

PATENT SPECIFICATION

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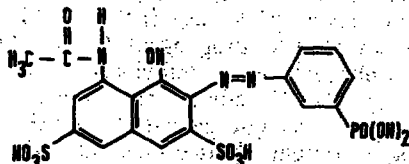
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(54) A PHOSPHONOPHENYLAZONAPHTHALENE
 DYESTUFF

(71) We, BURLINGTON INDUSTRIES, INC., a corporation organized under the laws of the State of Delaware, United States of America, of 3330 West Friendly Avenue, Greensboro, State of North Carolina, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention is concerned with a phosphonophenylazonaphthalene dyestuff. The invention provides salts of a dye having the structural formula:



whose chemical name is 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo)naphthalene with ammonia, alkali metals, and amines volatile under curing conditions, i.e. at 400°F. Also in accordance with the present invention, the compound 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo)naphthalene is prepared by reacting N - acetyl H - acid with diazotized m - aminobenzenephosphonic acid under acid conditions at below 10°C. The preparation of N - acetyl H - acid is described in Fierz-David, "Fundamental Processes of Dye Chemistry", Interscience Publishers, 1949, at pp. 263—264. The general reaction of certain naphthol sulfonic acids with 3 - aminobenzenephosphonic acid is described in Example 1 of United States Patent 3,202,550 to Grossman et al.

1 - Hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo)naphthalene and its said salts are bright red azo dyes. They exhibit properties improved over known

materials, i.e., good lightfastness and color strength; they are convenient to use in commercial dyeing operations, reasonably soluble in aqueous solutions (with or without surface active agents, organic solvents or the like) and convenient to synthesize.

We have found, for instance, that 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo)naphthalene and its said salts herein disclosed are lightfast and are more efficient than other commonly used materials. As an example, where one pound of 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo)naphthalene or its said salt is required to dye a given quantity of substrate (such as 100% cotton or another fiber), a greater amount, up to about 1.65 pounds, of another higher molecular weight dye is required to dye the same quantity of material.

1 - Hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo)naphthalene and its said salts, while useful as general dyestuff materials, are particularly suitable for reactive dyeing, that is in a process where the dye is reactively linked to cellulose fibers of the substrate to be dyed by means of a phosphorus ester link produced in the presence of a carbodiimide such as cyanamide. This procedure is described in detail in our German Offen. P. 25 05 497.1 of August 14, 1975, the disclosure of which is hereby incorporated by reference.

As already mentioned 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo)naphthalene may also be made and used as its alkali metal, ammonium or volatile amine salt. It is preferably used as the free acid or as the ammonium or an acid ammonium salt. The ammonium and acid ammonium salts are conveniently made by adding ammonium hydroxide to solutions of the free-acid dye. Correspondingly, upward adjustments of pH in the dyebath are preferably made with ammonia, although a volatile amines such as dimethylamine can

also be used. Downward adjustments of pH, if needed, preferably are made with hydrochloric acid or other acid volatile under curing conditions.

When used at low pH, as exemplified hereinafter, the free-acid dye is used in aqueous solution. At higher pH, the nature of the ammonium or alkali metal salt of the dye in solution will depend upon the ammonia or alkali metal content of the solution as measured by the pH. The ammonium salts are usually the tri- or tetra-ammonium salts, or mixtures thereof, within the general pH range. Mixtures of ammonium and alkali metal salts may also be used.

Of the following Examples, Example 1 illustrates the method of the invention, and the remaining Examples illustrate the use of the compound so prepared in dyeing. The words "Carbowax" and "Beckman" are trade marks.

EXAMPLE 1

H acid (Eastman product purified by reprecipitation, 175 g, 0.5 mole), sodium carbonate (30 g), and water (750 ml) were mixed and heated to 50°C to dissolve. Acetic anhydride (85 g, 0.83 mole) was added dropwise over 15 minutes and the solution then stirred for 1 hour at 50°C. Sodium carbonate (75 g) was then added and the solution heated for 1 hour at 95°C to reverse any acylation of the hydroxyl group. The solution was then cooled in ice.

m-Aminophenylphosphonic acid (86.5 g, 0.5 mole) and sodium carbonate (53 g, 0.5 mole) were dissolved in water (500 ml). Sodium nitrite (37 g, 0.54 mole) in water (100 ml) was added, and the solution cooled to 10°C. The solution was added to concentrated hydrochloric acid (125 ml) and ice (500 g). The solution was added all at once to the solution of acetyl H acid, and the solution stirred for 1 hour. Concentrated hydrochloric acid (500 ml) was then added (pH=0.5) and the solution filtered. The precipitated solid was washed with glacial acetic acid and dried under vacuum at 50°C.

Further purification to the free acid was effected by dissolving the dye in aqueous methanol and passing the solution through an acid ion exchange resin. Removal of the solvent yielded a dye which was, by titration, a tetrabasic acid of greater than 95% purity, thus confirming the structure illustrated above.

As a further means of analysis, the free acid was reacted in solution to make the tri-potassium salt and the solution evaporated to dryness giving the heptahydrated potassium salt having the empirical formula:

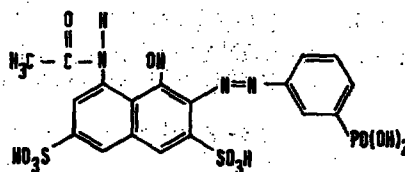


Results of elemental analysis are:

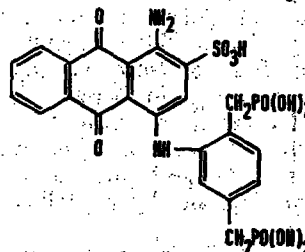
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	H ₂ O 16.0	Molecular Weight 785		
Found:	C 26.9	N 5.8	S 7.7	P 3.5
	H ₂ O 15.5	Molecular Weight 785		

EXAMPLE 2

A printing paste was prepared using 0.05 weight percent of the dye of the formula:



and 0.15 weight percent of a blue dye of the structure:



This dye is prepared by reacting bromaminic acid with *o*-amino-*p*-xylenediphosphonic acid as described in Example 25 of our German Offen. P 25 05 497.1.

The print paste also included 0.2 weight percent of a wetting agent (Igepal CO-710, nonylphenoxy poly - (ethyleneoxy) - ethanol having 10-11 ethyleneoxy units, sold by GAF), 0.1 weight percent (NH₄)₂HPO₄, 3.0 weight percent of dicyandiamide, 1.0 weight percent of sodium alginate, 33.0 weight percent of 70% Varsol emulsion and the remainder water. The resulting print paste was adjusted to a pH of 8.6 with ammonium hydroxide.

The print paste so prepared was screen printed on 100% cotton fabric at an add-on of about 5 grams per square yard (about a 100% average add-on). The fabric was dried and fixed at 400°F, at an exposure time of 60 seconds, to produce a printed cotton fabric having a good color fixation.

In the following Examples 3-5, all percentages are expressed on the weight of the bath.

EXAMPLE 3

A dye bath containing the following ingredients was prepared:

1.0%	Red dye of Example 1
3.0%	H ₃ PO ₄ (85%)
8.0%	Cyanamide AC-50 (50%)
2.0%	Carbowax 350
0.25%	Igepal CO-710
pH	1.5

The above bath was padded on 100% cotton at 70% pick-up, dried at 220°F, and cured for 60 seconds at 390°F. The cloth was rinsed; practically no color was removed.

EXAMPLE 4

A bath containing the following ingredients was prepared:

	0.5%	Red dye of Example 1
	5.0%	Cyanamide AC-50 (50%)
10	0.5%	Igepal CO-710
	0.3%	H ₃ PO ₄ (85%)
	pH	Adjusted to 5 with NH ₄ OH

This bath was padded on 100% cotton, steamed for 1 minute at 220°F and then cured 45 seconds at 390°F. When the cloth was scoured with 1.7 g/l soda ash and 1.5 g/l Synthrapol SP at the boil for 2 minutes, a fixation of 80% was obtained. Fixation is defined herein as that percentage of the color retained on the cloth after scouring, based on the color as it comes from the curing oven, both color measurements being taken on a Beckman DBG Spectrophotometer.

EXAMPLE 5

The following bath was prepared:

	2.0%	Red dye of Example 1
	4.0%	Dicyandiamide
	0.1%	Igepal CO-710
30	0.125%	H ₃ PO ₄ (85%)
	pH	5

This bath was padded on a 50/50 blend of polyester (T54)/cotton at 60% pick-up, infrared pre-dried and cured 75 seconds at 400°F. After scouring as in Example 4, color fixation was 70%.

As noted above, 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene and its said salts are unusually efficient, by which it is meant that the color yield per unit of dye weight is exceptional for a dye which is washfast on cellulosic fabrics and yarns. The exceptional efficiency stems from the fact that the dyes give inherently intense bright red dyeings, coupled with the fact that their molecular weights are very low by comparison with the large-molecule direct dyes which are substantive to cellulose. Hence each molecule, which is to say, each low molecular weight of it, provides a high yield of color on a pound-for-pound basis.

The low molecular weight, or expressed otherwise, the general simplicity and smallness of the molecule, provide yet another advantage to 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene and its said salts. Especially when a dye is permanently fixed to a substrate by chemical reaction, it is highly desirable that any of the dye which has failed to become reactively

bound should be readily washed away during process rinsing, to provide easy washoff, and reduce subsequent "washdown" during use. In 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene and its said salts the same phosphonic acid group that provides a site for reaction also serves as a strong water-solubilizing group for aiding removal of any dye molecules which are not fixed, thereby ensuring efficient removal of unfixed dye during present rinsing, and reducing or even eliminating subsequent drawn-out washdown during customer use. 1 - Hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene and its said salts are believed to be easier to wash off in process rinsing than any red dye being used in commercial continuous dyeing today.

The acetyl group is provided in the dyes as the smallest group capable of overcoming the inherent susceptibility to light of H-acid dyes. Other groups will furnish lightfastness properties, but no other so efficiently as the acetyl. In other words, the acetyl group supplies lightfastness in conjunction with minimum effect on the high redness per pound of the dyes of the invention.

1 - Hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene and its said salts have a distinct advantage, compared to conventional reactive dyes which are applied under strongly alkaline conditions, that they mostly are applied under acidic conditions and thus may be applied together with disperse dyes in the same dyebath. Alkaline conditions lead to flocculation of the majority of disperse dyes, which fact drastically limits the possibilities for simultaneous dyeings of polyester and cotton with disperse and conventional reactive dyes. In contrast, the acid fixing conditions used with 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene and its said salts have no adverse effect on disperse dyes, and the two types of dyes can be used together without difficulty.

WHAT WE CLAIM IS:—

1. The ammonium salt of 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene.
2. An alkali metal salt of 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene.
3. A salt of 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene with an amine that is volatile at 400°F.
4. A method of preparing 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene, that comprises reacting N - acetyl H - acid with diazotized m - aminobenzenephosphonic acid under acid conditions at below 10°C.



The above bath was padded on 100% cotton at 70% pick-up, dried at 220°F, and cured for 60 seconds at 390°F. The cloth was rinsed; practically no color was removed.

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2. An alkali metal salt of 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene.

3. A salt of 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene with an amine that is volatile at 400°F.

4. A method of preparing 1 - hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo) - naphthalene, that comprises reacting N - acetyl H - acid with diazotized m - aminobenzenephosphonic acid under acid conditions at below 10°C.

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5. A method as claimed in Claim 4 substantially as hereinbefore described in Example 1.

5 6. 1 - Hydroxy - 3,6 - disulfo - 8 - acetamido - 2 - (3' - phosphonophenylazo)-naphthalene when prepared by a method as claimed in Claim 4 or 5.

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