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Fibre-reactive disazo compounds containing two chlorotriazinyl groups

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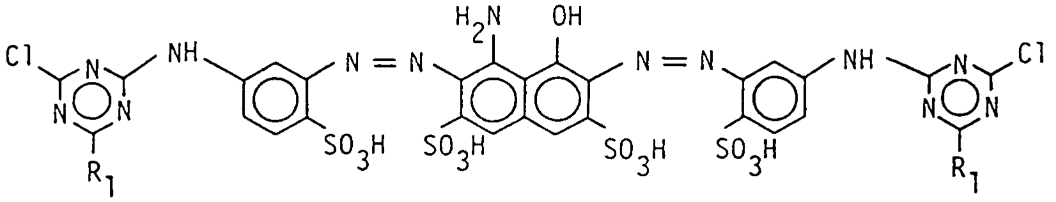
Case 150-4847

FIBRE-REACTIVE DISAZO COMPOUNDS CONTAINING TWO CHLOROTRIAZINYL GROUPS

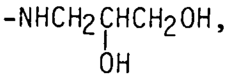
The present invention relates to monochlorotriazinyl disazo compounds, their preparation and their use as fibre-reactive dyestuffs.

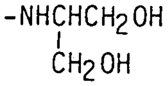
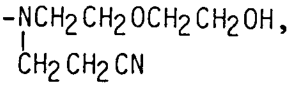
More particularly, this invention provides compounds which, in free acid form, correspond to formula I,



I

in which

each R_1 is $-NHCH_2CH_2OH$,

$-NHCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2OH$,


$-NH\underset{\displaystyle CH_2OH}{\underset{|}{C}}HCH_2OH$ or

$-\underset{\displaystyle CH_2CH_2CN}{\underset{|}{N}}CH_2CH_2OCH_2CH_2OH$,

and both R_1 groups are identical,

and mixtures of such compounds, which compounds are in free acid or salt form.

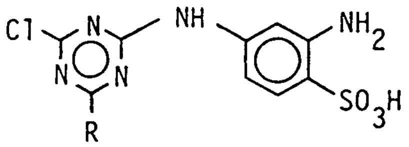
Most preferred is a compound of formula I in which both R_1 groups are $-NHCH_2CH_2OH$.

When a compound of formula I is in salt form, the cation associated with the sulpho groups is not critical and may be any one of those non-chromophoric cations conventional in the field of reactive dyes provided that the corresponding salts are water-soluble. In a compound of formula I, the cations of the sulpho groups may be the same or different, e.g., the compound may be in a mixed salt form.

Examples of suitable cations are alkali metal cations and unsubstituted and substituted ammonium ions, such as lithium, sodium, potassium, ammonium, mono-, di-, tri- and tetra-methylammonium, triethylammonium and mono-, di- and tri-ethanolammonium.

The preferred cations are the alkali metal cations and ammonium, with sodium being the most preferred.

The present invention further provides a process for the preparation of the compounds of formula I comprising coupling 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid on both sides with the diazonium salt of an amino compound of formula II,



II

in which R is chlorine or R_1 as defined above,
provided that for both coupling reactions identical amino compounds of formula II are employed,
and reacting the resultant coupling product, wherein R is chlorine, with the corresponding amine R_1-H.

Preferably, in any amino compound of formula II used as starting material, R is R_1 as defined above.

Diazotization of an amino compound of formula II and coupling reactions on both sides of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid may be effected in conventional manner. To carry out the coupling reactions the reaction mixture is first adjusted to an acid pH (of approximately 4), then, the first coupling having been completed, the mixture is adjusted to a weakly alkaline pH (of approximately 7-8). Advantageously, both coupling steps are carried out in a one step process without any isolation of the acid coupling intermediate. This one step process gives practically 100% yields of the end coupling product.

Likewise, the condensation reaction to introduce the R_1 group into the coupling product may be effected in accordance with conventional methods.

The compounds of formula I may be isolated in accordance with known methods, for example, by conventional salting out with alkali metal salt, filtering and drying in vacuo at elevated temperatures. Depending on the reaction and isolation conditions a compound of formula I is obtained in free acid or preferably salt form or even mixed salt form containing, for example, one or more of the above-mentioned cations. It may be converted from free acid form to a salt form or mixture of salt forms or vice versa or from one salt form to another by conventional means.

The compounds of formula II are either known or may be prepared in accordance with known methods from cyanuric chloride by stepwise replacement of the chlorine atoms, condensing with 1,3-diaminobenzene-4-sulphonic acid and an amine R_1-H, respectively. The amines R_1-H are either known or may be prepared in accordance with known methods.

The compounds of formula I and mixtures thereof are useful as fibre-reactive dyes for dyeing or printing hydroxy group- or nitrogen-containing organic substrates. Preferred substrates are leather and fibre materials containing or consisting of natural or synthetic polyamides and, particularly, of natural or regenerated cellulose such as cotton, viscose and spun rayon. The most preferred substrates are textile materials containing or consisting of cotton.

Dyeing or printing is effected in accordance with known methods. However, for the compounds of formula I it is preferred to use the exhaust dyeing method. Advantageously, dyeing with these dyestuffs is not temperature dependent in the usual dyeing temperature range. Therefore, dyeing may be effected almost equally well at 80°C as at 100°C without any essential loss of fixation yield.

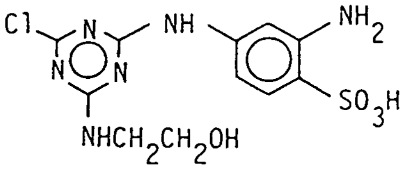
The compounds of this invention are well compatible with other reactive dyes; they may be applied per se or in combination with appropriate fibre-reactive dyestuffs of the same class having analogous dyeing properties, e.g., concerning common fastness properties, extent of ability to exhaust from the dyebath onto the fibre, etc. The dyeings obtained with such combination mixtures have good fastness properties and are comparable to those obtained with a single dyestuff.

In view of their notable build-up power the compounds of formula I give high exhaust and fixation yields. The portion of unfixed dyestuff can be easily washed off the substrate. The dyeings obtained show good light fastness and wet fastness properties such as wash-, water-, sea water- and sweat-fastness. They are stable to any oxidative influences, e.g., chlorinated water, hypochlorite bleach and peroxide or perborate containing wash liquors.

The following examples further serve to illustrate the invention. In the examples all parts and percentages are by weight or volume. The temperatures are in degrees Centigrade.

Example 1

180.25 Parts (= 0.5 mole equivalents) of the compound of formula III,

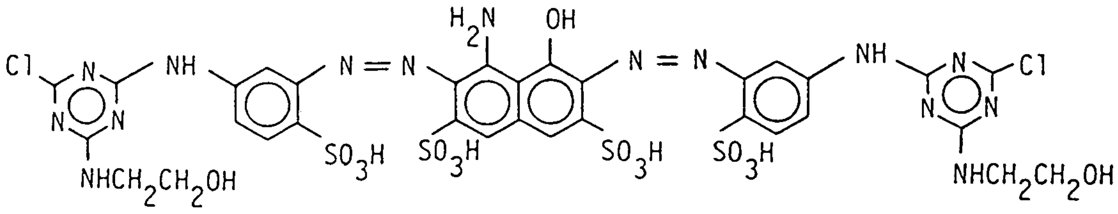


III

prepared in accordance with known methods by condensing cyanuric chloride with appropriate amounts of 1,3-diaminobenzene-4-sulphonic acid and ethanolamine, respectively, are dissolved in 1500 parts water at pH 7 and 35 parts sodium nitrite are added. This solution is cooled to 5° and is added dropwise to a mixture of 400 parts water, 120 parts concentrated hydrochloric acid and 500 parts ice whilst stirring. After two hours any excess nitrous acid is decomposed by the addition of a small amount of sulphamic acid.

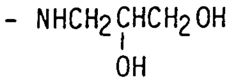
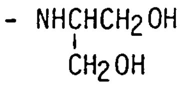
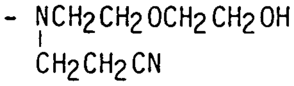
76 Parts (= 0.25 mole equivalents - 5%) 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid are sprinkled into the above obtained diazo mixture. The pH is adjusted to 4.2 - 4.4 by the addition of 50% sodium acetate solution and is kept in this range during the whole reaction by the addition of further amounts of sodium acetate solution. Reaction is effected at 5° until the pH of the mixture remains unchanged without any further addition of sodium acetate.

Subsequently, 30% sodium hydroxide solution is added dropwise to adjust the pH to 7.5 - 8.0. The coupling is completed when the addition of sodium hydroxide is no longer necessary to keep the pH in this range. Sodium chloride is then added in such an amount that the dyestuff thus prepared precipitates completely. It is filtered and dried in vacuo at 100°. The dyestuff obtained corresponding to the formula



dyes cellulose fibres in navy blue shades. The dyeings show good light fastness and wet fastness properties and are stable to any oxidative influences.

By analogy with the method described in Example 1, using appropriate starting compounds of formula II, further compounds of formula I may be prepared which are listed below. These compounds may be applied to cellulose fibres according to the conventional exhaust dyeing method. The dyeings obtained in all cases have navy blue shades; they show good light fastness and wet fastness properties and are stable to any oxidative influences.

Example No.	both R_1 groups
2	 $-\text{NHCH}_2\underset{\text{OH}}{\text{C}}\text{HCH}_2\text{OH}$
3	 $-\text{NH}\underset{\text{CH}_2\text{OH}}{\text{C}}\text{HCH}_2\text{OH}$
4	 $-\underset{\text{CH}_2\text{CH}_2\text{CN}}{\text{N}}\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$

In accordance with the method as described the dyestuffs of Examples 1 to 4 are obtained in the sodium salt form. They may, depending on the reaction/isolation conditions or by reacting the sodium salts in accordance with known methods, also be obtained in free acid form or in other salt forms, for example those salt forms containing one or more cations indicated in the description above.

In the following examples the application of the compounds of this invention is illustrated.

Application Example A

To a dyebath consisting of 1000 parts water, 20 parts Glauber's salt (calcined), 2.5 parts sodium carbonate (calcined) and 1 part of sodium 1-nitrobenzene-3-sulphonate are added 50 parts mercerized cotton fabric. The bath is heated to 40°, then 2.5 parts of the dye of Example 1 is added. The temperature is raised to 98° within 45 minutes; during this time 20 parts Glauber's salt (calcined) are added after 15 minutes and again 20 parts Glauber's salt (calcined) are added after further 15 minutes. At the end of this time 7.5 parts sodium carbonate (calcined) are added. Dyeing is continued at the boil for 45 to 60 minutes. Subsequently, the dyed fabric is rinsed hot and soaped at the boil for 20 minutes in 500 parts water and 0.5 parts sodium laurylsulphonate. After rinsing and drying a navy blue cotton dyeing with good light fastness and wet fastness properties is obtained.

When 2.5 parts of a dye mixture consisting of 93.23 parts of the dyestuff of Example 1 and 6.77 parts of the dyestuff C.I. Reactive Red 55 are employed according to the method of Application Example A a reddish navy blue cotton dyeing is obtained having good fastness properties.

Application Example B

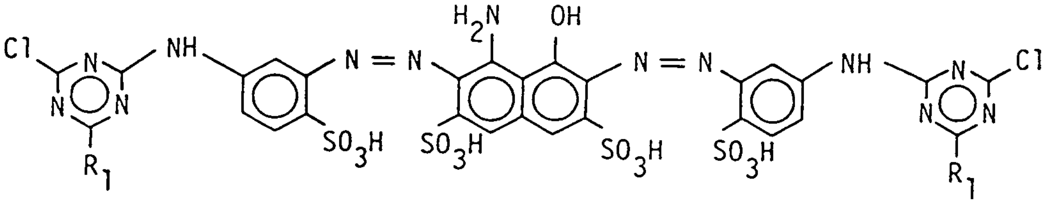
0.5 Parts of the dyestuff of Example 1 are dissolved in 300 parts water. 10 Parts cotton fabric are added and the temperature of the dyebath is raised to 80° within 10 minutes. 15 Parts Glauber's salt (calcined) are added and 30 minutes thereafter, 3 parts sodium carbonate (calcined). Dyeing is continued for one hour at 80°. Subsequently, the dyed fabric is rinsed cold, then hot, and is soaped according to the method given for Application Example A. After rinsing and drying a navy blue cotton dyeing having good fastness properties is obtained.

When 0.5 parts of the dye mixture consisting of 93.23 parts of the dyestuff of Example 1 and 6.77 parts of the dyestuff C.I. Reactive Red 55 are employed instead of 0.5 parts of the single dye of Example 1 a reddish navy blue cotton dyeing having good fastness properties is obtained.

Similarly, the dyes of Examples 2 to 4 or mixtures of the dyes of Examples 1 to 4 may be employed to dye cotton in accordance with the methods given for Application Examples A and B.

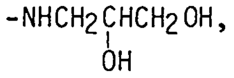
CLAIMS: -

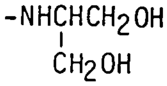
1. A compound which, in free acid form, corresponds to formula I,



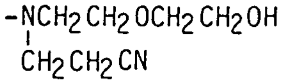
I

in which
each R_1 is $-NHCH_2CH_2OH$,


$-NHCH_2CH(OH)CH_2OH$,


$-NHCH(CH_2OH)CH_2OH$

or

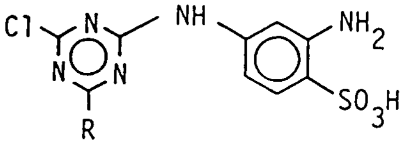

$-N(CH_2CH_2CN)CH_2CH_2OCH_2CH_2OH$

and both R_1 groups are identical,
or a mixture of compounds of formula I, which compound or mixture is in free acid or salt form.

2. The compound according to Claim 1, in which both R_1 groups are $-NHCH_2CH_2OH$.

3. A compound according to any one of Examples 2 to 4.

4. A process for the preparation of a compound of formula I defined in Claim 1, comprising coupling 1-amino-8-hydroxy-naphthalene-3,6-disulphonic acid on both sides with the diazonium salt of an amino compound of formula II,



II

wherein R is chlorine or R_1 defined in Claim 1, provided that for both coupling reactions identical amino compounds of formula II are employed,
and reacting the resultant coupling product, wherein R is chlorine, with the corresponding amine R_1-H.

5. A process according to Claim 4 using the diazonium salt of an amino compound of formula II, wherein R is R_1 defined in Claim 1.

6. A process for the preparation of a compound of formula I defined in Claim 1, substantially as herein described with reference to any one of Examples 1 to 4.

7. A compound of formula I, whenever obtained by a process according to any one of Claims 4 to 6.

8. A process for dyeing or printing hydroxy group- or nitrogen-containing organic substrates comprising applying a compound of formula I or a mixture thereof according to any one of Claims 1 to 3 or 7 as dyeing or printing agent.

9. A process according to Claim 8, wherein said substrates are leather or textile materials containing or consisting of natural or regenerated cellulose.

10. A process according to Claim 9, wherein said substrates are textile materials containing or consisting of cotton.

11. Dyed or printed substrates whenever obtained by a process according to any one of Claims 8 to 10.

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Title IMPROVEMENTS IN OR RELATING TO ORGANIC COMPOUNDS

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**** END OF REGISTER ENTRY ****