

1

2,867,494

METHOD OF METALLIZING AZOIC DYEINGS

Clemens Streck, Loudonville, N. Y., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application August 2, 1956
Serial No. 601,658

12 Claims. (Cl. 8—42)

This invention relates to an improved process of metallizing azoic dyeings.

The fiber may be impregnated with a coupling component and passed into a solution which contains an active diazo either in the form of freshly prepared diazo or as a Fast Color Salt solution under conditions suitable for coupling. Fast Color Salts are diazo compounds which, except for a few diazos which are sufficiently stable per se, are diazo compounds which are stabilized by salt formation such as with certain metallic salts, e. g. $MgCl_2$, $ZnCl_2$, $SnCl_2$, etc., arylsulfonic acids such as naphthalene-1,5-disulfonic acid and naphthalene-1,3,6-trisulfonic acid, and also borofluoric acid.

One of the outstanding advantages of azoic dyeings is their fastness in contrast to that of the usual azo dyes. The fastness of azoic dyeings has recently been improved by metallizing, i. e. by treating the previously dyed fibers with various metallizing agents such as Cu, Co, Cr, Ni and the like. In the art as now practiced, it is necessary to dye the fibrous material with an azoic dye devoid of solubilizing groups followed by an after treatment with a metallizing agent. The metallizing step represents an extra step and also requires at least about 20 minutes. To overcome this, satisfactory metallization of azoic dyeings is achieved by incorporating the metallizing agent in the soaping bath as taught in my United States patent (Serial No. 316,305).

I have found that fibrous material dyed with an azoic dye, free from solubilizing groups and capable of conversion into a complex metal compound, is endowed with improved light-, wash- and chlorine-fastness properties and of improved shades by carrying out azoic color formation in the presence of the metallizing agent. In other words, the metallizing agent may be dissolved in a naphtholating bath, the fibrous material impregnated with this bath, usually followed by drying, and the impregnated fiber padded or printed with an active diazo which includes a freshly prepared diazo or a diazo stabilized as a Fast Color Salt, and then metallizing with hot water or preferably with steam. The temperature and moisture conditions of the hot water or steam, are sufficiently drastic to yield complete metallization together with color development, even when exposed to steam for less than 1 minute. The important advantage of this improved method is that a satisfactory metallized product is obtained without any additional operations other than the usual dyeing steps. By this procedure, economical dyeings are obtained as contrasted with the present method of after metallizing which requires additional steps, over and above the dyeing steps, i. e., treatment with the metallizing agent and heating.

The diazos and the coupling components employed in accordance with this invention are those which produce dyes having hydroxy groups ortho to the azo linkage or groups which are convertible into hydroxy groups such as lower alkoxy, i. e. methoxy, ethoxy, propoxy and butoxy, which are free from solubilizing groups such as sulfonic and carboxylic acids.

2

Any aromatic diazotizable amine may be employed which does not contain solubilizing groups such as sulfonic and carboxylic acids and includes all of the conventional aromatic and heterocyclic amines that are customarily employed in the preparation of azoic dyes. Unless the coupler to be used contains the o,o'-dihydroxy configuration, the amine should also have an o-hydroxy or lower alkoxy group ortho to the amine group. As examples of such diazotizable amines, the following are illustrative:

o-Anisidine
5-chloro-o-anisidine
5-nitro-o-anisidine
o-Dianisidine
4-benzamido-2,5-dimethoxyaniline
2,5-dimethoxy-4-(p-nitrobenzeneazo) aniline
4-cyano-2,5-dimethoxyaniline
5-diethylsulfamyl-o-anisidine
4-phenylamino-o-anisidine
5-n-butylsulfamyl-o-hydroxyaniline
5-amino-6-hydroxyquinoline

In the case where the coupling component contains the o,o'-dihydroxy configuration, the above may be used, as also those free from the o-hydroxy and alkoxy configuration, e. g. p-chloroaniline, p-anisidine, benzidine.

The coupling components may, in general, be selected from the Naphthol AS compounds which are arylides of 2-hydroxy-3-naphthoic acid and related β -hydroxy carboxylic acid derivatives, acetoacetylides and related β -oxocarboxylic acid arylides and pyrazolones. However, other compounds may be employed which are capable of coupling to yield a component having the required metallizable group in ortho position to the azo linkage. Thus, in addition to the coupling components specifically set forth in the examples, the following coupling components may be employed; 2-naphthol, 3-hydroxy-2-(2',5'-dimethoxy) naphthanilide, 3-hydroxy-2-(N-naphthyl)naphthamide, 3 - hydroxy - 2 - (4'-chloro)-naphthanilide, 3 - hydroxy - 2 - (N-2-methoxy-3-dibenzofuryl)naphthamide, 3 - hydroxyanthraquinone - 2 - carbox-o-toluidide, 2-hydroxy-3-dibenzofurancarboxylic acid arylides such as 2 - hydroxy - 3 - dibenzofuran (2',5'-dimethoxy)carboxanilide, bis(acetoacet) benzidide, bis(acetoacet)tolidide, acylacetylides such as acetoacet-4-chloro-2,5-dimethoxyanilide, 3 - hydroxy - 2 - carbazolecarboxylic acid arylides such as 3-hydroxy-2-carbazole-(p-chloro)carboxyanilide, terephthaloyl bisacetoacet - (3'-chloro-2',4'-dimethoxy)-anilide, pyrazolones, such as 1-phenyl-3-methyl-5-pyrazolone, 3-hydroxy - 2 - naphthoic acid arylides, 3-hydroxy-2-anthoic acid arylides, 2-hydroxy-4-nitroaniline $\rightarrow$ 2-naphthol, o-hydroxy-aniline $\rightarrow$ resorcinol, 2-hydroxy-5-nitroaniline $\rightarrow$ resorcinol. In the case of the couplers in the last two examples listed, wherein the o-hydroxyazo linkage is present in the coupler per se, any ordinary diazo compounds may be employed, such as m-chloro-aniline, o-nitroaniline, 1-aminoanthraquinone and 2-amino-4,4'-dichlorodiphenyl oxide. Other similar couples may be employed, such as those listed in German Patent 618,748.

The process of the present invention is applicable to cotton, and regenerated cellulose, which can be dyed by the process of the present invention.

In practicing the present invention 0.1 to 10 parts of a naphthol-type coupling component is dissolved in 1 to 100 parts of water containing 0.1 to 5 parts of caustic on a 100% basis. To this solution is added 0.1 to 10 parts of a metal salt which was previously dissolved and coordinated. In order that the metal salt maintain solubility under the alkaline condition of a naphthol solution any one of the usual and commercially available chelat-

ing agents is used in conjunction with the metal salt. The chelating agent is capable of forming a complex with the metallizing agent and acts as a coordinating agent to maintain the soluble metal salt such as copper, cobalt or nickel in the form of chloride, nitrate, sulfate, acetate, and the like. Examples of such chelating agents (coordinating agents) include triethanolamine, tartaric acid, glycine, dimethylglycine, glycollic acid, aspartic acid, glutamic acid, lactic acid, α -hydroxybutyric acid and the like. The amount of chelating agent employed is that necessary to maintain solubility of the metal salt under alkaline conditions and may range from 50–250 parts by weight of chelating agent per 100 parts by weight of metal salt. Theoretically these chelating agents are added in approximately molecularly equivalent amounts to that of the metallizing compound, but in actual practice the aforementioned proportions may be departed from to obtain the most desirable results depending on conditions of dyeing and type of coordinating agent employed. Approximately one mole copper to two of dye also gives satisfactory improvement.

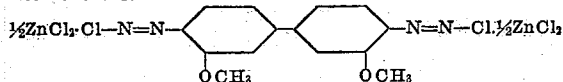
As stated above the metallizing compounds are salts and hydroxides of a metal selected from the group consisting of copper (cupic), nickel and cobalt. They are employed in the form of chlorides, sulphates, acetates, formates, nitrates, and the like. Those compounds are preferred which are relatively water soluble or dispersible. The amount of metal salt or metal hydroxide, to be employed will usually depend on the degree of metallizing desired. Molar ratios are necessary for complete metallization but the amount may range from about a fraction of an equivalent to an excess of one equivalent of metal per equivalent of dye.

The strength of dyeing is generally of the order of about 0.05–10% based on the weight of the fiber, depending on the shade desired, about 0.1–8% being the usual range to give sufficient and satisfactory dyeing.

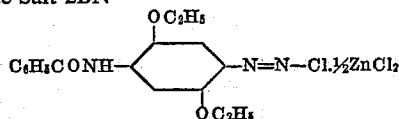
The diazo may be supplied by an amine freshly diazotized by treatment with nitrite in the customary manner, or the diazo may be a stabilized diazo, i. e., in the form of diazonium chloride or sulfate, or in the form of the diazo stabilized as a double salt, i. e., as a zinc chloride, boron trifluoride, tin chloride, naphthalenedisulfonic acid, etc.

As illustrative examples of Fast Color Salts the following are illustrative:

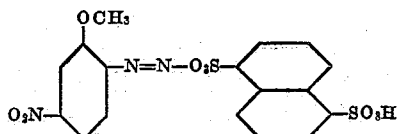
Fast Blue Salt BN



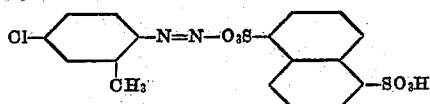
Fast Blue Salt 2BN



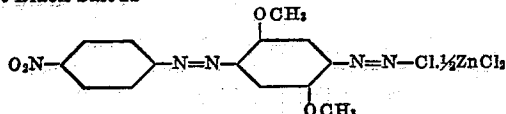
Fast Red Salt BN



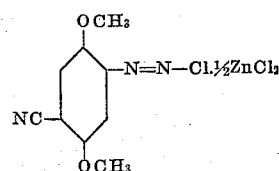
Fast Red Salt TRN



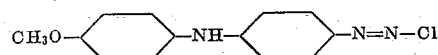
Fast Black Salt K



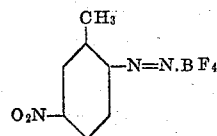
Fast Bordeaux Salt BD



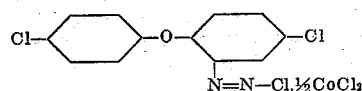
Variamine Blue Salt BD



Fast Red Salt RL



Fast Red Salt FR



The following examples will illustrate the preferred embodiments of the present invention. It is to be clearly understood that these examples are illustrative and are not to be considered as limitative.

All percentages and proportions given are based on the weight of the fibrous material employed unless otherwise indicated.

Example I

A naphthol coupling solution was made up by dissolving 3 grams of 3-hydroxy-2-naphthoic acid anilide in 6 cc. of isopropyl alcohol, 1½ cc. of caustic soda 34° Bé. and 2 cc. of water.

A metal containing solution was made by dissolving 25 grams of tartaric acid in 120 cc. of water. To this solution was added 25 grams of copper chloride, 75 cc. of caustic soda 34° Bé. and made up to 250 cc. with water.

The naphthol solution was poured into 50 cc. of water containing 2½ cc. of caustic soda 34° Bé., and 10 cc. of the aqueous alkaline copper chloride solution, and made up to 133 cc. by the addition of water.

A 100 gram sample of cotton was padded with the naphthol coupling and metal containing solution and dried. It was then padded with a solution made up by dissolving 6 grams of the zinc chloride salt of tetrazotized dianisidine, 0.5 cc. of commercial wetting agent, which is a 40% cc. solution of a fatty alcohol-ethylene oxide condensation product, and 2 cc. of 50% aqueous acetic acid and water added to make up to a volume of 133 cc. After padding, the material was exposed to steam at atmospheric pressure for 20–60 seconds.

A dyeing was obtained which was somewhat redder than a similar dyeing made without metallization with considerably better light-, wash- and chlorine-fastness.

Example II

Example I was repeated with the exception that in the metal containing solution copper chloride was replaced by 25 grams of cobalt chloride. The dyeing obtained was somewhat redder than a similar dyeing without metallization with considerably better light-, wash- and chlorine-fastness.

Example III

Example I was repeated with the exception that the tartaric acid in the metal containing solution was replaced by 25 grams of glycine. A dyeing was obtained which has considerable light-, wash- and chlorine-fastness.

Example IV

Example I was again repeated with the exception that the 3-hydroxy-2-naphthoic acid anilide was replaced by

5

2 grams of 1-phenyl-3-methylpyrazolone. A dyeing having excellent light-, wash- and chlorine-fastness properties was obtained.

Example V

Example I was again repeated with the exception that the 3-hydroxy-2-naphthoic acid anilide was replaced by an equivalent amount of 3-hydroxy-2-naphthoic acid o-toluidide, and the zinc chloride salt of tetrazotized dianisidine was replaced by an equivalent amount of the zinc chloride salt of diazotized 4-benzamido-2,5-dimethoxyaniline. A dyeing was obtained having excellent light-, wash- and chlorine-fastness properties.

Example VI

Example I was again repeated with the exception that the 3-hydroxy-2-naphthoic acid anilide was replaced by an equivalent amount of 3-hydroxy-2-naphthoic acid o-toluidide, and the zinc chloride salt of tetrazotized anisidine was replaced by an equivalent amount of the zinc chloride double salt of the diazo of 5-n-butylsulfamyl o-anisidine. A dyeing was obtained having excellent light-, wash- and chlorine-fastness properties.

Example VII

Example I was again repeated with the exception that the 3-hydroxy-2-naphthoic acid anilide was replaced by an equivalent amount of 2-hydroxybenzeneazo-4-resorcinol, and the zinc chloride salt of tetrazotized di-anisidine was replaced by an equivalent amount of the zinc chloride double salt of the diazo of 5-chloro-o-anisidine. A dyeing was obtained having excellent light fastness.

Example VIII

Example I was again repeated with the exception that in the metal containing solution copper chloride was replaced by an equivalent amount of nickel chloride. A dyeing of excellent light and wash fastness was obtained.

Example IX

Example I was again repeated with the exception that in the metal containing solution the copper chloride was replaced by an equivalent amount of copper sulfate. A dyeing of excellent light and wash fastness was obtained.

Example X

Example I was again repeated with the exception that the 3-hydroxy-2-naphthoic acid was replaced by 1.5 grams of β -naphthol. A deep navy shade was obtained of good light-, wash- and chlorine-fastness.

Example XI

3 grams of 3-hydroxy-2-naphthoic acid anilide and 1 gram of bis(acetoacet) o-toluidide were dissolved in 100 cc. boiling water containing 4½ cc. caustic soda 34° Bé. To this solution, cooled to to about 140° F., was added 10 cc. of the copper chloride solution of Example I.

Cotton was padded with this solution and dried.

It was then padded with a solution of 8.5 grams of zinc chloride double salt of tetrazotized dianisidine, 0.5 cc. of a 40% fatty alcohol-ethylene oxide condensation product, 3 cc. of 50% aqueous acetic acid solution and water added to make up to a volume of 133 cc., followed by treatment with steam for 25 seconds. A deep jet black was obtained of improved light fastness.

Example XII

Example I was again repeated with the exception that after the padding with the Fast Color Salt, the cotton was given a 30 second rinse in boiling water.

While the metallizing effect was not quite as good as the dyeing of Example I, i. e. exposed to steam, it was considerably better in light fastness than a dyeing which had not been metallized.

Example XIII

2.2 grams of 4-(o-hydroxyphenylazo)resorcinol were

6

dissolved in 6 cc. ethyl alcohol, 1½ cc. caustic soda 34° Bé. and 2 cc. of water.

A metal-containing solution was made up containing: 147 grams of copper sulfate, 683 cc. of water, 110 cc. of triethanolamine and 60 grams of dry caustic.

The naphthol solution was poured into a solution containing 50 cc. water, 2½ cc. caustic soda 34° Bé., and 10 cc. of the metallizing solution, and made up to 133 cc. with water.

Cotton was padded with this solution and dried. It was then padded with Fast Color Salt and treated with steam, as in Example I. A deep brown of good light fastness was obtained.

Example XIV

A solution was made up as follows:

I		A
		Parts
Naphthol AS soln. (25%)	120	
NaOH (dry)	6	

An additional metal-containing paste was made up as follows:

II		A
		Parts
Copper sulfate	14.7	
Triethanolamine	11.0	

I and II were mixed together.

A padding bath was made up as follows:

		A
		Oz.
Mixture of I and II	15	
Caustic (dry)	.8	
Water up to 1 gal.		

Cotton was padded with the above and dried.

The following padding bath was formulated:

		Parts
Dianisidine tetrazo, zinc chloride salt	8	
Alcohol-ethyleneoxide condensation product, 40% solution	.5	
Acetic acid 50%	2	
Water up to 1 gal.		

The cotton was padded with this solution and steamed for 25 seconds. A deep navy, fast to light, dyeing was obtained.

The metallizing compounds, i. e. metal salts, can be incorporated into the Rapidogen printing pastes and solutions, and on development in acidified steam the color is developed and metallizing occurs simultaneously.

The diazoamino compounds are the usual ones, free from solubilizing groups in the diazo portion, containing at least one solubilizing group in the amino portion, and in addition, containing a hydroxy or a lower alkoxy substituent ortho to the diazo group, except in the rare instance where the coupling components may contain an o,o'-dihydroxy-type azo configuration.

The following examples illustrate the foregoing embodiment:

Example XV

Two solutions were made up as follows:

	Solution	
	A	B
Commercially available Rapidogen solution which consists of 11 grams dianisidine tetrazotized and stabilized with methyl taurine, 11 grams 3-hydroxy-2-naphthanilide, 10 grams sodium hydroxide (100%), the usual solvents and water	120	120
Copper solution	50	50
Diethylene glycol		30

The copper solution contained 147 parts copper sul-

fate, 683 parts water, 110 parts triethanolamine and 60 parts dry caustic.

17 grams of A and 20 grams of B were thickened with starch tragacanth.

Cotton was printed with printing pastes A and B, steamed in acid steam in a normal manner for 2 minutes, rinsed and dried.

The dyeing from solution A was slightly redder, and had much better light fastness than a similar unmetallized dyeing. The dyeing from solution B was slightly less red than A, slightly stronger and showed a similar fastness to light.

Example XVI

A printing paste was made up as follows:

4 grams Rapidogen mix (cresidine diazotized and stabilized with sarcosine+3-hydroxy-3'-nitro-2-naphthanilide), 4 cc. ethylene glycol monoethyl ether, 24 cc. water, 3 cc. sodium hydroxide 34° Bé., 5 cc. copper solution, as employed in Example I, gum tragacanth to printing thickness.

Cotton cloth was printed with this paste and developed for 2 minutes in acidified steam. A yellower coloration, having excellent light fastness, was produced than in an unmetallized dyeing.

Example XVII

Example XVI was repeated with the exception that the Rapidogen mix was replaced by an equivalent amount of a Rapidogen consisting of dianisidine tetrazotized and stabilized with methyl taurine+phenyl methyl pyrazolone, and employing 10 cc. of the copper solution of Example XV. In this case a tan coloration was produced which had excellent light fastness properties.

Example XVIII

Example XVI was again repeated with the exception that the Rapidogen mix was replaced by an equivalent amount of a Rapidogen consisting of 4-benzoylamino-2-methoxy-5-methylaniline diazotized and stabilized with sarcosine+approx. equal parts of 3-hydroxy-2-naphthanilide and 3-hydroxy-2-naphth-o-toluidide. In this case a violet shade, somewhat redder than usual, was produced, having exceptionally good light fastness.

By the term "treatment at elevated temperatures with an aqueous medium having a pH of not more than 7" we include only the treatment of the padded fibrous material by means of steam, acidified steam, and hot water at or near the boil.

I claim:

1. The process of metallizing azoic dyeings which comprises impregnating a fibrous material selected from the class consisting of cotton and regenerated cellulose with an alkaline solution of an azoic coupling component, a coordinating agent selected from the class consisting of

aliphatic amino- and hydroxy-carboxylic acids, and a metallizing compound of the group consisting of soluble and dispersible salts of copper, cobalt, and nickel, and then treating the impregnated fiber with a diazo solution, in which the diazo is free from solubilizing groups, and simultaneously dyeing and metallizing in situ by treatment at elevated temperatures with an aqueous medium having a pH of not more than 7, the said azoic coupling component and the said diazo yielding an o, o'-dihydroxy configuration in the final dyestuff.

2. The process according to claim 1 wherein the metallizing compound is copper chloride.

3. The process according to claim 1 wherein the metallizing compound is cobalt chloride.

4. The process according to claim 1 wherein the metallizing compound is nickel chloride.

5. The process according to claim 1 wherein the metallizing compound is copper sulfate.

6. The process according to claim 1 wherein the metallizing compound is cobalt sulfate.

7. An alkaline azoic coupling bath for impregnating fibrous materials selected from the class consisting of cotton and regenerated cellulose prior to dyeing with a diazo compound, free from solubilizing groups, which converts to a complex metal compound comprising an alkaline solution of an azoic coupling component, a coordinating agent selected from the group consisting of aliphatic amino- and hydroxy-carboxylic acids, and a metallizing compound of the group consisting of salts and hydroxides of copper, cobalt, and nickel, the said azoic coupling component yielding upon coupling with the said diazo compound a dyestuff containing an o,o'-dihydroxy configuration.

8. A bath for impregnation of fibrous materials according to claim 7 wherein the metallizing compound is copper chloride.

9. A bath for impregnation of fibrous materials according to claim 7 wherein the metallizing compound is cobalt chloride.

10. A bath for impregnation of fibrous materials according to claim 7 wherein the metallizing compound is nickel chloride.

11. A bath for impregnation of fibrous materials according to claim 7 wherein the metallizing compound is copper sulfate.

12. A bath for impregnation of fibrous materials according to claim 7 wherein the metallizing compound is cobalt sulfate.

References Cited in the file of this patent

FOREIGN PATENTS

502,144	Great Britain	Mar. 7, 1939
531,470	Great Britain	Jan. 6, 1941