OFFICE

PATENT SPECIFICATION

1,120,367

NO DRAWINGS

1,120,367

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Int. Cl.:—C 09 b 29/16, C 09 b 43/18

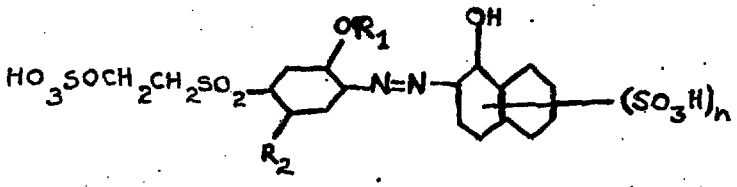
COMPLETE SPECIFICATION

Novel Water-Soluble Monoazo Dyes and method for the production thereof

We, SUMITOMO CHEMICAL COMPANY, LTD., a corporation organized under the laws of Japan, of 15, Kitahama-5-chome, Higashi-ku, Osaka, Japan, 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 relates to novel water-soluble monoazo dyes, a method for the production of the same and a method for dyeing fibers in characteristic deep red tints with the same.

More specifically, this invention relates to novel water-soluble monoazo dyes represented by the following formula,

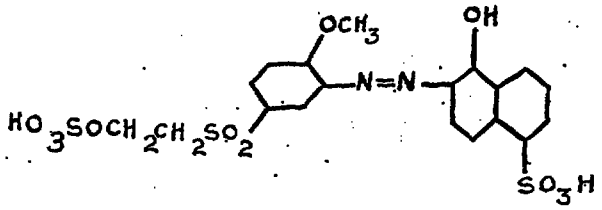


(I)

wherein R_1 means a methyl or ethyl radical, R_2 means a methyl, methoxy or ethoxy radical and n means an integer of 1 to 3, and a method for the production thereof.

It also relates to a method for dyeing fibers, especially fibers made from natural or regenerated cellulose materials such as cotton, hemp and viscose rayon, or polyvinyl alcohol materials, in characteristic deep red tint with the said dyes.

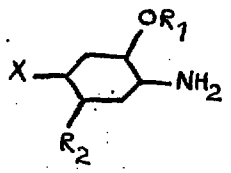
So far, dyes having a sulfatoethylsulfone radical, for example, a dye having the following formula,



are disclosed in specification No. 733,471 for dyeing fibers in red tint.

The present inventors have ~~broardly~~ broadly studied the dyes more suitable for dyeing fibers in characteristic deep red tints which has been strongly requested in this industry.

The present inventors have found that the requested tint in this industry can be obtained by the provision of the present novel monoazo dyes of the formula (I), comprising, as the diazo component, amines of the following formula,

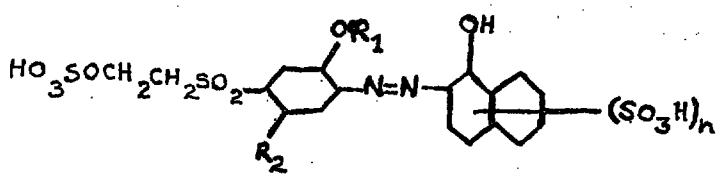


wherein R_1 and R_2 have the same meanings as defined above and X means a radical of $—SO_2CH_2CH_2OH$ or $—SO_2CH_2CH_2OSO_3H$. Besides, surprising is the finding that the present dyes can be employed with a higher color yield on fibers according to the impregnation dyeing method, compared with the known dyes mentioned above. Thus, one object of the present invention is to provide novel water-soluble monoazo dyes for dyeing fibers in characteristic deep red tints with high fastness, besides with a higher color yield on fibers according to the impregnation dyeing method, compared with the known dyes.

Another object of the present invention is to provide a method for the production thereof.

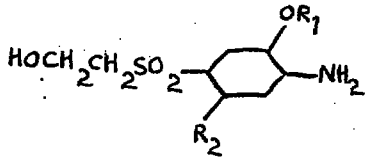
Further objects of the present invention will be apparent from the following detailed description.

The present inventors have found that these and other objects of the present invention can be accomplished by provision of novel water-soluble monoazo dyes represented by the following formula,



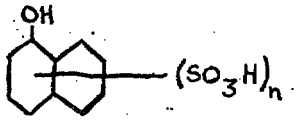
(I)

wherein R_1 means a methyl or ethyl radical, R_2 means a methyl, methoxy or ethoxy radical and n means an integer of 1 to 3, and ~~the~~ method for the production thereof which comprises reacting a diazotized amine of the formula,



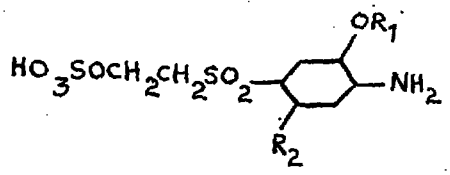
(II)

wherein R_1 and R_2 have the same meanings as defined above, with a 1-hydroxy-naphthalenesulfonic acid of the formula,



(III)

wherein n means an integer of 1 to 3, and esterifying the dyes derived with sulfuric acid at the hydroxy radical of the β-hydroxyethylsulfone radical according to the conventional esterifying procedures, or ~~by~~ reacting a diazotized amine of the formula,



(IV)

wherein R_1 and R_2 have the same meanings as defined above, with a 1-hydroxynaphthalenesulfonic acid of the formula (III).

A full understanding of the present invention can be given with reference to the following detailed illustrations.

As amines employed in the present invention, 2-methoxy-5-methylaniline-4-β-hydroxyethylsulfone, 2,5-dimethoxyaniline-4-β-hydroxyethylsulfone, 2-ethoxy-5-methylaniline - 4 - β - hydroxylethylsulfone and 2,5-diethoxyaniline-4-β-hydroxyethylsulfone or the sulfuric acid esters thereof are exemplified, but they are, of course, not to limit the scope of the present invention.

1-Hydroxynaphthalenesulfonic acids of the formula (III) employed in the present invention are as follows, which are, of course, not to limit the scope of the present invention.

1-hydroxynaphthalene-3-sulfonic acid
1-hydroxynaphthalene-4-sulfonic acid
1-hydroxynaphthalene-5-sulfonic acid
1-hydroxynaphthalene-3,6-disulfonic acid
1-hydroxynaphthalene-3,8-disulfonic acid
1-hydroxynaphthalene-3,6,8-trisulfonic acid

In carrying out the production methods of the present invention, 1 mol of the said amine (II) may be diazotized with hydrochloric acid and aqueous sodium nitrite solution according to the usual diazotizing procedures and the resulting diazo mixture is introduced dropwise into a solution previously prepared by dissolving at least 1 mol of 1-hydroxynaphthalenesulfonic acid in water, the reaction mixture being maintained within pH 4 to 7 during the reaction course by addition of sodium carbonate.

After the reaction is over, potassium chloride is added to the mixture to precipitate crystals, which are separated by filtration and dried.

The resulting crystals are added to sulfuric acid of 100% strength and the mixture is stirred for a sufficient period of time to complete the esterification reaction.

Amines of the formula (IV) are treated with a 1-hydroxynaphthalenesulfonic acid of the formula ~~(II)~~ according to the same procedure as mentioned above with the exception of esterification after the coupling reaction. Thus, the required dyes, which may be employed for dyeing fibers in characteristic deep red tint, are obtained. Hereon, the coupling reaction in the present invention may be advantageously controlled in the pH range of between 4 and 7.

In case of controlling the present reaction at higher pH range than that, the dyes suitable for dyeing fibers in required characteristic deep red tint can hardly be obtained in pure quality.

When a 1-hydroxynaphthalenesulfonic acid having no sulfonic acid radical at 4-position, for example, 1-hydroxynaphthalene-3-sulfonic acid, 1-hydroxynaphthalene-3,6-disulfonic acid, etc. is employed as the coupling component, the coupling reaction tends tc be orientated to 4-position at relatively high pH range. Besides, the amines of the formula (IV), namely amines previously esterified with sulfuric acid could not be employed without decomposition at such higher pH range. On the other hand, at a pH less than 4, the reaction takes too long for completion.

The dyes in the present invention are suitable for dyeing various kinds of fibers, especially fibers made from natural or regenerated cellulose materials such as cotton, hemp and viscose, rayon, and polyvinyl alcohol materials, in characteristic deep red tint.

The dyeing is effected by the known method applicable to the reaction dyes. Hereon, it is remarkable that a higher color yield, compared with the known dyes mentioned above can be obtained according to the impregnation dyeing method.

The dyeings obtained in accordance with the present invention are distinguished by characteristic deep red tint and high fastnesses to wet processing, light and chlorine resistance.

The present invention will be illustrated with reference to the following Examples, which are given by way of mere illustration and not by way of limitation of the scope of the present invention.

All parts and percentages are by weight.

EXAMPLE 1

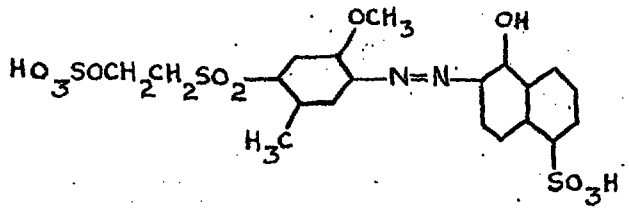
A mixture of 36.8 parts of 2-methoxy-5-methylaniline-4-hydroxyethylsulfone and 90 parts of 100% sulfuric acid is stirred for 2 hours at a temperature of 15° to 30°C. and the reaction mixture is poured onto 270 parts of ice and water, thereby to precipitate crystals, which are separated by filtration.

The resulting ester is introduced into 350 parts of ice and water and diazotized with 16 parts of hydrochloric acid and 8.3 parts of sodium nitrite in aqueous solution.

The thus obtained diazo mixture is introduced dropwise into a solution previously prepared by dissolving 34.0 parts of 1-hydroxynaphthalene-5-sulfonic acid in 300 parts of water which is neutralized wth 10.2 parts of sodium bicarbonate, the reaction mixture being maintained at the pH within 6 to 7 during the reaction course by addition of an aqueous solution containing about 20 parts of sodium carbonate.

After the reaction is over, 70 parts of potassium chloride is added thereto to precipitate crystals, which are separated by filtration and dried up.

The dye thus obtained having the following formula,



may be employed for dyeing cotton in brilliant bluish red tint with respectively 4—5 or higher degree of fastnesses to light, washing and chlorine resistance.

EXAMPLE 2

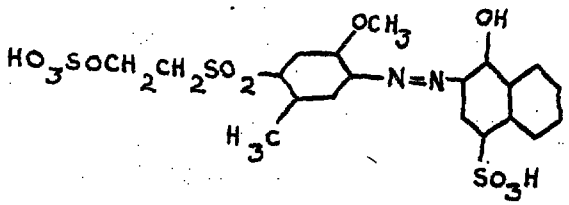
Ten point eight parts of 2-methoxy-5-methylaniline-4-hydroxyethylsulfone is dissolved in 100 parts of ice and water and 5.5 parts of 35% hydrochloric acid and the mixture is added with 2.8 parts of sodium nitrite in aqueous solution.

The resulting diazo mixture is introduced into a solution previously prepared by dissolving 10.5 parts of 1-hydroxynaphthalene-4-sulfonic acid in 100 parts of water together with 8 parts of sodium carbonate while being cooled. After the reaction is over, 20 parts of potassium chloride is added to precipitate crystals, which are separated by filtration and dried up.

The crystals obtained are dissolved in 100 parts of 100% sulfuric acid at temperature of 20°C.

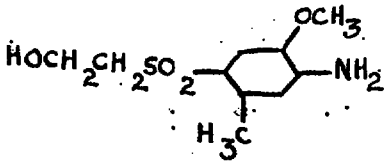
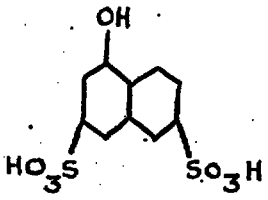
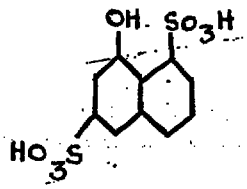
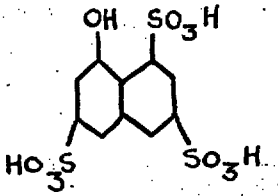
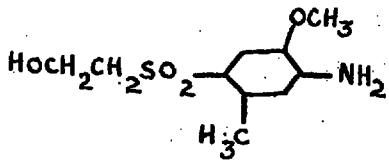
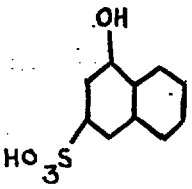
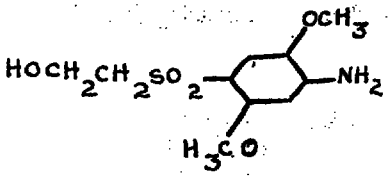
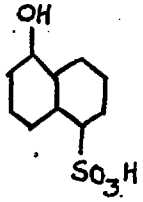
After 2 hour stirring, the mixture is poured onto 200 parts of ice and water and added with 15 parts of potassium chloride, thereby to isolate crystals, which are separated by filtration. The wet cake is dissolved in 150 parts of water and the pH is adjusted at 6 to 7 by addition of aqueous sodium carbonate. Thereafter, 15 parts of potassium chloride is added to the resulting solution to precipitate crystals, which are separated by filtration and dried up.

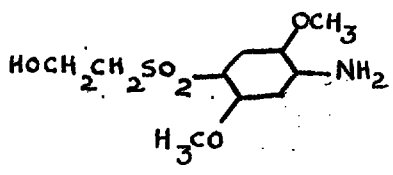
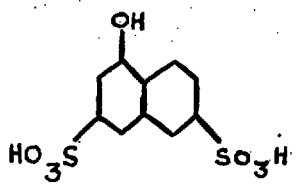
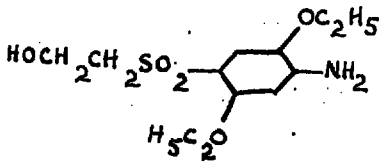
The dye thus obtained having the following formula,



may be employed for dyeing cotton in brilliant yellowish red tint with 5 or higher degree of fastnesses to light and washing and 4—5 degree of fastness to chlorine resistance.

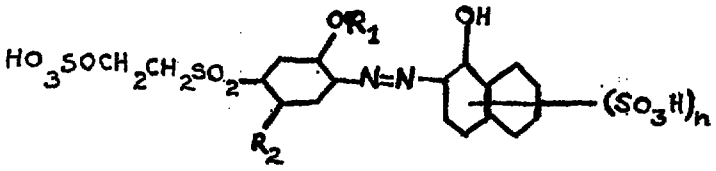
By use of amines shown in the column (A) and 1-hydroxynaphthalenesulfonic acids shown in the column (B) in the following table, the dyes suitable for dyeings cotton in characteristic red tint shown in the column (C) in the same table are obtained according to similar way as in Examples 1 to 2.

Example No.	A (amine)	B (1-hydroxynaphthalene-sulphonic acid derivatives)	C (tint)
3			yellowish red
4	"		red
5	"		red
6			yellowish red
7			bluish red

Example No.	A (amine)	B (1-hydroxynaphthalene-sulphonic acid ~~derivatives~~ derivatives)	C (tint)
8			red
9		"	red

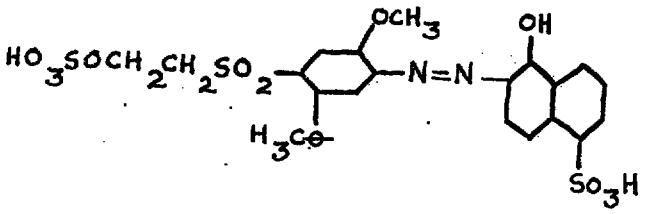
WHAT WE CLAIM IS:—

1. Novel water-soluble monoazo dyes represented by the following formula,

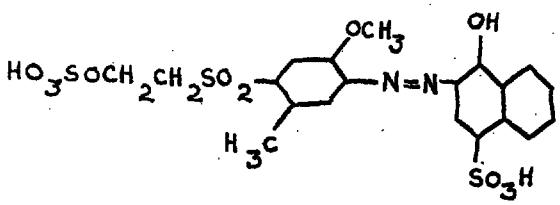


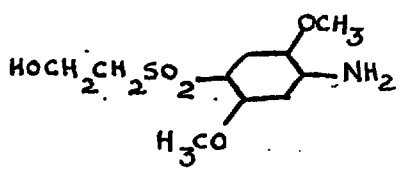
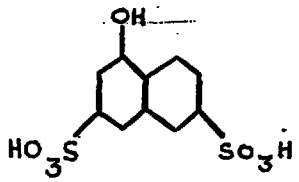
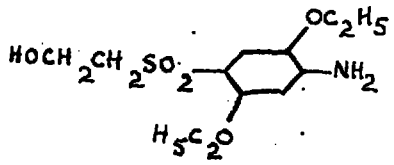
wherein R_1 means methyl or ethyl radical, R_2 means methyl, methoxy or ethoxy radical and n means an integer of 1 to 3.

2. A novel water-soluble monoazo dye represented by the following formula,



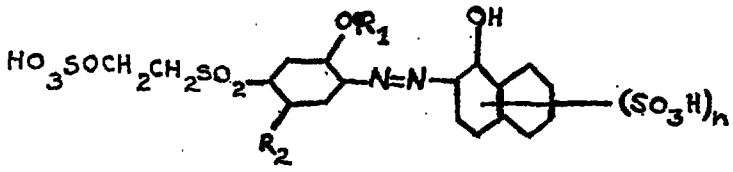
3. A water-soluble monoazo dye represented by the following formula,



Example No.	A (amine)	B (1-hydroxynaphthalene-sulphonic acid ~~derivatives~~)	C (tint)
8			red
9		"	red

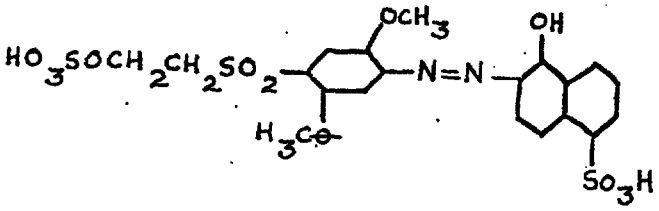
WHAT WE CLAIM IS:—

1. Novel water-soluble monoazo dyes represented by the following formula,

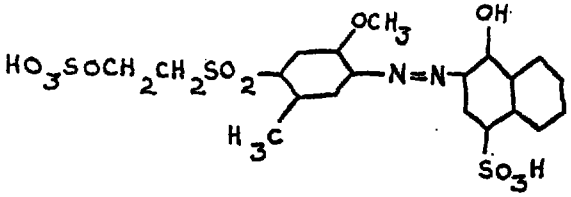


wherein R_1 means methyl or ethyl radical, R_2 means methyl, methoxy or ethoxy radical and n means an integer of 1 to 3.

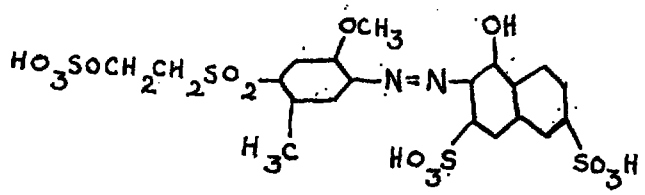
2. A novel water-soluble monoazo dye represented by the following formula,



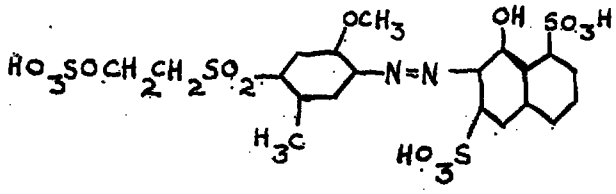
3. A water-soluble monoazo dye represented by the following formula,



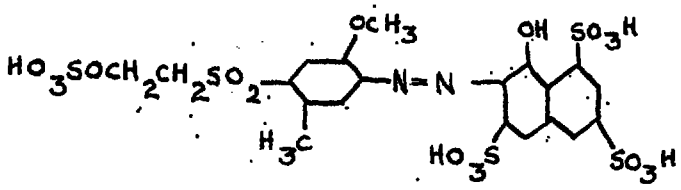
4. A novel water-soluble monoazo dye represented by the following formula,



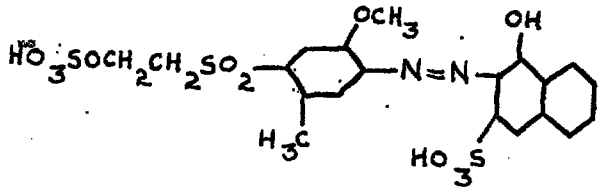
5. A novel water-soluble monoazo dye represented by the following formula,



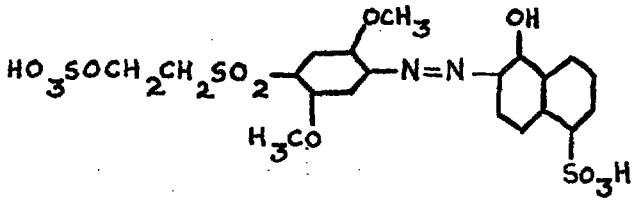
6. A novel water-soluble monoazo dye represented by the following formula,



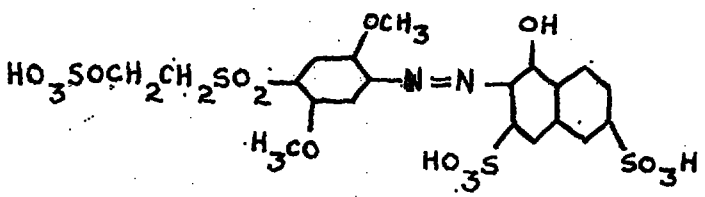
7. A novel water-soluble monoazo dye represented by the following formula,



8. A novel water-soluble monoazo dye represented by the following formula,

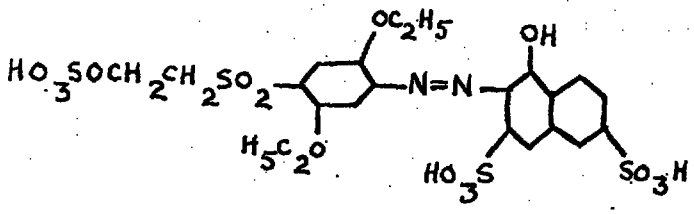


9. A novel water-soluble monoazo dye represented by the following formula,

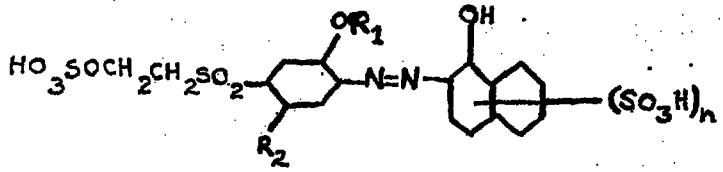


* C L M S *

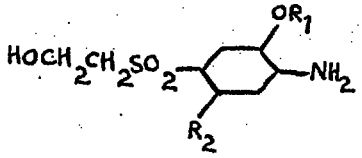
10. A novel water-soluble monoazo dye represented by the following formula,



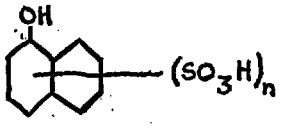
11. A method for the production of a novel water-soluble monoazo dye represented by the following formula,



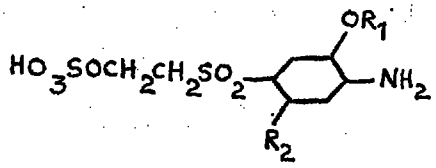
wherein R_1 means methyl or ethyl radical, R_2 means methyl, methoxy or ethoxy radical and n means an integer of 1 to 3, which comprises reacting a diazotized amine represented by the following formula,



wherein R_1 and R_2 have the same meanings as defined above, with a 1-hydroxynaphthalenesulfonic acid represented by the following formula,



wherein n has the same meanings as defined above and esterifying the dye derived with sulfuric acid at the hydroxy radical of the β-hydroxyethylsulfone radical, or reacting a diazotized amine represented by the following formula,



wherein R_1 anl R_2 have the same meanings as defined above, with a 1-hydroxynaphthalenesulfonic acid.

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* C L M S *