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Chloro-triazinyl monoazo compounds

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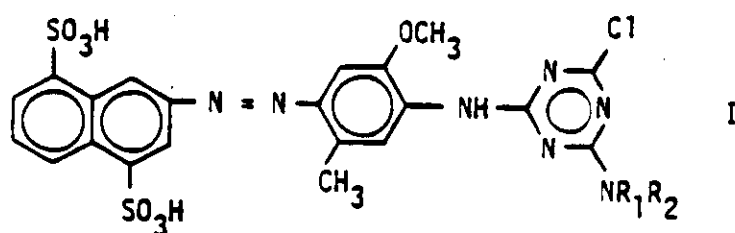
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CHLORO-TRIAZINYL MONOAZO COMPOUNDS

The present invention relates to chloro-triazinyl monoazo compounds, their preparation and use as fibre-reactive dyestuffs.

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



in which

either R_1 is hydrogen or hydroxy- C_{2-3} alkyl,

and R_2 is hydroxy- C_{2-3} alkyl

or, R_1 is hydrogen or 2-cyanoethyl,

10 and R_2 is $-CH_2CH_2OCH_2CH_2OH$,

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

In any hydroxysubstituted alkyl group the hydroxy group is bound to a carbon atom other than to the C_1 -atom.

15 Preferred compounds of formula I are those in which any hydroxy-

alkyl as R_1 and/or R_2 is 2-hydroxyethyl. More preferred are compounds of formula I, wherein R_1 is hydrogen or 2-hydroxyethyl and R_2 is 2-hydroxyethyl. Most preferred is the compound, wherein R_1 is hydrogen and R_2 is 2-hydroxyethyl.

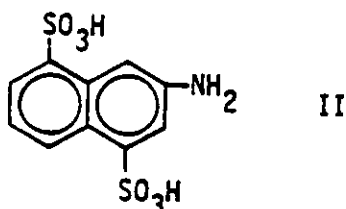
5 Preferred mixtures of compounds of formula I are those in which in a compound A R_1 is hydrogen and R_2 is 2-hydroxyethyl, and in a compound B R_1 and R_2 are both 2-hydroxyethyl. Preferably, these mixtures contain the compounds A and B in a molar ratio range of from 90:10 to 10:90, more preferably 75:25 to 25:75.

10 The cations of the sulpho groups when the compounds of formula I are in salt form may be any of those non-chromophoric cations common in the chemistry of reactive dyestuffs. Examples of suitable cations are alkali metal cations and unsubstituted or substituted ammonium ions, such as lithium, sodium, potassium, ammonium, mono-,
15 di-, tri- and tetra-methylammonium, triethylammonium and mono-, di- and tri-ethanolammonium.

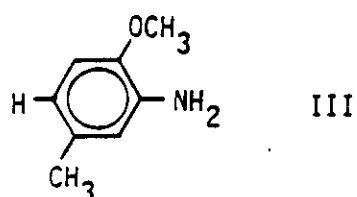
The preferred cations are the alkali metal cations and ammonium, with sodium being the most preferred.

20 The present invention further provides a process for the preparation of the compounds of formula I comprising reacting the following components: -

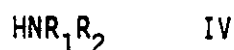
- the diazotized amino compound of formula II,



- the coupling component of formula III,



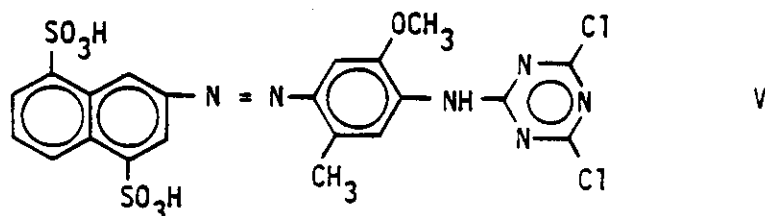
- cyanuric chloride, and
- a compound of formula IV,



or a mixture thereof;

- 5 which components must be present in the corresponding stoichiometric molar ratio to obtain a compound of formula I -
by coupling and condensing in any desired order.

More particularly, it is preferred to prepare the compounds of formula I by condensing a compound of formula V,



- 10 in free acid or salt form,
with a compound of formula IV



or a mixture thereof.

- 15 Diazotization and coupling reaction may be effected in conventional manner. The replacement of the chlorine atoms in cyanuric chloride by separate condensation steps may be effected in accordance with conventional methods, e.g., the replacement of the first chlorine atom may be carried out at temperatures of from 0° to 10°C, preferably at 0° to 5°C. The replacement of the second chlorine

atom may be effected at temperatures of from 20° up to 55°C in an alkaline medium.

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 a vacuo. 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 forms 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 starting materials, compounds of formula II, III and IV, are either known or may be prepared in accordance with known methods from available starting materials.

The compounds of formula I and mixtures thereof which are preferably in salt form, are useful as reactive dyestuffs for dyeing or printing hydroxy group- or nitrogen-containing organic substrates. Preferred substrates are leather and textiles containing or consisting of natural or synthetic polyamides such as wool, silk and nylon, natural or regenerated cellulose such as cotton, viscose and spun rayon. The most preferred substrate is textile material containing or consisting of cotton.

Dyeing or printing is effected in accordance with known methods. Since the compounds of formula I exhaust well from the dyebath they are suitable for all conventional dyeing processes using the exhaust dyeing method. They may be applied according to conventional methods per se or in combination with appropriate other fibre-reactive dyestuffs having analogous dyeing properties and, since they are well compatible, also in important three component dye mixtures. The dye-

ings obtained with such combination mixtures have good fastness properties and do not show catalytic fading.

Since the reactivity of the compounds of formula I to the substrate is not temperature dependent in the usual dyeing temperature ranges dyeing may be effected equally well at 100°C as at 80°C without any loss of fixation yield, even in some cases the fixation yield will be increased at 100°C. Evidently, the dyestuffs of the present invention are hydrolysis resistant at high temperatures and passing over the dyeing temperature will not be critical to the fixation yield.

Advantageously, a dyeing temperature at about 100°C may be applied because dyestuffs migrate better at high temperatures thus giving more even dyeings.

Furthermore, the compounds of this invention are notably well soluble in water, even in electrolyte-containing dyeing liquors. The dyeings obtained with the compounds of formula I show good light fastness and wet fastness properties, e.g., wash-, water- and sweat-fastness. Further, they have good fastness to chlorinated water, peroxide and 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 and the temperatures are in degrees Centigrade.

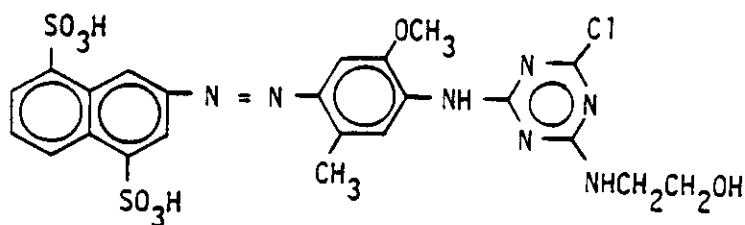
Example 1

75.8 Parts 2-aminonaphthalene-4,8-disulphonic acid are diazo-
tized in accordance with known methods. To the resulting diazo sus-
pension a solution of 34.3 parts 2-amino-1-methoxy-4-methylbenzene
5 in a mixture of water and hydrochloric acid are added dropwise, and
coupling is effected whilst gradually adding a total amount of
42.5 parts sodium bicarbonate with stirring. After four hours the
resulting monoazo dyestuff is isolated by heating the reaction mix-
ture to 60° and adding hydrochloric acid up to pH 1. The dyestuff
10 which precipitates is filtered and washed with a solution of a mix-
ture of water, sodium chloride and 30% hydrochloric acid.

The thus obtained product is stirred in 1000 parts water and
completely dissolved by the addition of ca. 25 parts 30% sodium hy-
droxide solution to give a medium with pH 8. This solution is
15 stirred overnight. After the addition of 500 parts ice the tempera-
ture is reduced to -1°. Subsequently, 46 parts cyanuric chloride
are added, the condensation reaction starts at about 7°. The reac-
tion is completed in approximately two hours whereby the tempera-
ture is raised to 30° for the last hour.

20 For the next condensation step 19.8 parts monoethanolamine di-
luted with 50 parts water are added to the reaction mixture within
5 minutes whereby the pH rises to 11.2. Stirring is effected for
15 minutes and the temperature is then elevated to 50°. After a
further 20 minutes stirring the pH falls to 7 and stirring is con-
25 tinued for approximately three hours. Then, further 2 parts mono-
ethanolamine diluted with water are added and stirring is continued
until a pH of ca. 8.8 is reached which remains unchanged.

The product is isolated by portionwise adding of 300 parts
sodium chloride, filtering and drying in a vacuo at 60°. The thus
30 obtained dyestuff which in form of the free acid corresponds to the
formula



is highly soluble in water and dyes cotton in yellow shades. The dyeings show good light fastness and wet fastness properties.

In analogy with the method described in Example 1 but using instead of monoethanolamine the corresponding amount of other mono- or disubstituted amines or a mixture of such amines further compounds of formula I are obtained which are listed in the following Table. These dyes or mixture of dyes also give yellow dyeings on cotton.

Example No.	R_1	R_2	
2	$-\text{CH}_2\text{CH}_2\text{OH}$	$-\text{CH}_2\text{CH}_2\text{OH}$	
3	$-\text{CH}_2\text{CH}_2\text{CN}$	$-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	
4	H	do.	
5	$\left\{ \begin{array}{l} \text{H} \\ -\text{CH}_2\text{CH}_2\text{OH} \end{array} \right.$	$\left\{ \begin{array}{l} -\text{CH}_2\text{CH}_2\text{OH} \\ \text{do.} \end{array} \right.$	75% by weight 25% by weight

The preparation of a dye mixture containing different groups $-\text{NR}_1\text{R}_2$, e.g., the mixture of Example 5, may be carried out by step-wise reaction first with 3/4 mole equivalent of monoethanolamine and second with 1/4 mole equivalent of diethanolamine but using a 30% excess of the last component. This condensation is effected at

40° and pH 7 during ten hours.

In accordance with the reaction and isolation conditions as described the dyestuffs of Examples 1 to 5 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 hereinbefore.

In the following examples the application of the dyestuffs 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 the sodium salt of 1-nitrobenzene-3-sulphonic acid 50 parts mercerized cotton fabric are added. The bath is heated to 40°, then 1 part 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 sodiumalkylsulphonate. After rinsing and drying a yellow cotton dyeing with good fastness properties is obtained.

Application Example B

To a dyebath consisting of 1000 parts water, 60 parts Glauber's salt (calcined), 15 parts sodium carbonate (calcined) and 1 part

of the sodium salt of 1-nitrobenzene-3-sulphonic acid 50 parts of cotton fabric are added. The bath is heated to 60°. Subsequently, 1.5 parts of the dye of Example 1 are added. The temperature is kept at 60° for 15 minutes and is then raised to 98° within 30 minutes. Dyeing is continued for 45-60 minutes at 98°. The dyed fabric is rinsed hot and soaped according to the method given in Application Example A. After rinsing and drying a yellow cotton dyeing is obtained having good fastness properties.

Application Example C

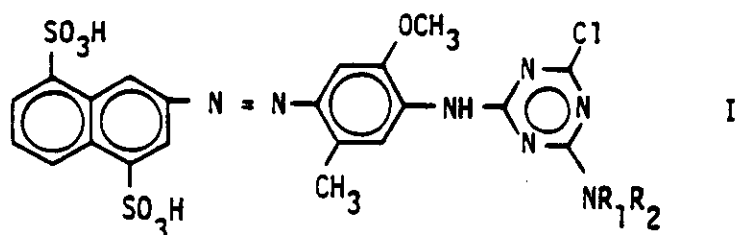
10 1 Part of the dyestuff of Example 1 is dissolved in 2000 parts water. 100 Parts cotton fabric are added and the temperature of the dyebath is raised to 80° within 10 minutes. 100 Parts Glauber's salt (calcined) are added and 30 minutes thereafter, 20 parts sodium carbonate (calcined). Dyeing is continued for one hour at 80°.

15 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 yellow cotton dyeing is obtained having good fastness properties.

20 Similarly, the dyes or mixtures of Example 2 to 5 may be employed to dye cotton in accordance with the method given for Application Examples A, B or C.

CLAIMS: -

1. A compound of formula I,



and mixtures thereof, in which

- either R_1 is hydrogen or hydroxy- C_{2-3} alkyl,
 5 and R_2 is hydroxy- C_{2-3} alkyl,
or, R_1 is hydrogen or 2-cyanoethyl,
 and R_2 is $-CH_2CH_2OCH_2CH_2OH$,

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

2. A compound or mixture according to Claim 1, wherein R_1 is
 10 hydrogen or 2-hydroxyethyl and R_2 is 2-hydroxyethyl.

3. A compound according to Claim 1, wherein R_1 is hydrogen
 and R_2 is 2-hydroxyethyl, which compound is in free acid or salt
 form.

4. A mixture according to Claim 2, consisting of compound A
 15 which is a compound of formula I wherein R_1 is hydrogen and R_2 is
 2-hydroxyethyl, and of compound B which is a compound of formula I
 wherein R_1 and R_2 are both 2-hydroxyethyl.

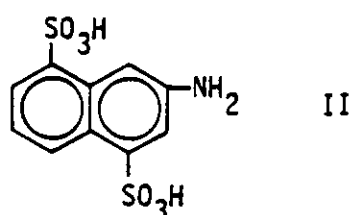
5. A mixture according to Claim 4, containing the compounds A
 and B in a molar ratio range of from 90:10 to 10:90.

- 20 6. A mixture according to Claim 5, wherein said molar ratio
 range is of from 75:25 to 25:75.

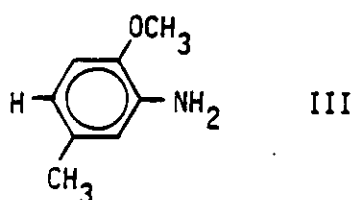
7. A compound or mixture according to any one of Examples 2 to 5.

8. A process for the preparation of a compound of formula I, as defined in Claim 1, or a mixture thereof, comprising reacting the following components: -

- the diazotized amino compound of formula II,



- the coupling component of formula III,



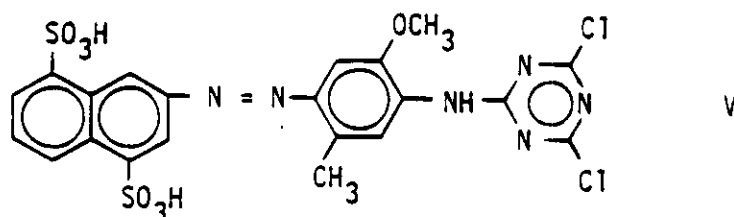
- cyanuric chloride, and
- a compound of formula IV,



or a mixture thereof, wherein R_1 and R_2 are as defined in Claim 1, which components must be present in the corresponding stoichiometric molar ratio range to obtain a compound of formula I -

by coupling and condensing in any desired order.

15 9. A process according to Claim 8, to prepare a compound of formula I by condensing a compound of formula V,



in free acid or salt form,
with a compound of formula IV,



wherein R_1 and R_2 are as defined in Claim 1,
5 or a mixture thereof.

10. A process for the preparation of a compound of formula I,
as defined in Claim 1, or a mixture thereof, substantially as here-
inbefore described with reference to any one of Examples 1 to 5.

11. A compound of formula I or a mixture thereof, whenever
10 obtained by a process according to any one of Claims 8 to 10.

12. A process for dyeing or printing hydroxy group- or nitrogen-
containing organic substrates comprising applying a compound of for-
mula I or a mixture thereof according to any one of Claims 1 to 7
or 11 as dyeing or printing agent.

15 13. A process according to Claim 12, wherein said substrate is
leather or a textile containing or consisting of natural or regene-
rated cellulose.

14. A process according to Claim 13, wherein said substrate
is a textile containing or consisting of cotton.

20 15. Dyed or printed substrates whenever obtained by a process
according to any one of Claims 12 to 14.

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