MALAYA

1,124,388

PATENT SPECIFICATION

NO DRAWINGS

1,124,388

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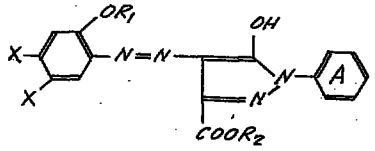
Int. Cl.:—C09 b 29/38, C 09 b 43/18

COMPLETE SPECIFICATION

Reactive Monoazo Dyes of the Benzene-Azo-Pyrazolone Series and process for their manufacture and use

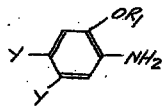
We, SUMITOMO CHEMICAL COMPANY LTD., a corporation organized under the laws of Japan, of 15, Kitahama-5-chome, Higashiku, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides monoazo dyes represented by the general formula:



wherein R_1 stands for a methyl or ethyl group, and R_2 stands for a hydrogen atom, methyl or ethyl group, one X stands for a group represented by $—SO_2CH_2CH_2OSO_3H$ and the other X stands for a hydrogen atom, methyl, methoxy or ethoxy group, and the ring A contains at least one sulfonic acid group, and may further contain one or more alkyl groups and/or halogen atoms.

The invention also provides a process for the manufacture of the aforesaid novel monoazo dyes, which comprise coupling a diazotised amine of the formula:



in which R_1 stands for a methyl or ethyl group, and one Y stands for a group represented by $—SO_2CH_2CH_2OH$, optionally in the form of its acid sulfuric acid ester and the other Y stands for a hydrogen atom, methyl, methoxy or ethoxy group; with a 1-phenyl-3-carboxylic acid-5-pyrazolone or its methyl or ethyl ester, in which the 1-phenyl radical contains at least one sulfonic acid group and may further contain one or more alkyl groups and/or halogen atoms, and after coupling when the one Y is a β-hydroxyethyl sulphone group, esterifying it with sulfuric acid.

Dyes within the present invention and represented by the above general formula are suitable for dyeing fibers, especially those made from natural or regenerated cellulose materials such as cotton, linen, viscose, and polyvinyl alcohol materials. They yield clear yellow or reddish yellow dyeings.

Dyeing is effected, as in the ordinary fiber reactive dyes, in the presence of acid-binding agents by a method such as impregnation, printing or padding. Dyeing is also possible by fixing the dyes with the acid-binding agents after printing or padding in the absence of such agents.

Dyeings obtained are distinguished by a brilliant yellow to reddish yellow tint and good fastness to light and wet processing. Dyes of the present invention are especially distinguished by a good solubility in water and a good stability of an alkaline paste used for printing.

[*Price 4s. 6d.*]

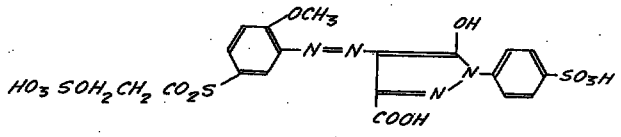
The following Examples illustrate the invention without limiting it. The parts are by weight.

EXAMPLE 1

27.8 parts of 2-methoxyanaline-5-β-hydroxyethylsulfone is added into 70 parts of sulfuric acid of 100% strength at 20°C. to 30°C. After complete dissolution the mixture is stirred for 1 hour and then introduced into 300 parts of ice and water. The precipitated sulfonic acid ester is filtered. The obtained 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 water.

34.2 parts of 1-(4'-sulfophenyl)-3-carboxy-5-pyrazolone are dissolved neutral in 300 parts of water and 15 parts of sodium carbonate, and into this solution the aforesaid diazo mixture is introduced dropwise, about 10 parts of sodium bicarbonate being added at the same time to maintain the reaction mixture at pH 6—7. After the reaction is over, 160 parts of sodium chloride are added thereto and the precipitated dye is filtered and dried at 70°C.

Thus 56 parts of the dye represented by the following formula are obtained.



The dye obtained is an orange-yellow powder which easily dissolves in water and gives, with the aid of acid-binding agents and using the usual dyeing method for fiber-reactive dyes, reddish yellow dyeings of good fastness to wet processing and light and of a high brilliancy on natural or regenerated cellulose fibers.

EXAMPLE 2

7 parts of 2-methoxyaniline-5-β-hydroxyethyl-sulphone are added to 70 parts of ice and water containing 5.5 parts of hydrochloric acid, and are diazotized with 2.8 parts of sodium nitrite.

11.4 parts of 1-(4'-sulfophenyl)-3-carboxy-5-pyrazolone are dissolved in 100 parts of water and 8 parts of sodium carbonate and into this solution the foresaid diazo mixture is introduced dropwise. After the coupling reaction is over, 20 parts of sodium chloride are added and the precipitated dye is filtered, dried and pulverized.

The dye obtained is added into 70 parts of sulfuric acid of 98% strength at 20°C. After complete dissolution, the mixture is stirred for 2 hours and then introduced into 200 parts of ice and water. 20 parts of potassium chloride are added and the precipitated dye is filtered. The cake obtained is dissolved in 150 parts of ice and water and the mixture is adjusted to pH 6—7 with aqueous potassium carbonate. The mixture is salted out with 15 parts of potassium chloride and the precipitated dye is filtered and dried at 70°C.

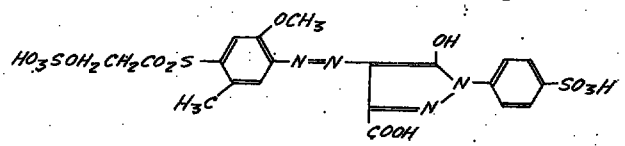
Thus 18 parts of the same dye as in Example 1 are obtained.

EXAMPLE 3

36.8 parts of 2-methoxy-5-methylaniline-4-β-hydroxyethylsulfone are added to 70 parts of sulfuric acid of 98% strength at 15°—30°C. After complete dissolution the mixture is stirred for 2 hours and then introduced into 300 parts of ice and water. The precipitated sulfuric acid ester is filtered. The obtained ester is introduced into 350 parts of ice and water and diazotized with 16 parts of hydrochloric acid and aqueous 8.3 parts of sodium nitrite.

34.2 parts of 1-(4'-sulfophenyl)-3-carboxy-5-pyrazolone is dissolved neutral in 300 parts of water and 10.2 parts of sodium bicarbonate, and into this solution the aforesaid diazo mixture is introduced dropwise, about 20 parts of sodium carbonate being added at the same time so as to maintain the pH at 6—7. After the reaction is over, 160 parts of potassium chloride are added and the precipitated dye is filtered and dried at 70°C.

Thus 65 parts of the dye represented by the following formula are obtained.



The dye obtained is an orange-yellow powder which easily dissolves in water and gives, with the aid of acid-binding agents and using a usual method of dyeing for fibre-reactive dyes, reddish yellow dyeings of good fastnesses to wet processing and light and of high brilliancy on natural or regenerated cellulose fibers.

EXAMPLE 4

10.8 parts of 2-methoxy-5-methylaniline-4-β-hydroxyethylsulfone are added to 100 parts of ice and water containing 5.5 parts of hydrochloric acid, and are diazotized with 2.8 parts of sodium nitrite.

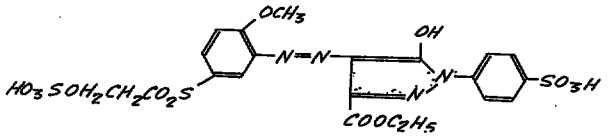
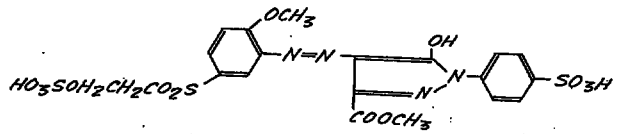
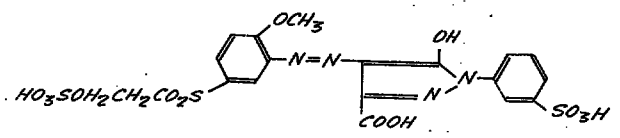
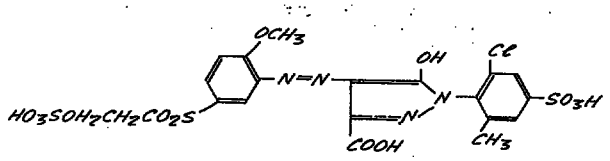
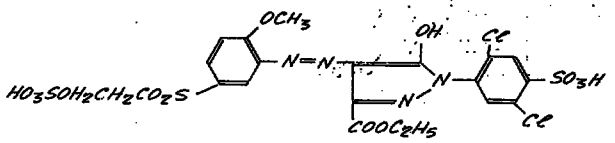
11.4 parts of 1-(4'-sulfophenyl)-3-carboxy-5-pyrazolone are added into 100 parts of water and 8 parts of sodium carbonate, and into this solution the aforesaid diazo mixture is introduced dropwise. After the coupling reaction is over, 25 parts of potassium chloride are added and the precipitated dye is filtered, dried and pulverized.

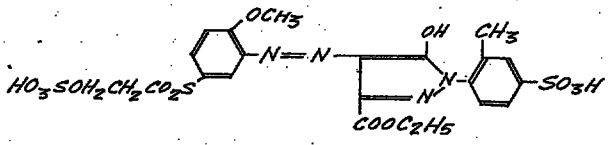
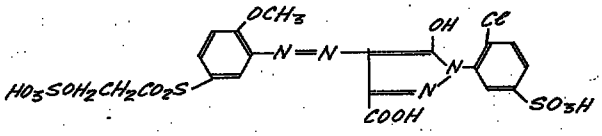
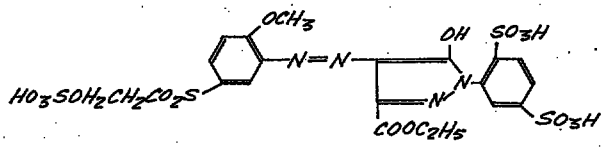
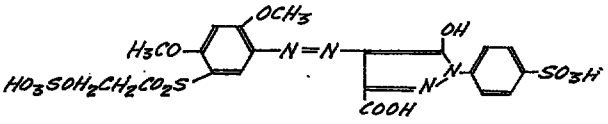
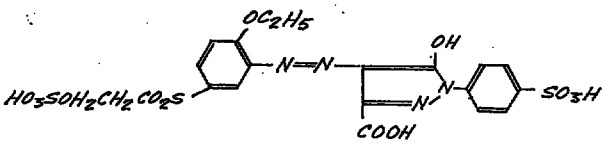
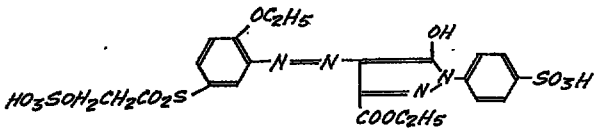
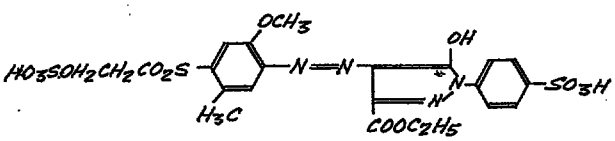
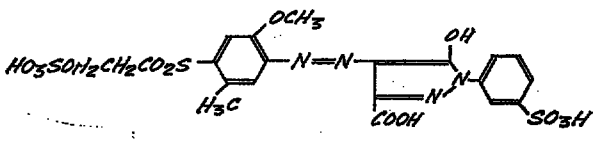
The dye obtained is added to 100 parts of 100% sulfuric acid at 20°C. After complete dissolution, the mixture is stirred for 2 hours and then introduced into 200 parts of ice and water, and neutralised to pH 6—7 with potassium carbonate. 15 parts of potassium chloride is added thereto and the precipitated dye is filtered and dried at 70°C.

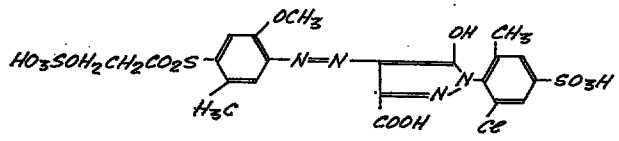
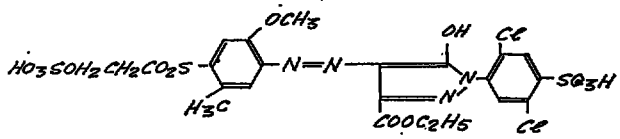
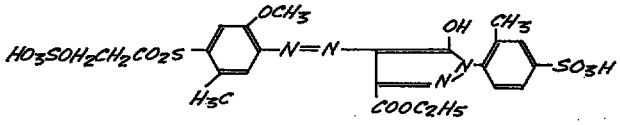
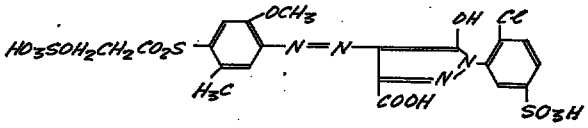
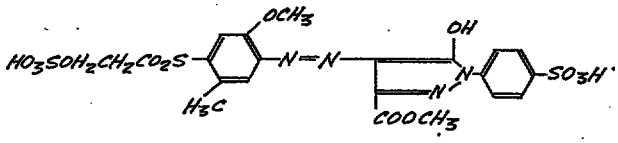
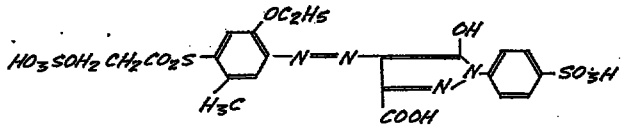
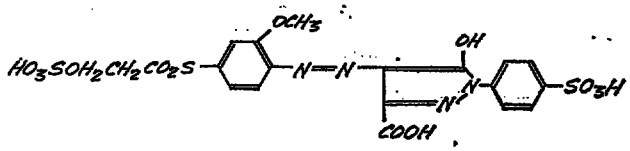
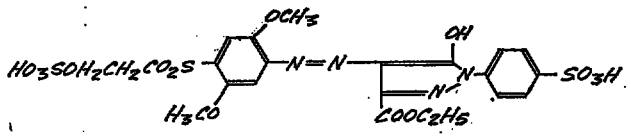
Thus 19 parts of the same dye as in Example 3 is obtained.

EXAMPLE 5

By methods similar to those of Examples 1 to 4, the dyes of the structures shown in column (I) in the following table are obtained and give dyeings of good fastnesses to light and to wet processing and of exceptional brilliancy, in the tints indicated in column (II).

(I) (Structure)	(II) (Tint)
	Reddish-Yellow
	"
	"
	Yellow
	"

(I) (Structure)	(II) (Tint)
	Yellow
	"
	Reddish-Yellow
	"
	"
	"
	"
	"

(I) (Structure)	(II) (Tint)
	Reddish-Yellow
	"
	"
	"
	"
	"
	"
	Orange-Yellow

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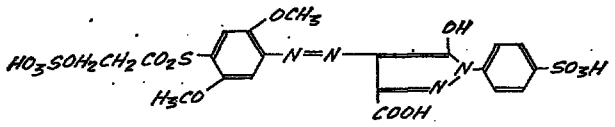
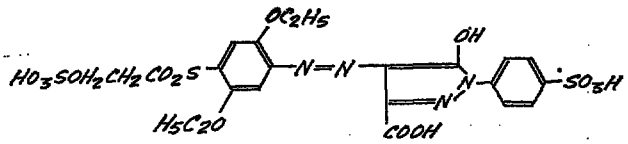
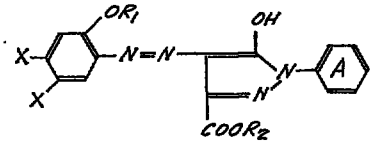
	Orange-Yellow
	"

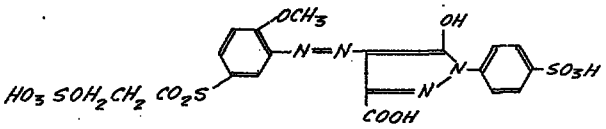
WHAT WE CLAIM IS:—

1. A monoazo dye represented by the following general formula:



wherein R_1 stands for a methyl or ethyl group, and R_2 stands for a hydrogen atom, methyl or ethyl group, one X stands for the group $-SO_2CH_2CH_2OSO_3H$ and the other X stands for a hydrogen atom, methyl, methoxy or ethoxy group, and the ring A contains at least one sulfonic acid group and may further contain one or more alkyl groups and/or halogen atoms.

2. A monoazo dye represented by the following formula:



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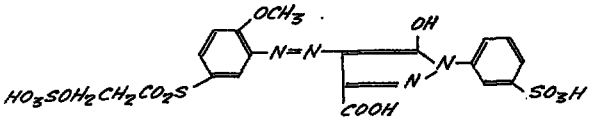

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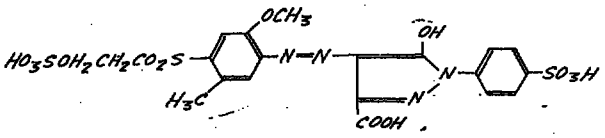
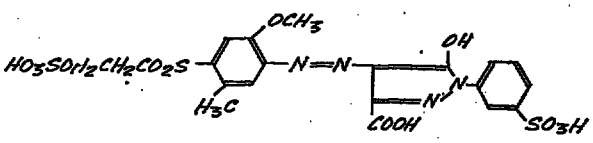


5. A monoazo dye represented by the following formula:



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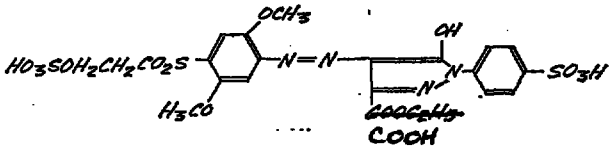

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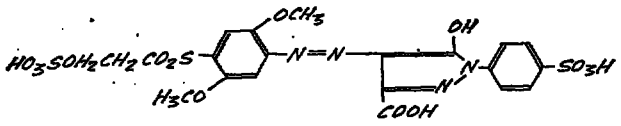
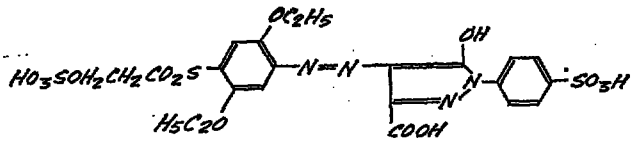
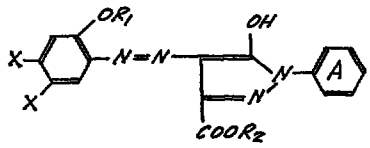
	Orange-Yellow
	"

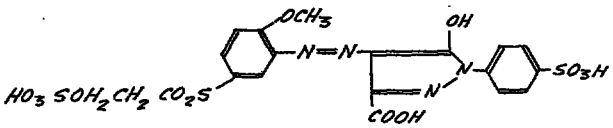
WHAT WE CLAIM IS:—

1. A monoazo dye represented by the following general formula:

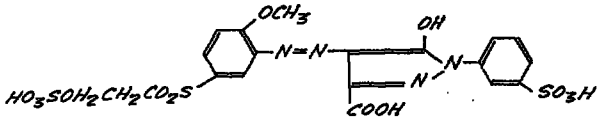


wherein R_1 stands for a methyl or ethyl group, and R_2 stands for a hydrogen atom, methyl or ethyl group, one X stands for the group $-SO_2CH_2CH_2OSO_3H$ and the other X stands for a hydrogen atom, methyl, methoxy or ethoxy group, and the ring A contains at least one sulfonic acid group and may further contain one or more alkyl groups and/or halogen atoms.

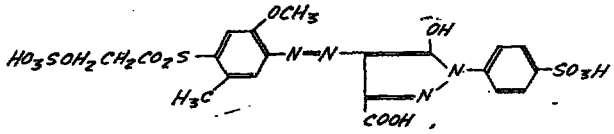
2. A monoazo dye represented by the following formula:



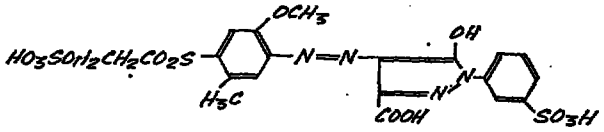
3. A monoazo dye represented by the following formula:



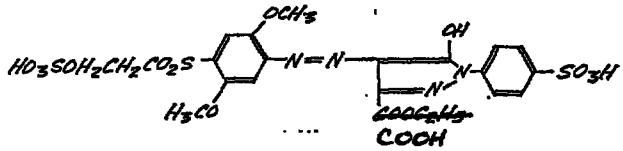
4. A monoazo dye represented by the following formula:



5. A monoazo dye represented by the following formula:



6. A monoazo dye represented by the following formula:



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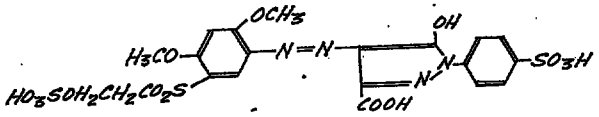

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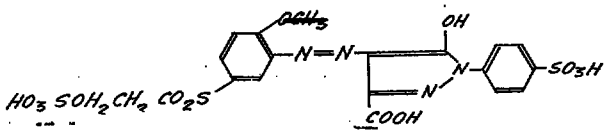
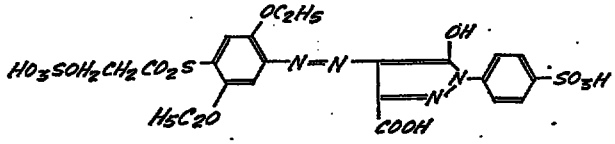
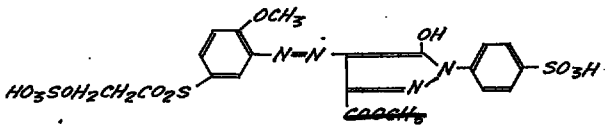


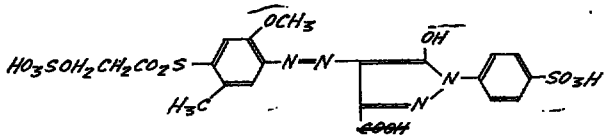
9. A monoazo dye represented by the following formula:



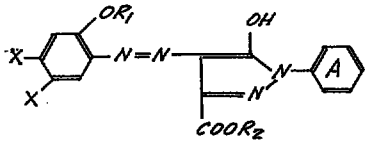
10. A monoazo dye represented by the following formula:



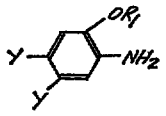
11. A monoazo dye represented by the following formula:



12. A process for the manufacture of a novel monoazo dye represented by the general formula:



wherein R_1 stands for a methyl or ethyl group; R_2 stands for a hydrogen atom, methyl or ethyl group, one X stands for the group $—SO_2CH_2CH_2OSO_3H$ and the other X stands for a hydrogen atom, methyl, methoxy or ethoxy group, and the ring A contains at least one sulfonic acid group and may further contain one or more alkyl groups and/or halogen atoms; which comprises coupling a diazotized amine of the following formula:



in which R_1 stands for a methyl or ethyl group, ~~and~~ one Y stands for ~~a~~ group ~~represented by~~ $—SO_2CH_2CH_2OH$, optionally in the form of its acid sulfuric acid ester and the other Y stands for a hydrogen atom, methyl, methoxy or ethoxy group; with a 1-phenyl-3-carboxylic acid-5-pyrazolone or its methyl or ethyl ester, in which the 1-phenyl radical contains at least one sulfonic acid group and may further contain one or more alkyl groups and/or halogen atoms, and after coupling when the one Y is a β-hydroxyethyl sulphone group, esterifying it with sulfuric acid.

* C L M S *

13. A process for the manufacture of a monoazo dye according to Claim 1 conducted substantially as described in any one of the Examples herein.

14. A process for dyeing or printing natural or regenerated cellulosic fibers in which a monoazo dye claimed in any one of Claims 1 to 11 is used.

15. Natural or regenerated cellulose fibers which have been dyed or printed with a dye claimed in any one of Claims 1 to 11.

16. Monoazo dyes according to Claim 1 whenever produced by a process according to Claim 12 or Claim 13.

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