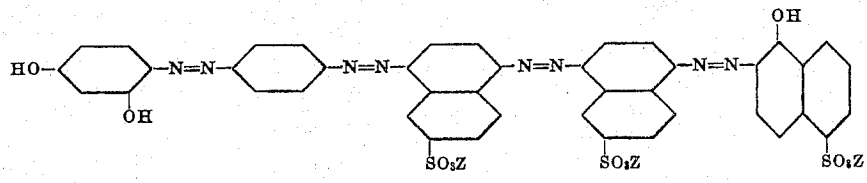


in which w is the residue of one of a group consisting of naphthols represented by the formulae



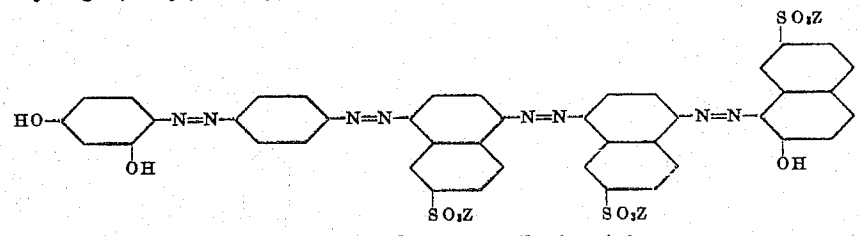
in which R_3 is one of a group consisting of hydrogen, alkyl and alkoxy, R_4 is at least one of a group consisting of hydrogen, alkyl, alkoxy, sulfonic acid and carboxy, m is an integer not greater than 2, one X_1 is a sulfonic acid group and the other is hydrogen, one Y_1 is hydroxy and the other is hydrogen, and the group $-SO_3Z$ is an alkali metal sulfonic acid group.

7. A compound represented by the formula



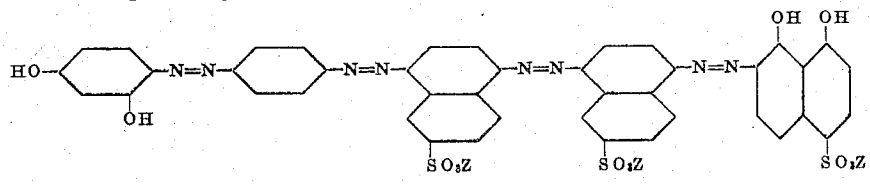
in which Z is an alkali metal.

8. A compound represented by the formula



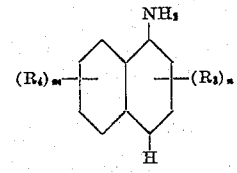
in which Z is an alkali metal.

9. A compound represented by the formula

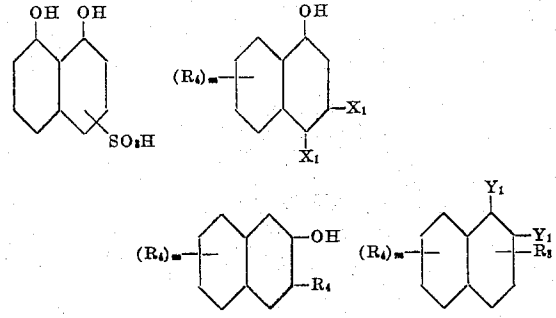


in which Z is an alkali metal.

10. The process which comprises diazotizing a meta- or para-diamino benzene in which one of said amino groups is blocked; coupling with a compound Y which is represented by the formula

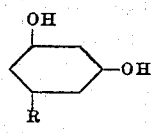


in which R_3 is at least one of a group consisting of hydrogen, alkyl and alkoxy, R_4 is at least one of a group consisting of hydrogen, alkyl, alkoxy, sulfonic acid and carboxy, n is an integer not greater than 2 and m is an integer not greater than 2; diazotizing the monazo compound and again coupling with one of said Y compounds; diazotizing the disazo compound and coupling with one of a group consisting of the naphthols represented by the formulae



in which R_3 is one of a group consisting of hydrogen, alkyl and alkoxy, R_4 is at least one of a group consisting of hydrogen, alkyl, alkoxy, sulfonic acid and carboxy, n is an integer not greater than 2 and m is an integer not greater than 2; one X_1 is sulfonic acid and the other is hydrogen and one Y_1 is hydroxy and the other is hydrogen; unblocking said blocked amino

group; diazotizing; and coupling with a dihydroxy benzene represented by the formula



in which R is one of a group consisting of hydrogen, alkyl, alkoxy, hydroxy, amino, halogen, nitrile, carboxyl and sulfonic acid.

SWANIE S. ROSSANDER.
CHILES E. SPARKS.