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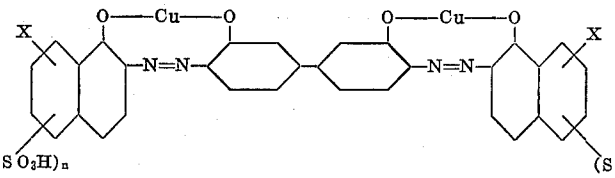
PROCESS FOR DYEING PAPER EMPLOYING METALIZED DYESTUFFS CONTAINING DIETHYLENE TRIAMINE

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ABSTRACT OF THE DISCLOSURE

Paper is dyed with dyestuffs of the formula:

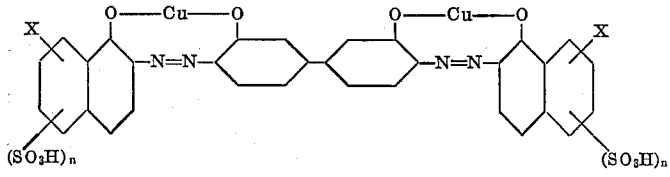


wherein *n* is 1–2, and X is hydrogen, chlorine or —NHR, wherein R is hydrogen, lower alkyl, benzyl, aryl or acyl, to which there has been added 5–20 parts of diethylene triamine and preferably 10–30 parts of (A) dialkali metal phosphate and/or (B) hexamethylene tetramine for 100 parts of dyestuff to obtain an even dyeing of true shade.

BACKGROUND OF INVENTION

This invention relates to the process of dyeing paper.

In the dyeing of paper employing dyestuffs of the following general formula:



wherein *n* is 1–2, and X is hydrogen, chlorine or —NHR, wherein R is hydrogen, lower alkyl, benzyl, aryl or acyl, a great deal of graniting (uneven splotchy dyeing having a granite-like appearance) frequently occurs. Such dyeings are not desirable and attempts to overcome this difficulty have not been wholly successful.

SUMMARY

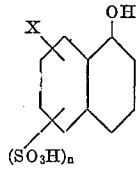
I have found that if a small amount, preferably from 5–20 parts by weight of diethylene triamine, is present in the dyebath per 100 parts of dyestuff, this problem of graniting is largely overcome. I have also found that if 10–30 parts by weight of a stabilizing material selected from the group consisting of (A) hexamethylene tetramine and (B) dialkali metal phosphate such as dilithium, disodium or dipotassium phosphate, or a mixture of (A) and (B) is present in the dyebath per 100 parts of dyestuff, decomposition of the dyestuff and resultant tendency to give a redder shade during dyeing of the paper web is very substantially inhibited.

While the diethylene triamine, and also the hexamethylene tetramine and/or dialkali metal phosphate if used, may be added to the dyebath, it is preferred to add these compounds to the dyestuff prior to standardization in order to produce the novel dyestuff composition of the present invention which has a softer physical form and which dissolves more readily in the dyebath.

Diethylene triamine appears to be quite unique in this action of overcoming graniting in dyeing paper with this class of dyestuffs since if an equivalent amount of closely related chemical compounds, ethylene diamine or triethylene tetramine, is present in the dyebath, then graniting is not reduced materially.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The dyestuffs of the formula given above which are included within the scope of this invention are known dyes and may be produced by tetrazotizing one molar proportion of o-dianisidine or o,o'-dihydroxybenzidine and coupling under alkaline conditions with approximately 2 moles of a coupler having the formula:



wherein X and *n* have the same definitions as above and coppering by any known method used to copper o,o'-dihydroxy type azo dyes.

Such couplers are exemplified by:

1-naphthol-3-sulfonic acid,
1-naphthol-4-sulfonic acid,
1-naphthol-5-sulfonic acid,
5-amino-1-naphthol-3-sulfonic acid,
6-amino-1-naphthol-3-sulfonic acid,
6-methylamino-1-naphthol-3-sulfonic acid,
6-benzylamino-1-naphthol-3-sulfonic acid,
6-anilino-1-naphthol-3-sulfonic acid,
6-p-anisidino-1-naphthol-3-sulfonic acid,
7-amino-1-naphthol-3-sulfonic acid,
7-anilino-1-naphthol-3-sulfonic acid,
8-amino-1-naphthol-3-sulfonic acid,
8-anilino-1-naphthol-3-sulfonic acid,
8-amino-1-naphthol-5-sulfonic acid,
8-anilino-1-naphthol-5-sulfonic acid,
8-(p-tolylsulfonamido)-1-naphthol-5-sulfonic acid,
1-naphthol-3,6-disulfonic acid,
1-naphthol-3,8-disulfonic acid,
1-naphthol-4,8-disulfonic acid,
6-amino-1-naphthol-3,5-disulfonic acid,
8-amino-1-naphthol-3,6-disulfonic acid,
8-acetylamino-1-naphthol-3,6-disulfonic acid,
8-amino-1-naphthol-5,7-disulfonic acid,
8-chloro-1-naphthol-3,6-disulfonic acid.

The amount of diethylene triamine employed is also critical. If less than 5% of diethylene trimine on the weight of dye is employed, there is practically no improvement in graniting. If more than 20% is employed, the product does not dry properly. Thus, 5–20% on the weight of dye is the critical amount.

In the preferred embodiment of the present invention the novel dyestuff composition thereof is formulated by mixing the dyestuff, preferably in the form of a dye paste taken directly from a filter press with about 5 up to 20% of diethylene triamine based on the weight of the dyestuff and also 10–30% based on the weight of the dyestuff of a material selected from the group consisting of (A) hexamethylene tetramine and (B) dialkali metal phosphate, or mixture of (A) and (B). Water or other inert solvent is preferably added in such an amount as to form a slurry for easy mixing. After mixing well, the paste may be used as such for dyeing paper, but preferably is dried in any suitable manner such as by spray drying, drum drying or oven drying. The dried material is then preferably standardized in known manner using the usual standardizing agents such as sodium sulfate, dextrin, Tamol, urea, sugar. The product thus obtained is in a soft physical form which dissolves quite readily in the paper pulp. It also shows little or no graniting when dyed on paper in contrast to such other formulations, and a further advantage is that the dyestuff in this formulation is relatively insensitive to alum, frequently used for sizing paper.

While it is preferred to prepare the novel dyestuff composition of the present invention containing both this type of dyestuff and diethylene triamine and also preferably hexamethylene tetramine and/or dialkali metal phosphate and add this to the dyebath (paper pulp), it will be understood that many of the advantages of the present invention may be obtained by adding the diethylene triamine and also preferably the dialkali metal phosphate to the dyebath (paper pulp) either before or after the dyestuff is added thereto. Especially in heavy dyeings, hexamethylene tetramine is preferred to the dialkali metal phosphate as the dialkali metal phosphate interferes with the size. The hexamethylene tetramine may be used without the dialkali metal phosphate, or in admixture in any proportion up to and including only the dialkali metal phosphate.

EXAMPLE 1

Preparation of dye composition

A series of 9 dyestuff formulations were prepared by slurrying 85 parts by weight of the dyestuff presscake obtained by coupling one molar proportion of tetrazotized dianisidine with two molar proportions of each of the couplers shown in the accompanying Table I and coppering in the usual manner, with 10 parts of diethylene triamine, 25 parts of disodium phosphate and a small amount of water to facilitate mixing. After the material was mixed well, it was spray dried. 75 parts by weight of this dried material was then mixed with 23 parts of dextrin to standardize the same, 1 part of Twitchell oil and 1 part of antifoam agent. The product is a soft, powdery material having a light appearance.

Dyeing on paper

200 mg. of each of the dry colors thus obtained was then mixed into 300 g. of bleached sulfite pulp (10% strength). After mixing well as in the beater, it was allowed to stand for 15 minutes and 1000 cc. of water at 40° F. was then added with agitation. After one minute, 2% of rosin size (1.7% solution) on the weight of the dry pulp was added and then after agitation for one minute, 2½% of alum (1.5% solution) was added. After agitating for 15 minutes, the pulp was made into a hand sample of paper on a screen. The particular dyestuffs employed and the shade on paper is shown in the following table:

TABLE I

	Tetrazo	Coupler	Metal	Shade on paper
Formulation:				
1	Dianisidine	8-amino-1-naphthol-3,6-disulfonic acid	Cu	Blue.
2	do	8-amino-1-naphthol-5,7-disulfonic acid	Cu	Do.
3	do	8-anilino-1-naphthol-5-sulfonic acid	Cu	Greenish blue.
4	do	6-amino-1-naphthol-3,5-disulfonic acid	Cu	Blue.
5	do	7-amino-1-naphthol-3-sulfonic acid	Cu	Blue-gray.
6	do	1-naphthol-3,6-disulfonic acid	Cu	Greenish blue.
7	do	8-amino-1-naphthol-5-sulfonic acid	Cu	Do.
8	do	6-anilino-1-naphthol-3-sulfonic acid	Cu	Blue.
9	do	6-amino-1-naphthol-3-sulfonic acid	Cu	Do.

Each of the dyeings thus obtained showed essentially no graniting as contrasted with a control dyeing using the same formulations and the same conditions but without the diethylene triamine and the disodium phosphate which showed considerable graniting. Also, the control dyeings were redder and duller than the dyeings obtained with the process of this invention.

Essentially the same results were obtained when disodium phosphate in the above formulations is replaced with equivalent amounts of either dipotassium phosphate or dilithium phosphate.

EXAMPLE 2

In order to better illustrate the decreased sensitivity to alum of the dye compositions of the present invention, the following experiment was carried out. It is to be noted that in the above examples the dye was on the fiber prior to treatment by alum, and thus, in a way "protected" from the alum. The dyeings employing the formulations of Example 1 were greener and brighter than the corresponding standard or control dyeing, but this difference was nowhere nearly as pronounced as in the case where the pulp is treated with alum first and then with dye so that the dye is not "protected" from the alum by combination with the fiber.

In carrying out this experiment, 300 g. of bleached sulfite pulp (10% pulp) is agitated with 2% rosin size (1.7% solution) on the weight of the dry pulp for 1 minute, then with 2½% alum (1.5% solution) on the weight of the dry pulp for 1 minute, and then with 200 mg. of color for 15 minutes, and then made into a hand sample.

Standard or control dyeings made without diethylene triamine and disodium phosphate showed considerable graniting in contrast to the dyeing made with the formulations of Example 1 according to this method. Also, the dyeings made employing the formulations of Example 1 were greener and brighter.

However, these dyeings were less green and duller than those of Example 1, thus demonstrating the sensitivity of the dye to alum, but at the same time also demonstrating the ability of the diethylene triamine to reduce alum sensitivity.

EXAMPLE 3

85 parts of the blue dyestuff obtained by coupling approximately 2 moles of 8-amino-1-naphthol-3,6-disulfonic acid with 1 mole of dianisidine tetrazo and copper (C.I. 24400) in the form of the presscake was slurried with 10

parts of diethylene triamine and a small amount of water to facilitate mixing. After the material was mixed well, it was spray dried. It was then finished in the manner of Example 1 to produce a soft powder. It was then applied to bleached sulfite pulp in the manner of Example 1. There was essentially no graniting.

EXAMPLE 4

Example 3 was prepared with the exception that 12.5 parts of hexamethylene tetramine and 12.5 parts of disodium phosphate were employed instead of the 25 parts of hexamethylene tetramine. The results were commensurate.

While in the foregoing examples the novel dyestuff composition of the present invention has been added to the paper pulp as a dry powder, it will be understood that if desired, the dyestuff composition can be metered into the paper pulp. It has been found that the aqueous solutions of the dyestuff compositions of this invention are quite stable, whether originally prepared in the form employing the moist dyestuff presscake or prepared before in the form employing the moist dyestuff presscake or prepared before use by dissolving the dyestuff compositions of the foregoing examples in water. The following examples illustrate preferred embodiments of aqueous solutions encompassed in the present invention.

EXAMPLES 5–7

The following formulations were prepared:

	5	6	7
Dyestuff of Example 3 (C. I. 24400), parts	100	100	100
Diethylene triamine	10	10	10
Hexamethylene tetramine		15	15
Triethylene tetramine			1
Water	90	75	74

These were mixed into bleached sulfite pulp and treated in the manner of Example 1.

The shade of Example 5 was greener and brighter, with less graniting, than a similar paper prepared without the diethylene triamine.

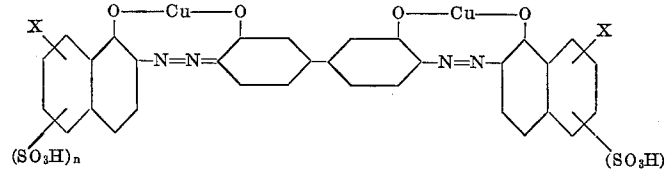
Example 6 had somewhat increased dye strength over Example 5, was slightly greener and brighter and had an improved storage stability over Example 5.

Example 7 had a better storage stability than that of Example 6 with practically no graniting. However, the shade shifted slightly to the redder side.

It will be understood that the foregoing examples are illustrative of the preferred embodiments of the present invention and various modifications will suggest themselves to those skilled in the art. Thus, in the examples the dyestuff was incorporated into the paper pulp so that in effect the pulp was the dyebath. It will be understood that if desired, the paper may be dyed after the web is formed by passing the web through a separate dyebath containing the dyestuff composition of this invention, or by wetting the web with an aqueous solution (dyebath) of a dyestuff of the composition such as spraying or roller-coating and the like.

I claim:

1. The process of dyeing paper comprises dyeing the paper in a dyebath containing a composition consisting essentially of about 100 parts by weight of dyestuff of formula:



wherein *n* is 1–2, and X is hydrogen, chlorine or —NHR, wherein R is hydrogen, lower alkyl, benzyl, aryl or acyl, and about 5 to 20 parts by weight of diethylene triamine.

2. The process as defined in claim **1** wherein the dyestuff composition contains about 10 to 30 parts by weight of a material selected from the group consisting of (A) hexamethylene tetramine and (B) dialkali metal phosphate and mixtures of (A) and (B).

3. The process as defined in claim **1** wherein the dyestuff composition contains about 10 to 30 parts by weight of hexamethylene tetramine.

4. The process as defined in claim **1** wherein the dyestuff composition contains about 10 to 30 parts by weight of dialkali metal phosphate per 100 parts of dyestuff.

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