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TRIAZINYL AZO DYESTUFFS

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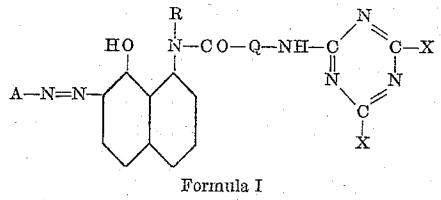
No Drawing. Filed Jan. 17, 1958, Ser. No. 709,453
Claims priority, application Great Britain Jan. 23, 1957
6 Claims. (Cl. 260—153)

This invention relates to new azo dyestuffs and more particularly it relates to new monoazo dyestuffs which are valuable for the production of fast red colourations on textile materials.

The present invention is a modification of the invention described in United Kingdom specification No. 785,222. In the said specification there are described certain monoazo dyestuffs containing a 1-(2':4'-dichloro-s-triazinylamino-)8-hydroxynaphthalene mono- or di-sulphonic acid residue which are valuable dyestuffs for cellulosic textile materials, especially when applied in accordance with the dyeing and printing processes described in Belgian specifications Nos. 543,218, 556,709 and 556,819. When so applied, the dyestuffs described in United Kingdom specification No. 785,222 are believed to become chemically bound to the textile material, the resultant coloured textile materials being very fast to severe washing treatments. However, further study of these dyestuffs has revealed that, when the coloured dyeings and prints obtained therefrom by the processes indicated above are stored in a slightly moist, acidic atmosphere, as is sometimes found in textile warehouses used for the storage of coloured textile materials, a small proportion of colouring matter, probably a decomposition product of the dyestuff, becomes loosely attached to the textile material, and may readily be removed therefrom by mild washing treatments. More particularly, in the case of the printed textile materials there is a tendency of such loosely attached colouring matter to migrate so that adjacent portions of the textile material become stained.

It is a purpose of the present invention to provide dyestuffs which, whilst having in the main the desirable properties of the dyestuffs of United Kingdom specification No. 785,222, are superior to those dyestuffs and dyestuffs of closely related structure thereto which are known from the prior art, in respect of the fastness to moist, acid atmospheres of the dyeings and prints obtained from said dyestuffs by the processes described in the Belgian specifications named above.

Thus according to the present invention there is provided the modification in or improvement of the invention described in United Kingdom specification No. 785,222 whereby there are provided, as new dyestuffs, the monoazo compounds represented in the free acid form by the formula:



Formula I

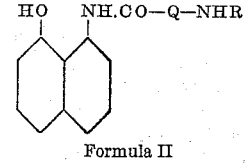
wherein A stands for an aryl radical which may be substituted other than with hydroxyl, amino or monoalkylamino groups, the naphthalene nucleus contains one or two sulphonic acid groups, R stands for a hydrogen atom or hydrocarbon radical, Q stands for a m- or p-phenylene radical which may be substituted for example by methyl and X stands for a halogen atom.

Thus in the above formula, A may represent, for example, a benzene or an alpha- or beta-naphthalene nucleus which may also be substituted, for example, by halogen such as chlorine, alkyl such as methyl, trifluoromethyl, alkoxy such as methoxy, aryloxy such as phenoxy, and more especially A may contain electronegative substituents, such as nitro groups, sulphamyl or mono- or di-substituted sulphamyl groups, carboxylic acid, carboxylic ester, carbamyl or mono- or di-substituted carbamyl groups and above all by sulphonic acid groups. Dyestuffs which contain an electronegative group, and in particular a sulphonic acid group, ortho to the azo group, form a preferred class of the new dyestuffs.

As hydrocarbon radicals represented by R there are preferred unbranched alkyl radicals of 6 carbon atoms or less, for example methyl, ethyl, n-butyl and n-hexyl radicals.

X may represent, for example a chlorine or a bromine atom.

According to a further feature of the invention there is provided a process for the manufacture of new monoazo dyestuffs from, as starting materials, substantially equimolecular proportions of a cyanuric halide, a compound which in its free acid state is represented by the formula:



Formula II

wherein the naphthalene nucleus contains one or two sulphonic acid groups, and Q and R have the meanings stated above, and a diazotised aromatic primary amine which may contain substituents other than hydroxyl or monoalkylamino groups, which comprises interacting the compound represented by Formula II with either of the two starting materials and then interacting the product so obtained with the third starting material.

Thus in the above process the compound represented by Formula II may be first used as a coupling component and interacted with the diazotised amine by the commonly-used methods for the manufacture of azo compounds and then the azo compound so obtained interacted with the cyanuric halide; or the compound represented by Formula II may be first interacted with a cyanuric halide and then the product so obtained is used as a coupling component and interacted with the diazotised amine, using the commonly-used methods for obtaining azo compounds.

As examples of cyanuric halides which may be used, there may be mentioned cyanuric chloride and cyanuric bromide.

As examples of aromatic primary amines which may be diazotised for use in the above process there may be mentioned orthanilic acid, sulphanilic acid, aniline-2:5-disulphonic acid, 4-chloroaniline-2-sulphonic acid, 5-chloro-4-methylaniline-2-sulphonic acid, 4-methylaniline-2-sulphonic acid, 4-chloro-5-methylaniline-2-sulphonic acid, 3-amino-4-sulphobenzotrifluoride, 3:4-dichloroaniline-6-sulphonic acid, 4-aminoanisole-3-sulphonic acid, 3-aminoanisole-4-sulphonic acid, 3-methylaniline-4-sulphonic acid, 1-naphthylamine-2-sulphonic acid, 2-naphthylamine-3:6-disulphonic acid and 2-naphthylamine-1-sulphonic acid.

As examples of amino compounds of Formula II which may be used there may be mentioned 1-(3'-aminobenzoylamino)-8-hydroxynaphthalene-3:6- and 4:6-disulphonic acids, 1-(4'-aminobenzoylamino)-8-hydroxynaphthalene-3:6- and 4:6-disulphonic acids, 1-(3'-aminobenzoylamino)-8-hydroxynaphthalene-2:4-disulphonic acid and 1-(3'-aminobenzoylamino)-8-hydroxynaphthalene-6-sulphonic acid.

Although, in general it is preferred to use equimolecular proportions of the reactants, it is sometimes found preferable, in order to improve the yield or quality of the product, to use a slight excess, up to 10% by weight, of one reactant over the weight which is theoretically equivalent to the weight of the other reactant present.

In carrying out the above process, the product obtained by the first interaction may, if desired, be isolated but in general, it is preferred to interact it in situ with the third starting material.

When the compound represented by Formula II is first interacted with the diazotised amine, the interaction is preferably carried out in the presence of an alkali, for example sodium carbonate. However, when the coupling is carried out as the second interaction, using as coupling component the interaction product of the cyanuric halide and the compound represented by Formula II, it is preferred to use a reaction medium as weakly alkaline as will allow the coupling to take place efficiently, so that side-reactions, especially the loss of halogen from the triazine residue, are reduced to a minimum. In general a reaction medium having a pH between 6 and 8 is preferred when the coupling is carried out as the second interaction.

Whether the cyanuric halide is employed as a reactant in the first or the second interaction of the process, the interaction is preferably carried out in aqueous medium at a temperature between 0° C. and 5° C. If desired, an acid-binding agent for example sodium carbonate, may be added to the medium.

It is generally preferable to isolate the new dyestuffs from the media in which they have been formed at a pH from 6 to 8 and it has been found that the loss of chlorine from the triazine rings in the dyestuffs can be reduced considerably by addition of certain buffering agents which give a pH value between 6 and 8 and in particular by those which give a pH of about 6.5. These buffering agents for example mixtures of disodium hydrogen phosphate and sodium dihydrogen phosphate or of disodium hydrogen phosphate and potassium dihydrogen phosphate may be added at any suitable time during the manufacture of the new dyestuffs, but a convenient procedure comprises addition of sufficient of an acid-binding agent such as sodium carbonate to the reaction mixture to give a pH between 6 and 8, then addition of buffering agent and then salt to precipitate the dyestuff, isolation of the latter by filtration and addition of more buffering agent to the dyestuff paste before drying.

The drying of the dyestuff paste is preferably carried out at a temperature below 65° C.

The new monoazo dyestuffs, in the form of the alkali metal salts are soluble in water, and like the dyestuffs described in United Kingdom specification No. 785,222 they may be used to colour silk, wool, regenerated protein and cellulosic textile materials for example cotton, linen and viscose rayon, by treating the textile material with an aqueous solution (which may be a thickened printing paste) of the dyestuff in conjunction with a treatment with an acid-binding agent, for example sodium hydroxide, potassium phosphate, sodium carbonate or sodium bicarbonate. The treatment with the acid-binding agent may be carried out prior to, simultaneously with or after the treatment with the dyestuff.

The new dyestuffs may also be applied to silk, wool, regenerated protein, polyamide and modified polyacrylonitrile textile materials, by the conventional dyeing methods used for those textile materials, that is by dyeing from weakly acid or neutral dyestuff solutions, for example dyestuff solutions containing acetic acid, formic acid, sodium sulphate or ammonium acetate.

The dyestuffs may also be applied to silk, wool and regenerated protein textile materials by the conventional printing methods used for those materials.

When so applied, they give fast level red shades, which have substantially the same degree of fastness to washing and to light, as those from the dyestuffs of the said specification.

The invention is illustrated but not limited by the following examples in which parts and percentages are by weight:

EXAMPLE 1

A solution of 18.6 parts of cyanuric chloride in 100 parts of acetone is added to a stirred mixture of 200 parts of water and 300 parts of crushed ice and then 2 parts of 2 N hydrochloric acid are added. To the suspension of cyanuric chloride so formed there is added in 40 minutes a solution of 48.2 parts of the disodium salt of 1-(3'-aminobenzoylamino)-8-hydroxynaphthalene-3:6-disulphonic acid in 240 parts of water made faintly alkaline to Brilliant Yellow paper by the addition of sodium carbonate. The temperature of the mixture is kept between 0° C. and 5° C. throughout the process.

The mixture is stirred for 2 to 3 hours until no cyanuric chloride is present and then there is added a suspension of the diazo compound from 16.45 parts of aniline-2-sulphonic acid.

The mixture is stirred at a temperature between 0° C. and 5° C. and sufficient sodium carbonate is added to change the pH of the mixture to 5. Common salt is then added at the rate of 15 lb. for every 10 gallons of mixture and then more sodium carbonate is gradually added over 2 hours to raise the pH of the aqueous medium to about 7.5 and to maintain it in this region until the coupling reaction is completed. A solution containing 7.0 parts of disodium hydrogen phosphate and 12.5 parts of potassium dihydrogen phosphate in 100 parts of water is then added. The mixture is then stirred for 30 minutes, filtered and the residue is dried at 30° C.

The dyestuff so obtained contains 1.88 organically bound chlorine atoms for each azo group. It may be applied to cotton by padding the fabric with an aqueous solution of the dyestuff, drying, subsequently passing the dried fabric through a 1% solution of caustic soda saturated with sodium chloride and afterwards steaming it for 1 minute. There is thus obtained a bright bluish-red colouration possessing good fastness to severe washing and to light.

EXAMPLE 2

If the process described in Example 1 is repeated, using 24.0 parts of aniline-2:5-disulphonic acid in place of the 16.45 parts of aniline-2-sulphonic acid, and the amount of common salt added to the coupling mixture is raised to 20 lb. for every 10 gallons of volume, a dyestuff is obtained which contains 2.0 organically bound chlorine atoms for each azo group present. It dyes cotton by the method described at the end of Example 1 in slightly yellower shades but having similar good fastness to severe washing and to light.

EXAMPLE 3

If in the process of Example 1 the 48.2 parts of the disodium salt of 1-(3'-aminobenzoylamino-)8-hydroxynaphthalene-3:6-disulphonic acid are replaced by 48.2 parts of the disodium salt of 1-(4'-aminobenzoylamino-)-8-hydroxynaphthalene-3:6-disulphonic acid and after adding the suspension of the diazo compound and adjusting the pH of the coupling mixture to 5, common salt is added at the rate of 20 lb. for every 10 gallons of mixture and the subsequent procedure is that described in Example 1, then a dyestuff is obtained which contains 1.90 organically bound chlorine atoms for each azo group present. This dyestuff when applied to cotton by the method described in Example 1 gives bright bluish red shades with good fastness to washing and to light.

EXAMPLE 4

A solution of 19 parts of cyanuric chloride dissolved in 108 parts of acetone is added to a stirred mixture of 300 parts of water and 300 parts of crushed ice. To the

suspension of cyanuric chloride so formed there is added in 40 minutes a solution of 48.2 parts of the disodium salt of 1-(3'-aminobenzoylamino)-8-hydroxynaphthalene-3:6-disulphonic acid in 800 parts of water made faintly alkaline to Brilliant Yellow paper by addition of sodium carbonate. The temperature of the mixture is kept between 0° C. and 5° C. throughout the process.

The mixture is stirred for 1 to 2 hours until no cyanuric chloride is present and then there is added a suspension of the diazo compound from 21.05 parts of 5-chloro-4-methylaniline-2-sulphonic acid.

The mixture is stirred at a temperature between 0° C. and 5° C. and sufficient sodium carbonate is added to change the pH of the mixture to 7. More sodium carbonate is gradually added to raise the pH to 7 and to maintain it in this region until the coupling reaction is completed. A solution containing 7.0 parts of disodium hydrogen phosphate and 12.5 parts of potassium dihydrogen phosphate in 100 parts of water is then added. The mixture is stirred for 30 minutes, filtered and the residue is dried at 25° C.

The dyestuff so obtained contains 1.96 organically bound chlorine atoms for each azo group. It dyes cotton by the method described at the end of Example 1 giving a bright bluish red colouration possessing good fastness to washing and to light.

In the following table there are described in column 2 the shades obtained from further dyestuffs of the invention, obtained by the procedure described in Example 4 but substituting the molecularly equivalent amount of the diazonium compound from the amine named in column 1. All dyestuffs so obtained contain 2.0 organically bound chlorine atoms for each azo group.

Table

Column 1—Diazo Components	Shade
5. 4-methylaniline-2-sulphonic acid	Bluish red.
6. 4-aminoanisole-3-sulphonic acid	Magenta.
7. 3:4-dichloroaniline-6-sulphonic acid	Bluish red.
8. 3-amino-4-sulphobenzotrifluoride	Red.
9. 3-methylaniline-6-sulphonic acid	Bluish red.
10. 2-naphthylamine-3:6-disulphonic acid	Do.
11. 2-naphthylamine-1-sulphonic acid	Do.
12. 1-naphthylamine-2-sulphonic acid	Reddish purple.
13. 4-chloroaniline-2-sulphonic acid	Bluish red.

EXAMPLE 14

A solution of 18.6 parts of cyanuric chloride in 130 parts of acetone is added to a stirred mixture of 170 parts of water and 170 parts of crushed ice. To the suspension of cyanuric chloride so formed there is added during 40 minutes a solution of 73.4 parts of the trisodium salt of the aminoazo dyestuff obtained by coupling, in the presence of sodium acetate, diazotised aniline-2-sulphonic acid with 1-(N-n-butyl-N- 3'-aminobenzoylamino)-8-hydroxynaphthalene - 3:6 - disulphonic acid in 850 parts of water made faintly alkaline to Brilliant Yellow paper by the addition of sodium carbonate. The temperature of the mixture is kept between 0° C. and 5° C. throughout the process.

The mixture is stirred for 1 hour, neutralised to pH 7 by the addition of sufficient sodium carbonate and stirring is continued for a further 2 hours until no cyanuric chloride is present, the pH being maintained at 7 by further additions of sodium carbonate. A solution containing 7.0 parts of disodium hydrogen phosphate and 12.5 parts of potassium dihydrogen phosphate in 100 parts of water is then added. The dyestuff contain 2.0 organically bound chlorine atoms for each azo link and dyes cotton by the method described at the end of Example 1 in reddish orange shades.

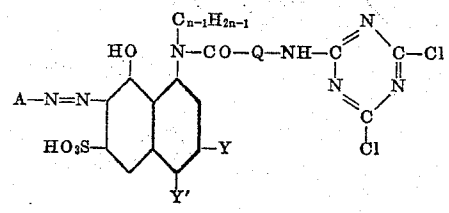
EXAMPLE 15

If the process described in Example 1 is repeated using

48.2 parts of the disodium salt of 1-(3'-aminobenzoylamino)-8-hydroxynaphthalene-4:6 - disulphonic acid in place of the 1-(3'-aminobenzoylamino)-3:6-disulphonic acid, and the amount of common salt added to the coupling mixture is increased to 20 lb. for every 10 gallons of volume, a dyestuff is obtained which contains 2.0 organically bound chlorine atoms for each azo group present. It dyes cotton by the method described at the end of Example 1 in yellower shades having good fastness to washing and light.

What I claim is:

1. Dyestuffs represented in their free acid form by the formula:



wherein:

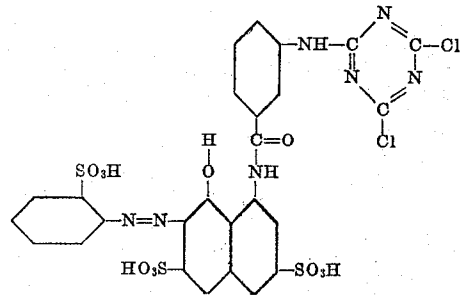
A stands for a radical selected from the group consisting of unsubstituted naphthyl and sulfonated naphthyl radicals, phenyl radicals and phenyl radicals carrying up to three substituents selected from the group consisting of chlorine, methyl, trifluoromethyl, methoxy, phenoxy, nitro, sulfamyl, carbamyl, carboxy, and sulfonic acid groups;

n is a small whole number having a value from 1 to 7;

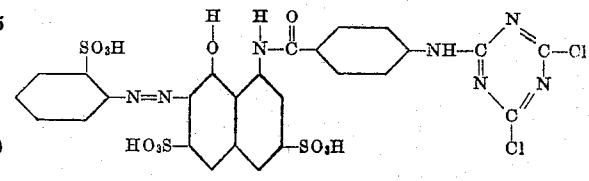
Q is a member selected from the group consisting of m- and p-phenylene radicals; and,

one of the radicals represented by Y and Y' is selected from the group consisting of hydrogen and sulfonic acid, and the other is hydrogen.

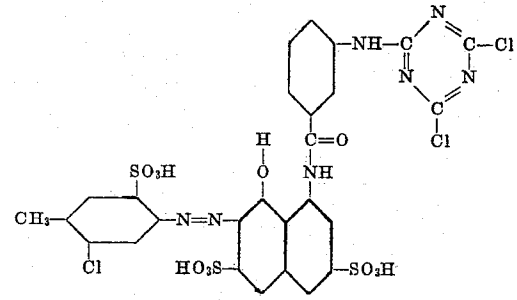
2. The dyestuff having the formula:



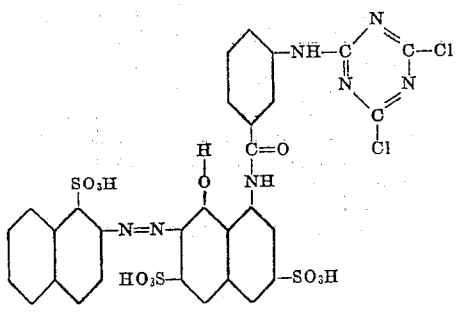
3. The dyestuff having the formula:



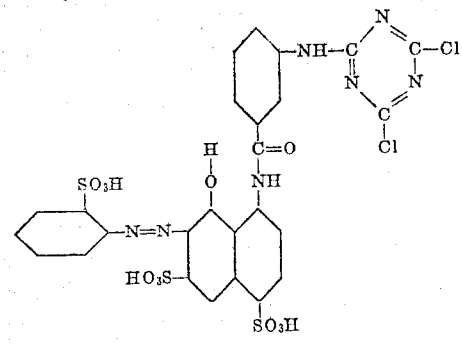
4. The dyestuff having the formula:



5. The dyestuff having the formula:



6. The dyestuff having the formula:



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