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3,184,284

DYE-PAD, HOT-CHEMICAL-TREATMENT DYEING PROCESS

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The present invention is directed to novel dyeing processes for the application of quinoxaline fiber-reactive dyes to cellulosic materials wherein the fabric is padded, optionally dried, treated with hot alkali and washed. The novel processes afford significantly uniform results in the dyeing of all reactive dyes containing a 2,3-dichloro-6-quinoxalinecarbonylamino group and amino dye bases. The dyes employed in the present processes are more fully described in the specification which follows.

With fiber-reactive dyes, it is a well known fact that time, temperature and nature and concentration of acid acceptor are the variables which are important for reaction with the cellulosic textile materials. Although it is possible with all fiber-reactive dyes to get some dye-fiber reaction by varying these variables over an extremely wide range, it is well known that the reactivity among the various reactive dye types, and even among the dyes of the same type, cannot be predicted. Thus, if possible, it is necessary and of advantage to determine for each type of reactive dye a unique method of dyeing, which is compatible with all of the dyes of that type.

In other words, since it is impossible to predict dyeing characteristics from chemical composition, one must find the unique and novel dyeing method for each reactive dye type.

It is, therefore, an object of the present invention to provide, for the first time, dye-pad, hot-chemical-treatment dyeing processes for the two-bath dyeing application of a most recent type of fiber-reactive dyes, those which contain a 2,3-dichloro-6-quinoxalinecarbonylamino group. Such a method must be compatible with all dyes which contain said group, and must achieve the significant results described herein.

It is a further object of this invention to provide dye-pad, hot-chemical-treatment processes for dyeing said dichloroquinoxaline dyes by either continuous or batch operations in which Williams or jig dyeing equipment, respectively, can be used. A Williams dyeing unit is described in "The Application of Vat Dyes," pages 119–120, Americal Association of Textile Chemists and Colorists Monograph No. 2, 1953, Mack Printing Company, Easton, Pennsylvania. A dye jig unit is also illustrated in the same Monograph on page 109.

Still a further object of this invention is to provide processes for obtaining attractive and fast dyeings in high fixation yields, said dyeings reflecting good wash-fastness properties, resistance to acid perspiration and fully acceptable light fastness.

These and other objects of the invention will become apparent in the following description and claims.

The novel processes of dyeing embodied by this invention are characterized by padding the dye solution onto the fabric, optionally drying, treating the padded fabric with a hot aqueous solution of electrolyte and acid acceptor, and washing the dyed fabric. More specifically, the present invention comprises the following combination of steps:

(1) the cellulosic material is padded with said dichloroquinoxaline dye from an aqueous solution thereof maintained at pH 6 to 7.8. Urea is often advantageously added to this padding solution. The dye-padded fabric is then dried, if desired, or is passed directly into the hot-chemical bath;

(2) the dye-padded fabric is treated for at least five seconds with an aqueous alkaline liquor comprising 2 to 15 g./l. of sodium hydroxide and 200 to 300 g./l. of electrolyte selected from the group consisting of NaCl and Na_2SO_4, the temperature of said liquor being 80° to 218° F.;

(3) the dyed fabric from step (2) is washed for removal of salts and any unfixed dye, as normally performed by one skilled in the art of dyeing.

There are various ways of operating the novel dye-pad, hot-chemical-treatment processes outlined above.

When the fabric is dried, following the dye-pad step, the residence time of the fabric in the hot-chemical-treatment bath is usually 5 to 10 seconds. A longer time period may be used without harm to the dyeing, but more time than that mentioned is not required to obtain high fixation yields. This modification of the invention affords a continuous process which assures high speed dyeing, being a definite advantage in the trade when long yardages of goods are being dyed.

On the other hand, when short yardages of goods are being dyed, it is sometimes convenient to adapt the dye pad, hot-chemical-treatment process of this invention to the well known jig equipment for the hot-chemical-treatment step. In this modification of the invention, one operates the two liquid treatments with or without intermediate drying of the fabric. Since the time factor can be varied conveniently over a wide range in the jigger, depending on the number of times the fabric is passed through the hot chemical bath, it is convenient to operate at temperatures as low as 80° F. and extend the number of passes of cloth through the alkaline liquor. Generally, 2 or 4 passes, or "ends," are sufficient to obtain excellent fixation of the quinoxaline dyes. When the hot chemical treatment is performed in the jig and the quinoxaline dyes are applied together with other types of fiber-reactive dyes which are slower to react with the fiber, the number of passes would be increased to 6, or even more.

The present novel processes afford combinations of the following technically significant features:

(*a*) *Compatibility*—all of the dyes which contain a 2,3-dichloro-6-quinoxalinecarbonylamino group can be applied without sacrificing any of the desired application properties of one specific dye.

(*b*) *High-fixation*—thus economy; since one obtains efficient utilization of the reactive dye.

(*c*) *Convenience*—The process can be operated in dye houses which do not have continuous steaming equipment but are equipped with jigs and/or Williams units.

(*d*) *Good fastness* properties are maintained by this method.

In order to take full advantage of all of the features of this invention, the described processes must be operated in the defined limits during the hot alkaline treatment. For

instance with certain dyes weaker alkali, or lower temperatures or shorter times are effective, but to have a reproducible dyeing and compatibility of all the quinoxaline dyes, the preferred ranges must be maintained. Long times e.g. beyond about 10 seconds during alkaline treatments are of course impractical in continuous operations. Temperatures higher than the boiling point of the alkaline liquor, about 218° F., are impossible to obtain without special equipment. Stronger alkali than 15 g./l. of sodium hydroxide lowers fixation and at times depreciates the fastness properties of the dyeing.

It will be understood by those skilled in the art that additives, for example surface active agents and migration inhibitors, and dyeing aids, are sometimes used in the practice of this invention. Typical additives are:

Urea

"Keltex"—sodium salt of alginic acid (Kelco Co., Clark, New Jersey)

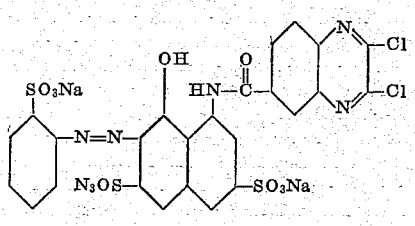
"Cassofix AS"—benzol derivative and resin precondensate (1962 AATCC Yearbook p. E–205) (Sou-Tex Chemical Co., Inc., Mount Holly, N.C.)

Representative examples illustrating the present invention follow:

PART I—DYEING

Example I

Twenty parts of the quinoxaline dye of the structure



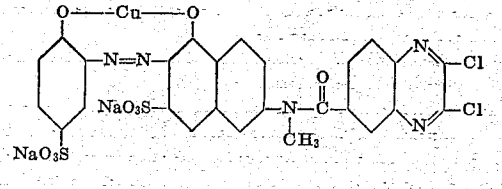
are dissolved at pH 6.2 in 1000 parts of water. This solution is padded at 78° F. onto cotton poplin at 65% pickup. The fabric is dried in a flue dryer, passed with a residence time of five seconds through a 172° F. aqueous bath containing 12 g./l. of sodium hydroxide and 300 g./l. of sodium sulfate, washed (hot water rinse, cold water rinse, hot soap scour, hot water rinse and cold water rinse, in turn) and dried. There results a bright red shade which is fast to washing, acid perspiration and light.

Example II

The padded material of Example I without drying is passed on a jig for 2 ends of five minutes each (the immersion time is four seconds for each end), through an aqueous liquor at 160° F. (4:1, cloth: liquor ratio) containing 2 g./l. of sodium hydroxide and 300 g./l. sodium sulfate, washed and dried. There results a dyeing of similar shade, strength and fastness to that obtained in Example I.

Example III

Thirty parts of the quinoxaline dye of the structure



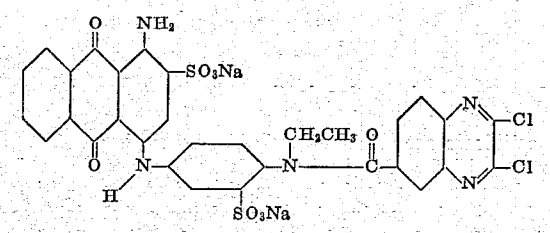
are dissolved at pH 7.2 in 1000 parts of water containing 30 parts of "Cassofix AS" and 150 parts of urea. This solution is padded at 75% pickup onto cotton broadcloth. The impregnated fabric is dried over heated cans, passed with a residence time of seven seconds through a 210° F. aqueous bath containing 10 g./l. of sodium carbonate, 2 g./l. sodium hydroxide and 200 g./l. of sodium sulfate, washed and dried. The resulting ruby shade is fast to washing and light.

Example IV

One yard of the dye-impregnated wet fabric of Example III is passed twice (the immersion time for each pass is three seconds) through a 218° F. aqueous bath (10:1 liquor:fabric ratio) containing 15 g./l. of sodium hydroxide, 150 g./l. of sodium chloride and 100 g./l. of sodium sulfate, washed and dried to give a dyeing similar to that from Example III.

Example V

Twenty-five parts of the quinoxaline dye of the structure



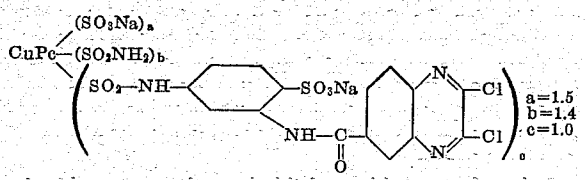
are dissolved at pH 7.8 in 1,000 parts of water. This solution is padded at 70% pickup onto cotton twill. The fabric is dried and passed with a residence time of ten seconds through a 190° F. aqueous solution of 5 g./l. of sodium hydroxide, 100 g./l. of sodium chloride and 150 g./l. of sodium sulfate, washed and dried. There results a bright blue dyeing which is fast to washing and light.

Example VI

One thousand yards of the dye-impregnated twill from Example V are passed for six ends (20 minutes per end, immersion time 2.5 seconds per end) through an aqueous 80° F. solution of 5 g./l. of sodium hydroxide and 200 g./l. of sodium chloride. After washing and drying the cotton twill, a dyeing similar to that obtained in Example V is obtained.

Example VII

Twenty parts of the dye of the structure



are dissolved in 1000 parts of water. This solution is padded onto one yard of cotton poplin at 68% pickup. The poplin fabric is passed for four ends (3 seconds for each pass) through a 120° F. aqueous solution (4:1 liquor:fabric ratio) containing 5 g./l. of sodium hydroxide and 250 g./l. of sodium sulfate, washed and dried. There results a torquoise shade which is fast to washing and light.

Example VIII

A dye-impregnated poplin fabric prepared as in Example VII is dried, passed with a residence time of five seconds through a 188° F. aqueous bath containing 10 g./l. of sodium hydroxide and 270 g./l. of sodium chloride, washed and dried. There results a dyeing similar to that obtained in Example VII.

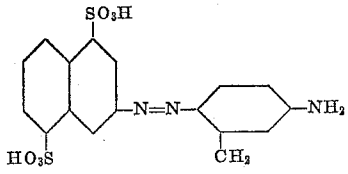
PART II—PREPARATION OF THE REACTIVE DYES

As shown in the preceding examples, the process of the present invention gives good dyeings regardless of

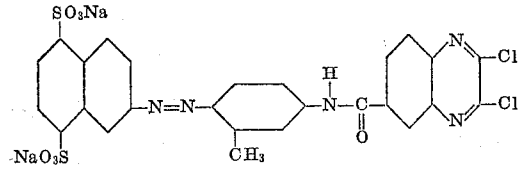
the type of dye chromophore which is attached to the 2,3-dichloro-6-quinoxalinecarbonylamino group. It has been found that a large variety of said quinoxaline dyes can be used in the invention. This variety is illustrated further by the following examples, numbers 1 through 8 which disclose the preparation of dyes which are applicable in the novel dyeing process.

Example 1

42 parts of an azo-dye base having the following formula



are dissolved in 700 parts of water at 40° C. to give a yellow solution. After adjusting the pH to 7.5–8 (using sodium carbonate), 30 parts of finely powdered 2,3-dichloro-6-quinoxalinecarbonyl chloride are added, and the mixture is stirred overnight while maintaining a temperature of 35°–40° C. and a pH of 7.5–8 by the addition of sodium carbonate. The yellow solution is then clarified by filtration, salted with 10 parts of sodium sulfate, and the precipitated solid is filtered and washed with a 12% sodium sulfate solution. The filter cake is pressed to 58% dye content, and dried as a thin layer in an oven at 80° C. for 24 hours. The dried product is then ground to a free-flowing light-yellow powder. This powder contains approximately 82% dye, 11% water, and 7% Na_2SO_4 by weight. The dye has the formula

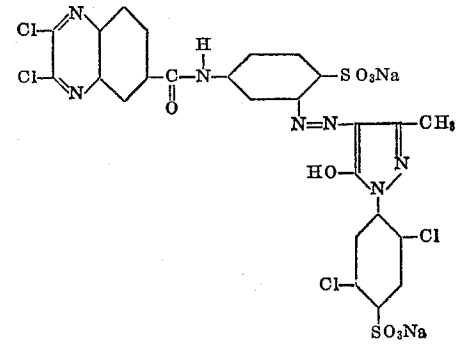


and dyes cotton by the above procedure in yellow shades.

Example 2

To 120 parts of 2,4-diaminobenzenesulfonic acid in 1000 parts of water at 35° C. and pH 7.5–8 (maintained using dilute sodium hydroxide solution) are added 163 parts of finely powdered 2,3-dichloro-6-quinoxalinecarbonyl chloride. The slurry is maintained for 4 hours at 35°–40° C. and pH 7.5–8.0 and the precipitated solid is filtered. This solid is dissolved in 10,000 parts of 50° C. water, clarified, cooled to 5°–10° C., and slowly added to a solution consisting of 150 parts of 10 N sulfuric acid, 110 parts of 5 N sodium nitrite and 500 parts of water. After completion of the addition, the reaction is stirred at 5°–15° C. for 4 hours, the excess nitrite is destroyed by the addition of sulfamic acid, as shown by a negative test on starch iodide paper, the solid is allowed to settle, and about 10,000 parts of the water layer are removed by decanting.

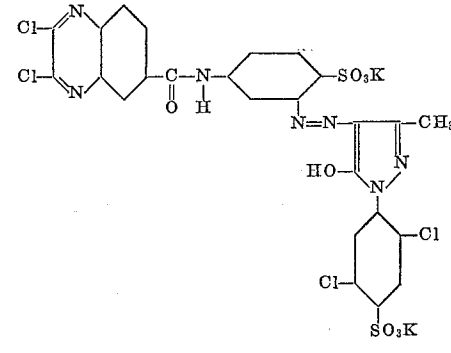
To the remaining slurry is added a solution consisting of 161 parts of 1-(2',5'-dichloro-4'-sulfophenyl-3-methyl-5-pyrazolone dissolved in 450 parts of water at pH 7.0 (obtained by adding sodium hydroxide as necessary) and this bright yellow slurry is stirred at pH 4.5–6 (adding sodium acetate as needed) to effect complete solution. The pH of the brown yellow solution is adjusted to 8.2 with sodium hydroxide, the temperature is increased to 40°–45° C., and sodium sulfate is slowly added to salt the solution. The precipitated yellow solid is filtered, washed with 20% sodium sulfate solution, and dried at 60° C. The dye thus obtained has the formula:



Example 3

To 500 parts of water are added 188 parts of 2,4-diaminobenzenesulfonic acid and 100 parts of 30% sodium hydroxide. This slurry is stirred to effect solution, cooled to 25° C., and diluted with 1400 parts of water. To this solution are added all at once 112 parts of acetic anhydride and stirring is continued 1 hour, after which the pH is adjusted to 8±0.5, and 69 parts of a 31% sodium nitrite solution are added. This solution is then added, over ½ hour, to a solution of 500 parts of water, 500 parts of ice, and 120 parts of 30% hydrochloric acid. The resulting slurry is stirred for ½ hour before the excess nitrite is destroyed with sulfamic acid as shown by a negative test on starch iodide paper. This diazo slurry is added with stirring at 5°–15° C. over 1 hour to a solution of 500 parts of water, 323 parts of 1-(2'-5'-dichloro-4'-sulfophenyl)-3-methyl-5-pyrazolone, 72 parts of 30% sodium hydroxide, 100 parts of sodium acetate, and 500 parts of ice. To this yellow-brown solution are added 120 parts of hydrochloric acid, the temperature is then raised to 90° C. over 1 hour, held at this temperature for 2 hours, cooled to 40° C., and the precipitated solid dye-base is collected by filtration and washed with a dilute hydrochloric acid solution.

This wet dye-base cake is dissolved in a solution of 5000 parts of water and 165 parts of sodium hydroxide. To this rapidly-stirred solution at 30°–35° C. are added 230 parts of 2,3-dichloro-6-quinoxalinecarbonyl chloride dissolved in 700 parts of xylene. This mixture is stirred for 3 hours at 35°–40° C., while maintaining the pH at 5.5–8.0 by the addition of a sodium hydroxide solution. The reaction mass is then clarified by filtration, 150 parts of potassium chloride in 2000 parts of water are added over 1 hour, and the precipitated insoluble (in cold water, slightly soluble in boiling water) potassium salt of the formula:

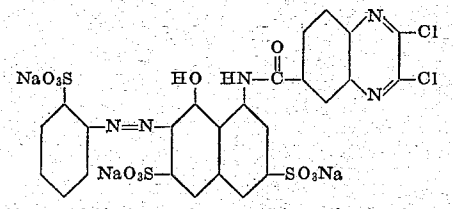


is filtered. This wet press cake is prepared for commercial use by drying below 60° C., adding 4.2% K_2SO_4 based on weight of dye, and grinding.

Example 4

26 parts of 2,3-dichloro-6-quinoxalinecarbonyl chloride dissolved in 70 parts of xylene are added to a rapidly

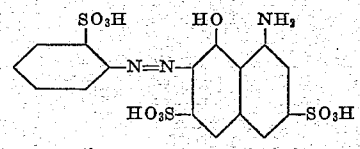
stirred solution of 37.5 parts of H acid (8-amino-1-naphthol-3,6-disulfonic acid) at pH 6 (adjusted with sodium hydroxide) in 400 parts of 35° C. water. The mixture, which converts to a greenish gel, is stirred at 25°–35° C. and at pH 4–5 (maintained with sodium hydroxide) for 3–4 hours. 720 parts of water are added and the pH is adjusted to 8.5±0.2 with sodium hydroxide. The reaction mass is then clarified by filtration and the filtrate is cooled to 5°–15° C. To this brownish solution is added at 5°–15° C. and at pH 7.5±0.2 (maintained with sodium hydroxide) over a 1-hour period the cold diazo slurry prepared in the usual manner from 130 parts of water, 22.5 parts of orthanilic acid, 5.9 parts of hydrochloric acid, 9.0 parts of sodium nitrite, and 100 parts of ice. This coupling requires 2–3 hours. The red dye of the structure



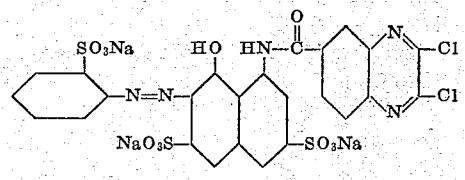
is salted to 10% by volume with solid sodium sulfate over a 2-hour period, filtered, washed with 10% sodium sulfate solution, dried below 100° C. in an oven, and standardized to 65% active ingredient by intimate mixing with sodium sulfate.

Example 5

50.3 parts of the azo-dye base

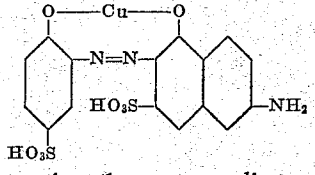


(prepared by coupling acetyl H acid with orthanilic acid followed by hydrolysis) are dissolved in 1100 parts of water at pH 7–7.5 (using sodium hydroxide) and 28.6 parts of 2,3-dichloro-6-quinoxalinecarbonyl chloride dissolved in 80 parts of xylene are added. The resulting mixture is vigorously stirred at pH 6–8 (maintained with sodium hydroxide) and at 35°±5° C. for about 3 hours, clarified, salted with sodium sulfate and isolated as in Example 4 to give the dye of formula:

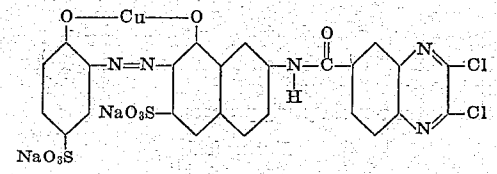


Example 6

25 parts of the dye base



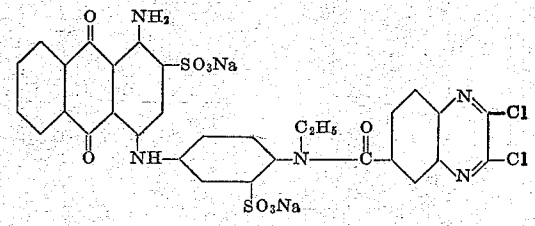
prepared by treating the azo coupling product of 2-amino-1-phenol-4-sulfonic acid and J acid (6-amino-1-naphthol-3-sulfonic acid) with a copper-containing agent, are dissolved at 40±5° C. in 1000 parts of water at pH 7.5 (maintained with sodium hydroxide), and 14.3 parts of 2,3-dichloro-6-quinoxalinecarbonyl chloride dissolved in 45 parts of xylene are added. The resulting mixture is vigorously stirred at pH 7.5–8.0 (maintained with sodium hydroxide solution) and at 40±5° C. for about 3 hours, then filtered, and the filtrate is salted with a mixture of 60 parts of sodium sulfate and 60 parts of sodium chloride. The precipitated rubine dye of the structure



is filtered off and washed with 300 parts of a 15% sodium sulfate solution. The filter cake is pressed to about 30% dye content and dried at 80° C.

Example 7

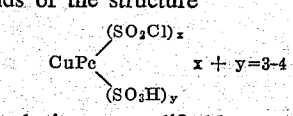
160 parts of water are stirred with 29 parts of sodium bicarbonate and 22.3 parts of 5-amino-2-ethylaminobenzenesulfonic acid at 60° C. for 15 minutes and cooled to 40° C. At this temperature are added 0.9 part of cupric sulfate, 0.4 part of copper powder, and, slowly over a 2-hour period, 39.8 parts of the sodium salt of bromamine acid (1-amino-4-bromo-2-anthraquinonesulfonic acid). The blue slurry is stirred for an additional 2 hours, clarified, and then salted carefully to a 14% salt solution, using sodium chloride. The precipitated needles are filtered, washed free of the green-brown color with 15% sodium chloride solution, and redissolved at 30°–35° C. in 1500 parts of water at pH 7.6±0.2 (using sodium hydroxide). To this solution are added 60 parts of xylene containing 24.2 parts of 2,3-dichloro-6-quinoxalinecarbonyl chloride, and the pH and temperature are maintained at 5.5–8 (with sodium hydroxide) and 30°–35° C., respectively, until the pH is steady (usually 3 hours). The solution is clarified by filtration and the filtrate is slowly salted to 4% with sodium chloride and 6% with sodium sulfate, which affords, after stirring for 14 hours, a blue crystalline precipitate. The product of the structure



is filtered, washed with a solution of 4% sodium chloride and 10% sodium sulfate, and dried at 100° C.

Example 8

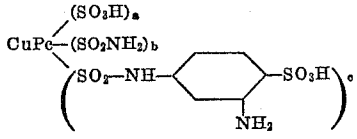
To 160 parts of chlorosulfonic acid cooled to 5° C. are added 23 parts of copper phthalocyanine at such a rate as not to exceed 25° C. This slurry is stirred 15 minutes, heated over 1.5 hours to 135±5° C. and stirred at this temperature for 3.5 hours. The dark green solution is cooled to room temperature and is drowned in a mixture of ice and water below 5° C. The solid, which is collected by filtration and washed with 5° C. aqueous 1% hydrochloric acid solution, corresponds to a mixture of compounds of the structure



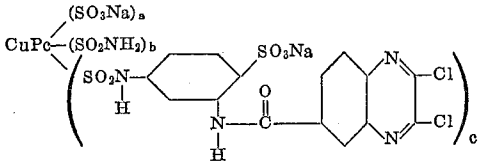
in which all substituents modified by x and y are primarily located in the 3, 3′, 3″, and 3‴ positions.

To this wet sulfonyl chloride filter cake slurried in 1200 parts of ice water are added 22.5 parts of 2,4-diaminobenzenesulfonic acid, and the pH is adjusted to 7.5 with ammonium hydroxide. The mixture is heated to 40° C. and stirred at this temperature, maintaining the pH at 7.5–8.0, by addition of ammonium hydroxide until the pH remains constant, usually 3–4 hours. The resulting dye base is filtered off after acidification of

the solution to pH 2 with hydrochloric acid. After washing the filter cake with dilute hydrochloric acid, the dye base, of formula

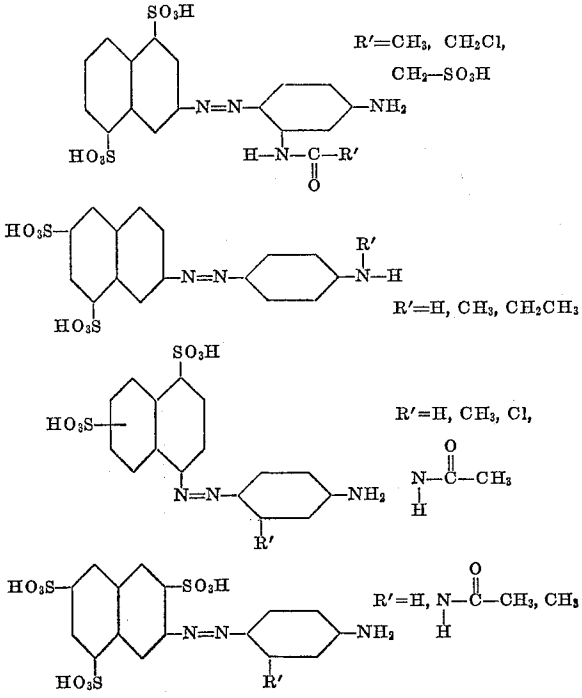


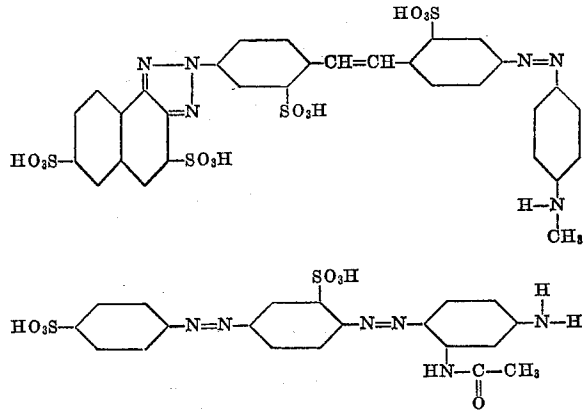
is reslurried in 1500 parts of 45° C. water at pH 7.5–8.0 using sodium hydroxide. To this solution is added with vigorous stirring at 40°–45° C. and pH 7.5–8.0 (maintained with sodium hydroxide) a solution of 21.0 parts of 2,3-dichloro-6-quinoxalinecarbonyl chloride and 45 parts of xylene. After the pH holds constant, about 4 hours, the solution is clarified and 100 parts of sodium sulfate are added. The turquoise solution is salted carefully with solid sodium chloride to about 16%, the precipitated dye is filtered, washed with a 10% sodium sulfate and 10% sodium chloride solution, and dried in an oven below 80° C. This dye mixture of the structure



on analysis is found to contain 1.0 dichloroquinoxaline radical, 1.4 sulfamoyl radicals, and 2.5 sodium sulfonate groups. Thus, the values of *a*, *b*, and *c* are 1.5, 1.4, and 1.0, respectively. This dye is standardized to 55% active ingredients by the addition of anhydrous sodium sulfate. When applied to cellulosic textile materials by the procedures shown in the examples of Part I above, bright turquoise shades have good light and wash fastness are obtained.

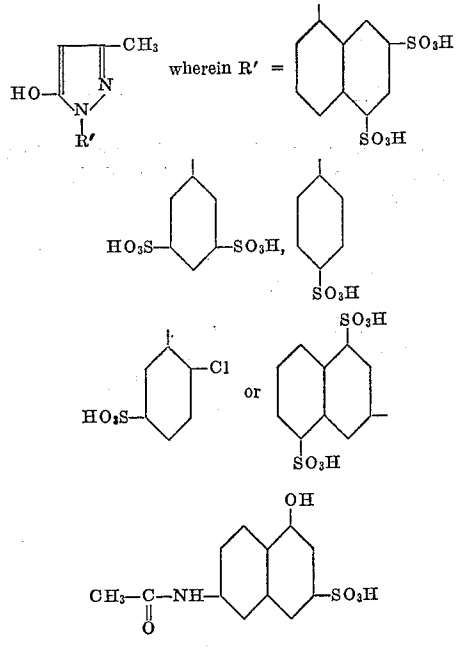
Additional dyes applicable in the present invention are obtained by employing other dye bases in condensation with 2,3-dichloro-6-quinoxalinecarbonyl chloride according to procedures described in the above preparative Examples 1–8. For instance, the dye base used in Example 1 (3-amino-1,5-naphthalenedisulfonic acid→meta-toluidine) may be replaced by equimolar proportions of any of the following dye bases:





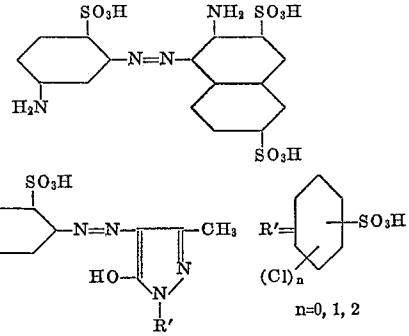
It should be further pointed out that one skilled in the art can also replace the dye bases of the examples with equimolar proportions of dye bases which are similar to those used in the specific examples. In Example 2, one or more of the following substitutions can be made. The dye can be prepared by using 2,5-diaminobenzenesulfonic acid instead of the 2,4-isomer which is specified in Example 2. Moreover, in place of the pyrazalone which was used to prepare the dye of Example 2, one could use the following compounds:

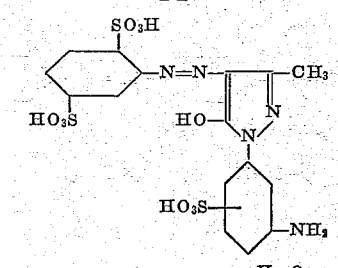
(1)

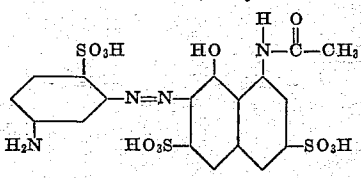


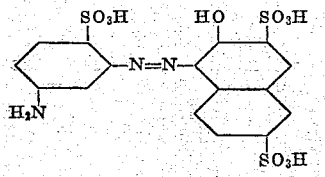
(2)

In Example 3, the following dye bases may be substituted for the dye base which was used therein:

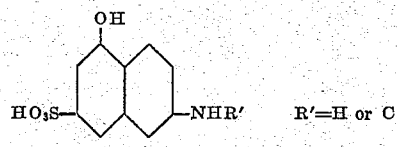






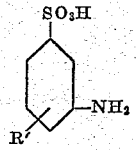


In Example 4, either the coupler or the diazo component or both may be changed. For instance, the 8-amino-1-naphthol-3,6-disulfonic acid used in Example 4 may be replaced with equimolar amounts of

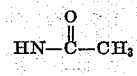


R′=H or CH_3

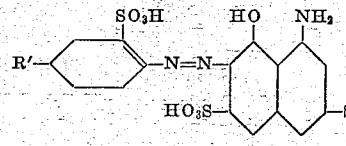
Moreover, a dye can be formed according to the procedure of Example 4 if the orthanilic acid is replaced with equimolar amounts of

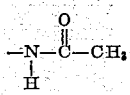


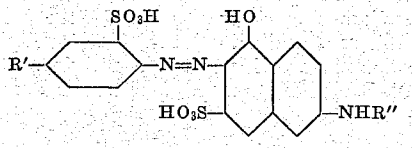
R′=Cl, CH_3, SO_3H or



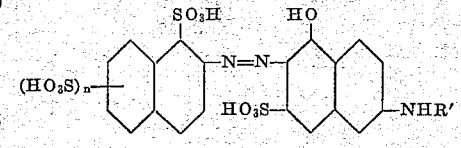
In Example 5, the dye base is formed by coupling acetyl H acid (8-amino-1-naphthol-3,6-disulfonic acid) with orthanilic acid. In place of this dye base, one can use equimolar proportions of the following dye bases:



R′=Cl, CH_3, SO_3H, 

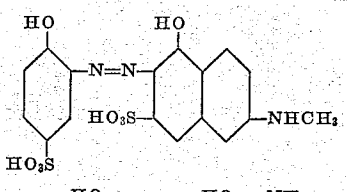
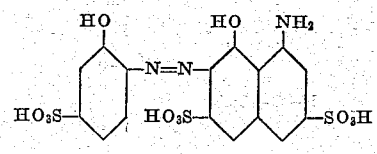
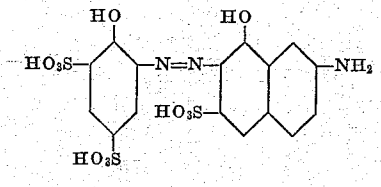


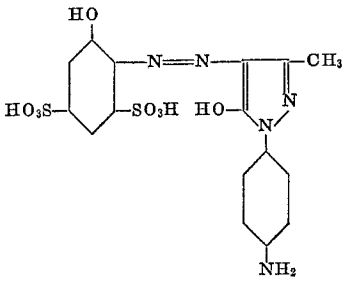
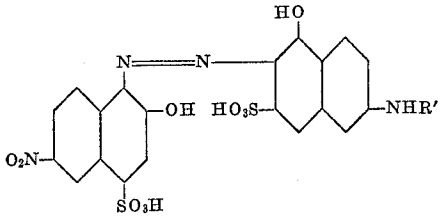
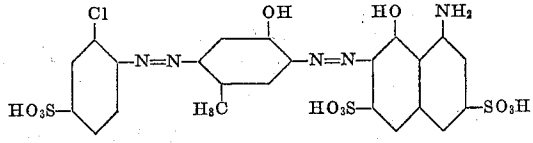
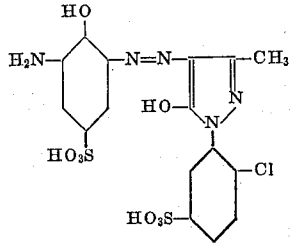
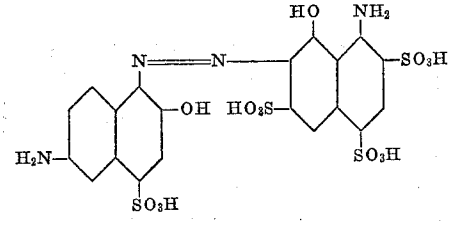
R′=Same as immediately above
R″=H, CH_3, CH_2CH_3,
CH_2CH_2OH,
$CH_2CH_2OSO_3H$



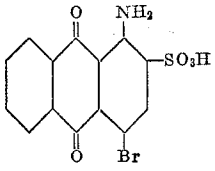
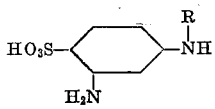
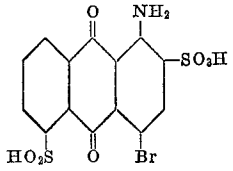
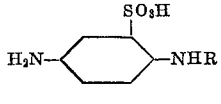
R′=H, CH_3, CH_2CH_3
CH_2CH_2CN
n=1 or 2

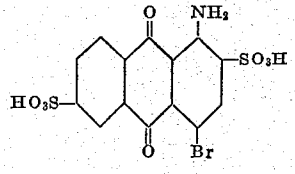
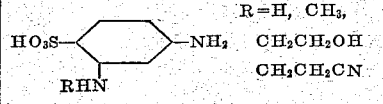
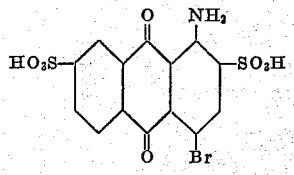
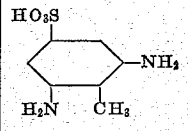
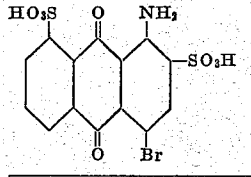
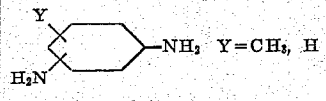
Example 6 shows a quinoxaline dye in which the dye chromophore is a radical of a metallized azo coupling product of 2-amino-1-phenol-4-sulfonic acid with 6-amino-1-naphthol-3-sulfonic acid. It is possible to substitute for this dye base equimolar parts of one or a mixture of the following metallized azo dye bases:

Azo Dye Base	Metallized with
	Cu or Co.
	Cu or Cr.
	Cu.

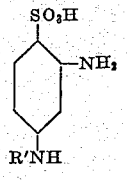
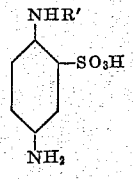
Azo Dye Base	Metallized with
	Cu.
 R'=H, CH_2CH_3, CH_2CH_2CN	Cu.
	Cu or Co or Cr.
	Cu.
	Cu.

Substitutions can also be made for the anthraquinone dye base of Example 7. The following anthraquinone components and diamine components can be condensed interchangeably to form dye bases which may be used in place of the dye base which is specified in Example 7:

Anthraquinone Component	Diamine Component
	 R=H, CH_3, CH_2CH_2OH, CH_2CH_2CN
	 R=H, CH_3, CH_2CH_3, $CH_2CH_2CH_3$, CH_2CH_2OH, $CH(CH_3)_2$

Anthraquinone Component	Diamine Component
	 R=H, CH_3, CH_2CH_2OH, CH_2CH_2CN
	
	 Y=CH_3, H

The use of a phthalocyanine dye base has been illustrated in Example 8. Typical phthalocyanine dye bases which are useful in this example are prepared by reacting a metal phthalocyanine tri- or tetrasulfonyl chloride wherein the sulfo groups are in the 3, 4 or 3 and 4 positions and the metal is Cu, Ni, or Co, with a diamine in the presence of a monoamine. The diamine used most frequently is

 or 

R'=H, CH_3, $CH(CH_3)_2$, CH_2CH_2CN, CH_2CH_2OH, $CH_2CH_2OSO_3H$

Ammonia is the preferred monoamine, but other amines such as methylamine and β-hydroxyethylamine are also useful.

The preceding representative examples may be varied within the scope of the present total specification disclosure, as understood and practiced, by one skilled in the art, to achieve essentially the same results.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for applying fiber-reactive dyes which contain a 2,3-dichloro-6-quinoxalinecarbonylamino group to cellulosic materials which process consists essentially of the following steps:

(1) the cellulosic material is padded with said fiber-reactive dye from an aqueous solution of said dye, said solution being maintained at a pH of from 6 to 7.8;

(2) the resulting dye-padded material is then treated for at least five seconds with an aqueous alkaline liquor consisting essentially of from 2 to 15 g./1. of sodium hydroxide and 200 to 300 g./1. of electrolyte selected from the group consisting of NaCl and Na_2SO_4, the temperature of said liquor being 160° to 218° F.;

(3) the dyed fabric of step (2) is then washed.

2. A process according to claim 1, step (1), wherein urea is added to said dye solution.

3. A process according to claim 1 wherein step (1) is followed by drying the dye-padded fabric prior to step (2).

4. A process according to claim 1 wherein step (1) is followed by drying the dye-padded fabric prior to step (2), the aqueous alkaline liquor treatment of step (2) being conducted at a temperature within the range of 180°–212° F. for from 5 to 10 seconds.

References Cited by the Examiner

UNITED STATES PATENTS

1,886,480	11/32	Haller et al.	8—54.2 X
3,043,650	7/62	Wegmann et al.	8—1.20
3,088,790	5/63	Schultheis et al.	8—54.2

FOREIGN PATENTS

315,451	7/29	Great Britain.
1,247,660	10/60	France.

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