1,132,759

PATENT SPECIFICATION

NO DRAWINGS

1,132,759

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Int. Cl.:—C 09 b 29/16

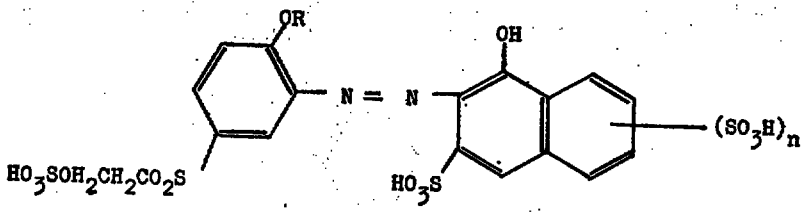
COMPLETE SPECIFICATION

Novel Scarlet Monoazo Dyes and process 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 deplace the invention, for which we pray that a patent may be granted to us, and by the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to novel scarlet monoazo dyes, process for the production thereof and process for dyeing textile fibers in scarlet tint with the same.

More specifically, this invention relates to novel scarlet monoazo dyes represented by the following formula,



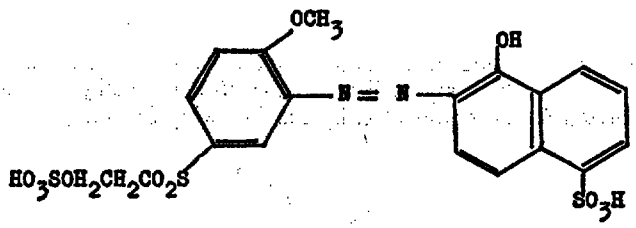
(I)

wherein R means methyl or ethyl radical and n means an integer of 1 to 2, and process for the production thereof. It also relates to process for dyeing textile fibers, especially fibers made from a member of natural or regenerated cellulose materials such as cotton, hemp and viscose rayon and polyvinyl alcohol materials in scarlet tint with the said dyes of the formula (I).

So far, several kinds of reactive dyes have been known having different characteristics distinguished by each reactive radical.

The kind of reactive dyes characterised by a sulfatoethyl-sulfone radical are, however, lacking in dyes suitable for dyeing textile fibers in valuable scarlet tint.

For example, a dye having the formula,

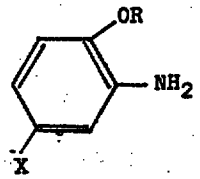


has been disclosed in British Patent Specification No. 733,471, which has been employed for dyeing textile fibers in red tint.

broadly

The present inventors have ~~broardly~~ studied the dyes for dyeing textile fibers in scarlet tint, which have been strongly requested in this industry.

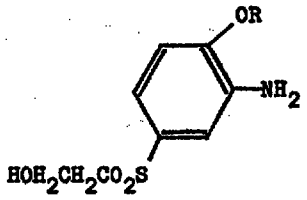
Surprising is the finding that the requested dyes, namely those suitable for dyeing textile fibers in scarlet tint, can be obtained by employing, as the coupling component, a 1-hydroxynaphthalene-polysulfonic acid having one sulfonic acid radical at 3-position of the said napthalene nucleus and one or two other sulfonic acid radicals at other optional position or positions, and as the diazo component, amines of the formula,



wherein R has the same meanings as defined above and X means a radical of $-SO_2CH_2CH_2OH$ or $-SO_2CH_2CH_2OSO_3H$, and, when X is $SO_2CH_2CH_2OH$, esterifying the —OH group to $-OSO_3H$. Thus one object of the present invention is to provide a novel monoazo dye suitable for dyeing fibers in scarlet tint with high fastnesses.

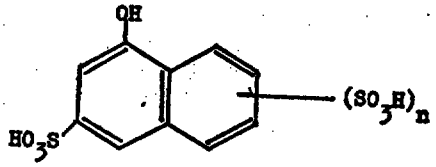
Another object of the present invention is to provide processes for the production of the said dyes.

The present inventors have found that these and other objects of the present invention can be accomplisted by provision of novel scarlet monoazo dyes represented by formula I, and process for the production of the same, which comprises contacting a diazotized amine represented by the following formula,



(II)

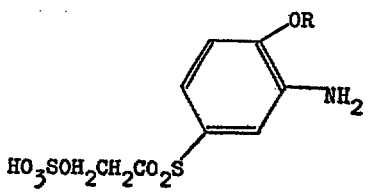
wherein R has the same meanings as defined above, with a 1-hydroxynaphthalene-polysulfonic acid represented by the following formula,



(III)

wherein n has the same meanings as defined above, and esterifying the thus-formed dye with sulfuric acid at the hydroxy radical of the β-~~hydroxyethylsulfonic~~ radical or contacting a diazotized amine represented by the following formula,

hydroxyethylsulfone



(IV)

wherein R has the same meanings as defined above, with a 1-hydroxynaphthalene-polysulfonic acid as defined above.

In the present invention, 2-methoxyaniline-5-β-hydroxyethylsulfone, 2-ethoxyaniline-5-β-hydroxyethylsulfone and the sulfuric acid esters thereof are advantageously employed as the diazo component.

As 1-hydroxynaphthalenepolysulfonic acids (III) employed in the present invention, 1-hydroxynaphthalene-3,6-disulfonic acid, 1-hydroxynaphthalene-3,8-disulfonic acid, 1-hydroxynaphthalene-3,6,8-trisulfonic acid are exemplified, but they are, of course, not to limit the scope of the present invention.

In carrying out the present invention, 1 mol of the amine of the formula (II) is diazotized with hydrochloric acid and aqueous sodium nitrite solution the resulting diazo mixture is successively introduced into the solution previously prepared by dissolving at least 1 mol of a 2-hydroxynaphthalene-polysulfonic acid of the formula (III) in water, the reaction mixture being maintained within pH 4 to 7 during the course of the reaction by addition of an aqueous sodium carbonate solution.

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

The resulting dyestuff 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. Alternatively, amines of the formula (IV) may be diazotised and coupled with a 1-hydroxynaphthalenepolysulfonic acid of the formula (III) as mentioned above.

Thus dyes which may be employed for dyeing textile fibers in scarlet tint are obtained.

The coupling reaction may be advantageously controlled at the pH range of between 4 and 7. At pH values higher than that, the dyes suitable for dyeing fibers in requested scarlet tint are not obtained in pure quality since the coupling reaction tends to be oriented at the 4-position at relatively high pH values. Also the amines of the formula (IV), namely amines previously esterified with sulfuric acid could not be employed without decomposition at such higher pH values. On the other hand, at pH values less than 4, it takes too much time for the completion of the coupling reaction.

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

The dyeing is effected by the known method applicable to reactive dyes.

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

The present invention will be further 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

23.1 parts of 2-methoxyaniline-5-β-hydroxyethylsulfone is introduced into 114 parts of sulfuric acid of 98% strength at a temperature of 15° to 30°C. and the mixture is stirred for 1 hour.

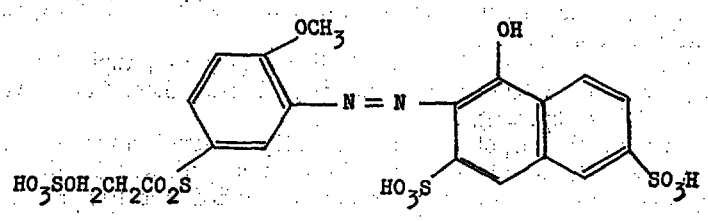
Thereafter, the reaction mixture is poured onto 342 parts of ice and water, thereby to precipitate crystals, which are separated by filtration.

The sulfuric acid ester obtained is introduced into 120 parts of ice and water and diazotized with 8.4 parts of hydrochloric acid and 6.35 parts of sodium nitrite in aqueous solution under cooling.

The resulting diazo mixture is added dropwise into a solution previously prepared by dissolving 31.5 parts of 1-hydroxynaphthalene-3,6-disulfonic acid in 300 parts of water, together with 5.3 parts of sodium carbonate, the reaction mixture being maintained within the pH 6 to 7 during the course of the reaction by addition of about 11 parts of sodium bicarbonate.

After the reaction is over, 110 parts of potassium chloride is added thereto to precipitate crystals, which are separated by filtration and dried.

Thus, a monoazo dye having the following formula,



is obtained.

The dye obtained gives characteristic scarlet dyeings of 5 degree of fastnesses to light, washing, chlorine resistance and acid boiling respectively, and of a high brilliancy on cotton with the aid of sodium carbonate as an acid binding agent using the usual dyeing method for the fibre reactive dyes.

If, 1-hydroxynaphthalene-3,8-disulfonic acid instead of 1-hydroxynaphthalene-3,6-disulfonic acid employed above is treated in similar way as mentioned above, a similar dye is obtained.

Furthermore, by employing 2-ethoxyaniline-5-β-hydroxyethylsulfone, instead of 2-methoxyaniline-5-β-hydroxyethylsulfone employed above, a similar dye may be also obtained.

EXAMPLE 2

23.1 parts of 2-methoxyaniline-5-β-hydroxyethylsulfone is dissolved in 200 parts of ice and water with 10 parts of 35% hydrochloric acid and diazotized with 6.9 parts of sodium nitrite in aqueous solution under cooling.

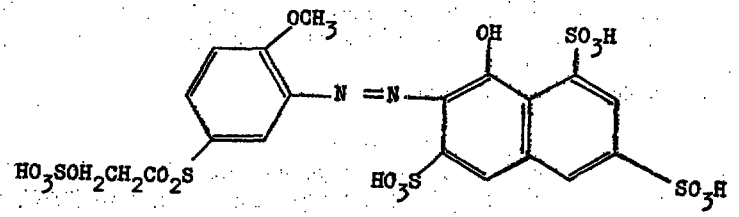
The resulting diazo mixture is introduced dropwise into a solution previously prepared by dissolving 42 parts of 1-hydroxynaphthalene-3,6,8-trisulfonic acid in 300 parts of water, together with 15 parts of sodium carbonate, while being cooled. After the reaction is over, 100 parts of potassium chloride is added to precipitate crystals, which are separated by filtration and dried.

The crystals obtained above are dissolved in 150 parts of 100% sulfuric acid at temperature of 20°C.

After 2 hour stirring, the reaction mixture is poured onto 300 parts of ice and water and 40 parts of potassium chloride is added thereto to precipitate crystals, which are separated by filtration. The separated crystals are dissolved in 300 parts of water by addition of potassium carbonate to adjust the pH to 6 to 7.

Thereafter, 45 parts of potassium chloride are further added thereto to precipitate crystals, which are separated by filtration and dried.

Thus a novel dye having the following formula,



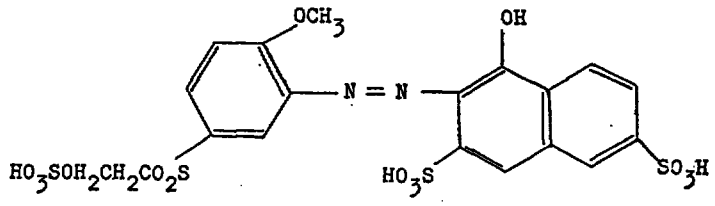
is obtained.

The dye obtained gives characteristic scarlet dyeing of 5 degree of fastnesses to light, washing, chlorine resistance and acid boiling respectively and of a high brilliancy on cotton with the aid of sodium hydroxide as an acid binding agent through the usual dyeing method for the fiber reactive dyes.

While, by employing 2-ethoxyaniline-5-β-hydroxyethylsulfone, instead of 2-methoxyaniline-5-β-hydroxyethylsulfone employed above, a similar dye for the same purposes may be also obtained according to the process mentioned above.

WHAT WE CLAIM IS:—

1. A scarlet monoazo dye represented by the following formula,



is obtained.

The dye obtained gives characteristic scarlet dyeings of 5 degree of fastnesses to light, washing, chlorine resistance and acid boiling respectively, and of a high brilliancy on cotton with the aid of sodium carbonate as an acid binding agent using the usual dyeing method for the fibre reactive dyes.

If, 1-hydroxynaphthalene-3,8-disulfonic acid instead of 1-hydroxynaphthalene-3,6-disulfonic acid employed above is treated in similar way as mentioned above, a similar dye is obtained.

Furthermore, by employing 2-ethoxyaniline-5-β-hydroxyethylsulfone, instead of 2-methoxyaniline-5-β-hydroxyethylsulfone employed above, a similar dye may be also obtained.

EXAMPLE 2

23.1 parts of 2-methoxyaniline-5-β-hydroxyethylsulfone is dissolved in 200 parts of ice and water with 10 parts of 35% hydrochloric acid and diazotized with 6.9 parts of sodium nitrite in aqueous solution under cooling.

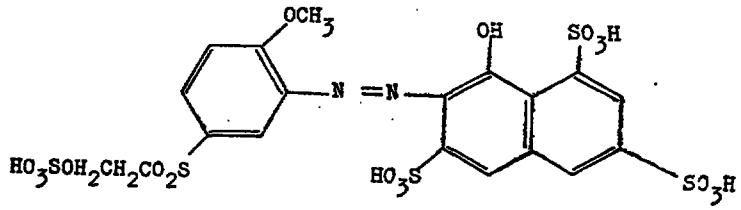
The resulting diazo mixture is introduced dropwise into a solution previously prepared by dissolving 42 parts of 1-hydroxynaphthalene-3,6,8-trisulfonic acid in 300 parts of water, together with 15 parts of sodium carbonate, while being cooled. After the reaction is over, 100 parts of potassium chloride is added to precipitate crystals, which are separated by filtration and dried.

The crystals obtained above are dissolved in 150 parts of 100% sulfuric acid at temperature of 20°C.

After 2 hour stirring, the reaction mixture is poured onto 300 parts of ice and water and 40 parts of potassium chloride is added thereto to precipitate crystals, which are separated by filtration. The separated crystals are dissolved in 300 parts of water by addition of potassium carbonate to adjust the pH to 6 to 7.

Thereafter, 45 parts of potassium chloride are further added thereto to precipitate crystals, which are separated by filtration and dried.

Thus a novel dye having the following formula,



is obtained.

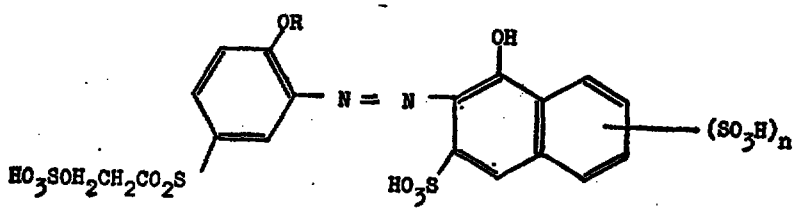
The dye obtained gives characteristic scarlet dyeing of 5 degree of fastnesses to light, washing, chlorine resistance and acid boiling respectively and of a high brilliancy on cotton with the aid of sodium hydroxide as an acid binding agent through the usual dyeing method for the fiber reactive dyes.

While, by employing 2-ethoxyaniline-5-β-hydroxyethylsulfone, instead of 2-methoxyaniline-5-β-hydroxyethylsulfone employed above, a similar dye for the same purposes may be also obtained according to the process mentioned above.

WHAT WE CLAIM IS:—

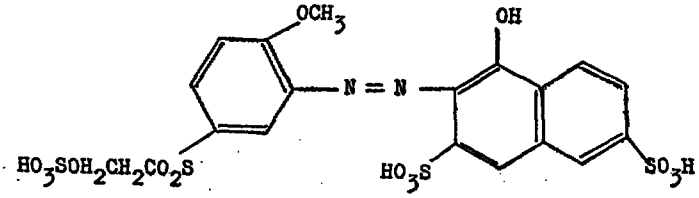
1. A scarlet monoazo dye represented by the following formula,

* C L M S *

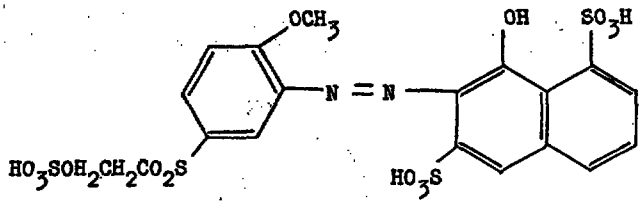


wherein R means methyl or ethyl radical and n means an integer of 1 to 2.

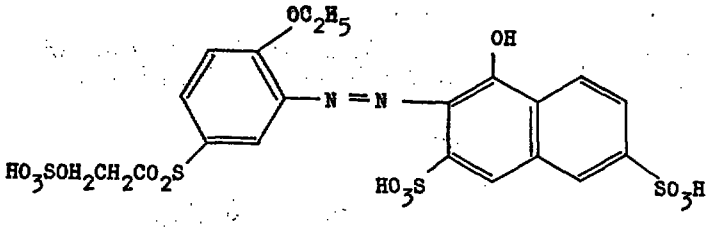
2. A scarlet monoazo dye represented by the following formula:



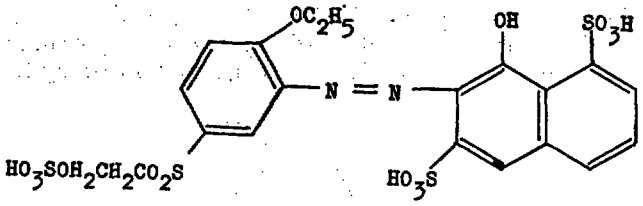
3. A scarlet monoazo dye represented by the following formula:



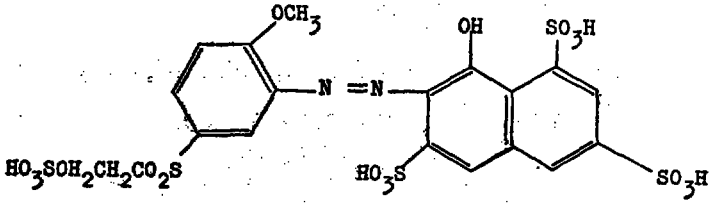
4. A scarlet monoazo dye represented by the following formula:



5. A scarlet monoazo dye represented by the following formula:

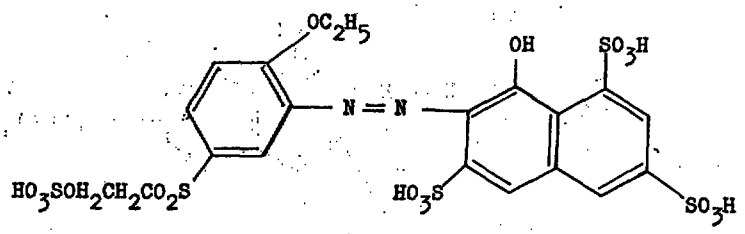


6. A scarlet monoazo dye represented by the following formula:

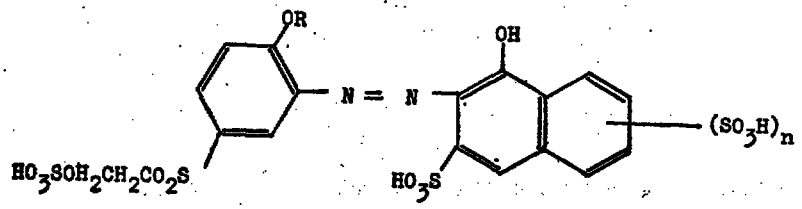


* C L M S *

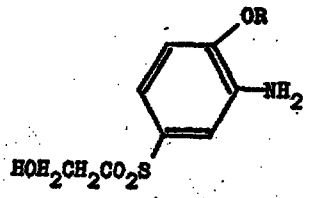
7. A scarlet monoazo dye represented by the following formula:



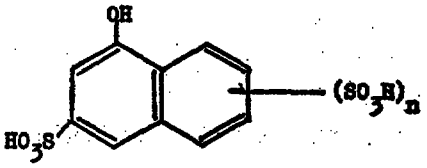
8. A method for the production of a scarlet monoazo dye represented by the following formula,



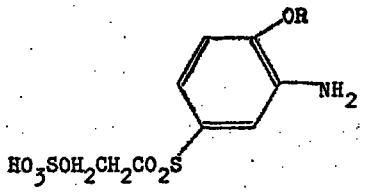
wherein R means methyl or ethyl radical and n means an integer of 1 to 2, which comprises contacting a diazotized amine represented by the following formula,



wherein R has the same meanings as defined in claim 1 above, with 1-hydroxy-naphthalene-polysulfonic acid represented by the following formula,



wherein n has the same meaning as defined in Claim 1 above, and esterifying the thus-formed dye with sulfuric acid at the hydroxy radical of β-hydroxyethylsulfone radical or contacting a diazotized amine represented by the following formula,



wherein R has the same meaning as defined above, with a 1-hydroxynaphthalenepoly-sulfonic acid same as defined above.

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