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3,061,397

METALLIZING AZOIC DYEINGS

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This invention relates to an improved process of metallizing azoic dyeings without the precipitation of free metal on the fibre and dyeing apparatus and at the same time yielding brighter and more desirable shades.

It is known that fibres may be impregnated with a coupling component and passed into a solution which contains an active diazo, either in the form of a 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 fibres 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 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 application Serial No. 316,305, filed on October 22, 1952 (now U.S. Patent 2,768,053, issued October 23, 1956).

In my United States patent application Serial No. 601,658, filed on August 2, 1956, for "Method of Metallizing Azoic Dyeings" (now U.S. Patent 2,867,494, issued January 5, 1959), I disclose and claim a novel process whereby the azoic color formation is carried out in the presence of the metallizing agent. By this process 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 shade. In this process the metallizing agent may be dissolved in a naphtholating bath, the fibrous material impregnated with this bath, usually followed by drying, and the impregnated fibre 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.

Despite the fact that economical dyeings having desirable characteristics are obtained, the latter process nevertheless lacks one factor which is highly desirable in the dye trade. In conducting numerous experiments with the process described in my patent, U.S. 2,867,494, I found

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that under certain conditions, free copper is precipitated. The precipitation may be on the fibre, causing splotchy dyeings, or in the dyeing apparatus, such as glass, wood, etc. (parts of which contain steel or iron), and the usual stainless steel, etc. resulting in a metal plating problem. The precipitation is believed to be due to the presence of certain impurities or by-products which are readily oxidizable and in oxidation cause a reduction of the loosely coordinated copper salt to free copper. Cleaning off deposited copper from equipment is difficult in addition to the poor, uneven dyeings resulting therefrom.

In my United States patent application Serial No. 631,062, filed on December 28, 1956, for "Method of Metallizing Azoic Dyeings," now Patent No. 2,893,814, I disclose and claim a novel process whereby the precipitation of free metal on the fibre and dyeing apparatus is very readily and economically remedied by the addition of an inorganic or organic oxidizing agent to the metallizing solution. The metallizing solution and other details with regard to the diazo and coupling components employed in azoic dyeings are fully described in my aforementioned patent application (Serial No. 601,658), the disclosure of which is incorporated herein by reference thereto. The inorganic and organic oxidizing agents which I have found particularly useful include all of those which are soluble in alkaline aqueous solution, and are sufficiently stable to withstand the temperature of padding which ranges from room temperature to 212° F., and will not destroy the diazo components. The disclosure of my application Serial No. 631,062 contains illustrative examples not only of the various inorganic and organic oxidizing agents but also complete details of avoiding precipitation of the free metal during metallizing azoic dyeings. Accordingly therefore, all such illustrations and working examples are incorporated herein by reference thereto.

I have found that the process disclosed in my pending application Serial No. 631,062 is surprisingly improved by yielding brighter and more desirable shades during the dyeing-metallization step by the presence of 1% to 30%, based on the dye solution, of a sulfonated vegetable oil, a phenylphenol, such as for example, o-, m- and p-phenylphenols or their alkali metal salts, and a mixture of the sulfonated vegetable oil and phenylphenol or its alkali metal salt. The sulfonated vegetable oil or the phenylphenol or its alkali metal salt or a mixture of the two can be added to the solution or paste at any time during the process so long as it is present during the dyeing-metallization step.

The sulfonated vegetable oils which may be employed include sulfonated oils obtained from any non-drying and semi-drying vegetable oils having (prior to sulfonation) an iodine number ranging from 48 to 160. As examples of such oils which are readily sulfonated and utilized in accordance with the present invention, the following are illustrative: castor oil, cashew nut oil, olive oil, palm oil, peanut oil, pecan nut oil, corn oil, cottonseed oil, mustardseed oil, pine nut oil, sesame seed oil, sunflower seed oil and the like. The method of sulfonating these oils is well known to those skilled in the art and need not be repeated herein. Any one of the conventional sulfonating methods may be employed to yield sulfonated vegetable oils which would be useful for the purpose of the present invention.

In experimenting with all of the above sulfonated vegetable oils, I have found that sulfonated castor oil, commercially available under the brand name of Monopol oil, is unique since when added to the solution or paste at any time during the process yields much brighter and more desirable shades than the other sulfonated vegetable oils, the alkali metal salts of the phenylphenols

and mixtures of such phenylphenols with sulfonated vegetable oils. This uniqueness may be attributable to the fact that the sulfonated castor oil is partially sulfonated and partially sulfated. The ricinoleic acid derived from castor oil contains both an unsaturated bond and a hydroxy group and for this reason on sulfonation yields a final product which is partially sulfonated and partially sulfated.

The alkali metal salts of the phenylphenols include sodium and potassium o-, m- and p-phenolates. The phenylphenols and their alkali metal salts are also well known to those skilled in the art and are commercially available under various trade and brand names.

In practicing the present invention, a Rapidogen solution is first prepared which normally comprises about 10 parts of a Naphthol type of coupling component and an approximately equivalent part of an azoic type of amine (free from solubilizing groups such as sulfonic and carboxylic acid groups) diazotized and stabilized with a primary or secondary amine together with a sufficient amount of caustic to dissolve the Naphthol, 5 to 30 parts of an alkaline glycol type solvent and 70-130 parts of water. The alkaline glycol solvents that may be employed include ethylene glycol, diethylene glycol, propylene glycol, glycol monomethyl ether, glycol monomethyl ether, glycol monobutyl ether. Preferably a mixture of a glycol, e.g. glycol and diethylene glycol and a glycol monoether, e.g. Cellosolve, is employed. To this is then added 1-30% of a sulfonated vegetable oil, an alkali metal salt of phenylphenol or a mixture of the two based on the weight of the dye solution.

To the dye solution is then added 0.1-10 parts of a copper salt which was previously dissolved and coordinated. As examples of such coordinating or chelating agents, the following are illustrative: triethanolamine, tartaric acid, glycine, dimethylglycine, glycollic acid, aspartic acid, glutamic acid, lactic acid, α -hydroxy-butyric 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 5-25 parts of chelating agent per 10 parts by weight of metal salt. Theoretically, the chelating agents are added in approximately 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 of copper to two of dye gives satisfactory improvement, although frequently the ratio of copper to dye is much less, i.e. as low as 0.1 mole of copper to 2 moles of dye.

The solution as above prepared may contain 10-20% of an oxidizing agent, as disclosed in the aforementioned application Serial No. 631,062, based on the weight of the metallizing agent.

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 parts given are by weight unless otherwise stated.

EXAMPLE I

A metallizing solution containing an oxidizing agent was prepared as follows:

Copper Solution

- .3 part of cupric chloride crystals
- .35 part of triethanolamine
- .18 part of caustic soda (dry)
- 2.0 parts of water

After formation of a blue solution, 0.3 part of sodium chromate anhydrous was added.

A concentrated solution was prepared from 120 parts of a commercially available Rapidogen Blue GN solu-

tion consisting of 11 parts of tetrazotized and stabilized o-dianisidine, i.e. stabilized with methyl taurine, 10 parts of 3-hydroxy-2-naphthanilide, 6 parts of sodium hydroxide (100%), 71 parts of combined water and solvent consisting of 7 parts of diethylene glycol, 10 parts of Cellosolve and 54 parts of water.

To 12 parts of the above concentrated solution, 3.13 parts of the above copper solution was added with stirring and 2 parts of sulfonated castor oil, commercially available under the brand name of Monopol oil, was added. The resulting solution was thickened with 70 parts of starch tragacanth and adjusted with 12.87 parts of water to yield a printing paste.

A 10 gram sample of cotton was printed with the paste, steamed in acid steam in a normal manner for 2 minutes, rinsed and dried. A very bright blue shade obtained was much brighter and greener in color than a similar dyeing obtained with a printing paste containing no sulfonated castor oil.

EXAMPLE II

Example I was repeated with the exception that .3 part of cupric chloride crystals was replaced by .45 part of copper sulfate. The results obtained were identical.

EXAMPLE III

Example I was again repeated with the exception that 2 parts of sulfonated castor oil were replaced by 2 parts of sodium p-phenylphenolate. The results obtained were identical with those of Example I.

EXAMPLE IV

Example I was repeated with the exception that 2 parts of sulfonated castor oil were replaced by 2 parts of sodium o-phenylphenolate. The results obtained were identical with those of Example I.

EXAMPLE V

Example I was again repeated with the exception that 2 parts of sulfonated castor oil were replaced by a mixture consisting of 1 part of sulfonated castor oil and 1 part of sodium p-phenylphenolate. The results obtained were similar as in the previous examples with the exception that in this case the dyeings were a little brighter and greener.

EXAMPLE VI

Example I was again repeated with the exception that 2 parts of sulfonated castor oil were replaced by a mixture consisting of 1 part of sulfonated corn oil and 1 part of sodium o-phenylphenolate. The results were similar to but a little brighter and greener than those obtained in Examples I to IV inclusive.

EXAMPLE VII

Example I was again repeated with the exception that 2 parts of sulfonated castor oil were replaced by 0.5 part of sodium p-phenylphenolate.

EXAMPLE VIII

A metallizing solution containing an oxidizing agent was prepared as follows:

Copper Solution

- 147 grams of copper sulfate
- 643 grams of water
- 110 grams of triethanolamine
- 60 grams of caustic soda (dry)

After formation of a blue solution, 40 grams of sodium chromate anhydrous was added.

A padding solution was prepared by mixing the following components:

- 3 grams of Naphthol AS (3-hydroxy-2-naphthanilide)
- 6 cc. of ethyl alcohol
- 1.5 cc. of caustic soda 34° Bé.
- 1.5 grams of sulfonated castor oil

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The padding solution was poured into 10 cc. of the above copper solution together with 2.5 cc. of caustic soda 34° Bé. and water to yield a total volume of 133 cc.

A 10 gram sample of muslin was padded with the above solution, dried and padded with a solution consisting of:

7 grams of o-dianisidine which had been tetrazotized and stabilized with zinc chloride

.5 cc. of Diazopon AN (fatty alcohol-ethylene oxide condensation product used as a protective colloid), and

2 cc. of acetic acid 50% aqueous solution

Sufficient water was added to give a total volume of 133 cc.

The padding was carried out on a 3-roll padder consisting of rubber rolls and stainless steel pad base.

The muslin was skyed (passed through the atmosphere) for a few seconds and then aged in neutral steam at atmospheric pressure for 20 seconds. A deep, rich blue coloration was obtained having excellent wash-, light- and chlorine-fastness without the minutest evidence of copper precipitation.

EXAMPLE IX

Example VIII was repeated 7 times. In the first example identified as "A" no sulfonated vegetable oil or phenylphenols or their alkali metal salts were added to the padding solution. In repeat examples "B" to "G" inclusive, 1.5 grams of sulfonated castor oil of Example VIII were replaced by "B," a mixture consisting of 1 gram of sulfonated castor oil and 1 gram of sodium o-phenylphenolate; "C," 1.5 grams of potassium p-phenylphenolate; "D," 1.5 grams of sodium p-phenylphenolate; "E," 1.5 grams of potassium o-phenylphenolate; "F," 1.5 grams of sodium o-phenylphenolate; and "G," 1.5 grams of sulfonated castor oil, respectively.

The repeat example "A," i.e. containing no sulfonated vegetable oil or phenylphenol or its alkali metal salt, after color development, gave a deep, rich blue coloration having excellent wash-, light- and chlorine-fastness without any evidence of copper precipitation. The repeat examples "C" to "G" gave more desirable brighter and greener colorations and shades whereas repeat example "B" showed a considerable improvement, i.e. much brighter and greener over repeat examples "C" to "G" inclusive.

EXAMPLE X

Example VIII was repeated with the exception that the Naphthol AS in the padding solution was replaced by 2 grams of phenylmethyl pyrazolone and 1.5 grams of sulfonated castor oil were replaced by 1.5 grams of sodium p-phenylphenolate. A tan coloration was produced which was very much brighter than the dyeing in which the padding solution contained no sodium p-phenylphenolate.

EXAMPLE XI

Example VIII was again repeated with the exception that the Naphthol AS was replaced by an equivalent amount of 2-hydroxy benzene-azo-4-resorcinol and the o-dianisidine tetrazotized and stabilized with zinc chloride, was replaced by an equivalent amount of zinc chloride double salt of diazotized 5-chloro-o-anisidine. A brown dyeing was obtained which showed excellent light-, wash- and chlorine-fastness with no precipitation of metallic copper on the fibre or in the padding solution. The shade was very much brighter and stronger than the dyeing without sulfonated castor oil in the padding solution.

EXAMPLE XII

Example VIII was again repeated with the exception that the Naphthol-AS in the repeated padding solution was replaced by an equivalent amount of 3-hydroxy-2-naphthoic acid o-toluidide and the o-dianisidine, tetrazotized and stabilized with zinc chloride, was replaced by an equivalent amount of zinc chloride double salt of the

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dialzo from 5-n-butylsulfamyl-o-anisidine. 1 gram of sodium-p-phenylphenolate was added to the padding solution. After color development, a real dyeing of improved properties was obtained which showed excellent light-, wash- and chlorine-fastness with no evidence whatsoever of copper precipitation on the fibre or in the padding solution.

EXAMPLE XIII

Example VIII was repeated with the exception that the sulfonated castor oil was replaced by 1.5 grams of sodium o-phenylphenolate and the copper solution was replaced by the following copper solution:

100 grams of glycine
400 grams of water
100 grams of copper chloride
300 cc. of caustic soda 34° Bé.
100 grams of sodium perborate

After color development, a much greener shade of blue was obtained than with a similar dyeing without the presence of sodium o-phenylphenolate in the padding solution.

EXAMPLE XIV

Example VIII was again repeated with the exception that the copper solution was replaced by the following copper solution:

100 grams of glutamic acid
400 grams of water
100 grams of copper sulfate
300 grams of caustic soda 34° Bé.
100 grams of m-nitrobenzenesulfonic acid sodium salt

A much brighter, greener shade of blue was obtained after color development than when a dyeing was made in identical manner without the presence of sulfonated castor oil.

EXAMPLE XV

Example I was repeated with the exception that 2 grams of sulfonated castor oil were replaced by 2 grams of sulfonated cottonseed oil in the Rapidogen solution. A much brighter and greener shade of blue was obtained than in a similar dyeing without the presence of the sulfonated cottonseed oil in the concentrated Rapidogen solution.

EXAMPLE XVI

A printing paste was prepared as follows:

4 grams of a Rapidogen mix, consisting of equivalent amounts of cresidine diazotized and stabilized with sarcosine, and 3-hydroxy-3'-nitro-2-naphthanilide, 4 cc. of ethylene glycol monoethyl ether, 24 cc. of water, 3 cc. of sodium hydroxide 34° Bé. and 5 cc. of copper solution of Example I were combined and 70 grams of gum tragacanth added to printing thickness. To the printing paste were added 1.5 grams of sodium o-phenylphenolate.

A 10 gram sample of cotton cloth was printed with the above paste and developed for 2 minutes in acidified steam. The Bordeaux print showed very excellent light-, wash- and chlorine-fastness with no evidence of metallic copper on the printed cotton fibre.

EXAMPLE XVII

Example XVI was repeated with the exception that 4 grams of the Rapidogen mix was replaced by 4 grams of a Rapidogen mix consisting of an equivalent amount of o-dianisidine tetrazotized and stabilized with methyl taurine and phenyl methyl pyrazolone, and 10 cc. of the copper solution of Example VIII together with 1.5 grams of sulfonated peanut oil. A very bright tan shade was produced, after color development, having excellent light-, wash- and chlorine-fastness with no evidence of metallic copper on the printed cotton fibre.

EXAMPLE XVIII

Example XVI was again repeated with the exception that 4 grams of the Rapidogen mix was replaced by 4 grams of a Rapidogen mix consisting of an equivalent amount of 4-benzoylamino-2-methoxy-5-methylaniline diazotized and stabilized with sarcosine and Naphthol AS, together with a mixture consisting of 1 gram of sulfonated cottonseed oil and 2 grams of sodium o-phenylphenolate. After color development, a very bright violet print was obtained which showed excellent light-, wash- and chlorine-fastness with no evidence of metallic copper on the printed fibre.

I claim:

1. The process of producing metallized azoic prints and dyeings in situ which comprises treating a fibrous material with an azoic coupling component which is free from solubilizing groups and a diazo component derived from an amine base free from solubilizing groups and which both azoic dye components are capable of yielding an o,o'-dihydroxy azo configuration, followed by a treatment at elevated temperatures in the presence of a coordinating agent selected from the class consisting of lower alkylolamines and aliphatic amino- and hydroxy-carboxylic acids, and a metallizing copper compound from the class consisting of soluble and dispersible salts and hydroxides of copper, and an oxidizing agent equivalent to 10-100% based on the weight of the metallizing agent, selected from the class consisting of alkali perborates, alkali chromates, hydrogen peroxide, alkali peroxides and nitrobenzenesulfonic acids and their alkali salts, and in the presence of a compound selected from the class consisting of o-, m-, and p-phenylphenols and the alkali metal salts thereof in an amount ranging from 1% to 30% based on the weight of the dye solution.

2. The process according to claim 1 wherein the compound is sodium o-phenylphenolate.

3. The process according to claim 1 wherein the compound is sodium p-phenylphenolate.

4. A composition of matter for use in azoic dye manufacture which comprises a dye solution of an azoic cou-

pling component free from solubilizing groups, a diazo-amino compound derived from an amine base free from solubilizing groups which has been diazotized and stabilized with a primary and secondary amine containing at least one solubilizing group, said azoic dye components yielding an o,o'-dihydroxy azo dye configuration in the final dye, a coordinating agent selected from the class consisting of lower alkylolamines and aliphatic amino- and hydroxy-carboxylic acids, a metallizing copper compound from the class consisting of soluble and dispersible salts of hydroxides of copper, an oxidizing agent equivalent to 10-100% based on the weight of the metallizing agent selected from the class consisting of alkali perborates, alkali chromates, hydrogen peroxide, alkali peroxides and nitrobenzenesulfonic acids and their alkali salts, and a phenylphenol compound selected from the class consisting of o-, m- and p-phenylphenols and the alkali metal salts thereof in an amount ranging from 1% to 30% based on the weight of the dye solution.

5. A composition of matter according to claim 4 wherein the phenylphenol compound is sodium o-phenylphenolate.

6. A composition of matter according to claim 4 wherein the phenylphenol compound is sodium p-phenylphenolate.

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