

PATENT SPECIFICATION

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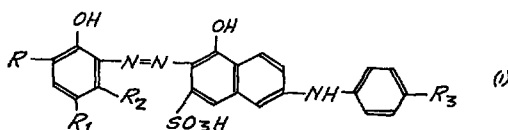
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(54) MONOAZO COMPOUNDS, PROCESSES FOR THEIR PRODUCTION, AND THEIR USE FOR THE DYEING OF NATURAL AND SYNTHETIC POLYAMIDE FIBRES

(71) We, SANDOZ LTD. of Lichtstrasse 35, Basle/Switzerland, a Body Corporate organised according to the laws of Switzerland, 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:—

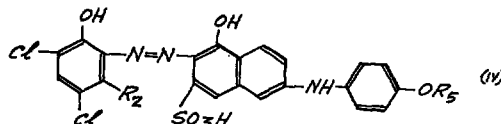
This invention relates to monoazo compounds, processes for their production, and their use for dyeing natural or synthetic polyamide fibres of textiles consisting of or containing such fibres comprising applying to the fibre a monoazo dye of formula I,



where each of R and R₁ signifies halogen, R₂ signifies hydrogen or halogen, R₃ signifies halogen or —OR₄ and R₄ signifies an unsubstituted or substituted alkyl radical, and a chromium donating compound, thereby forming a 1:1 or 2:1 dye:chromium complex or a mixture thereof on the fibre.

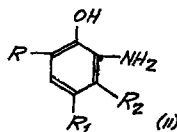
1-Hydroxy-2-(phenylazo)-6-phenylaminonaphthalene sulphonate compounds have been disclosed as a broad class but have not been disclosed for forming metal complexes of the fibre, and for such purpose the generality of such compounds do not possess the advantageous properties of the compounds of formula I.

Good dyeings are obtained using a monoazo compound of formula

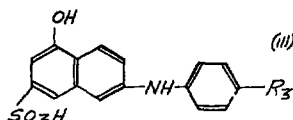


where R₅ represents an unsubstituted lower alkyl radical and R₂ is hydrogen or halogen atom.

The compounds of formula (I) can be obtained by coupling the diazo compound of an amine of formula



with a coupling component of formula



The coupling reaction can be carried out in an aqueous neutral to alkaline medium, preferably at pH 10.0 to 11.0, and at temperatures of -10°C to 60°C , preferably $0-20^{\circ}\text{C}$, if necessary in the presence of a coupling accelerant.

In each instance halogen represents a bromine, fluorine or iodine, or more especially a chlorine atom.

The alkyl radicals are preferably lower alkyl radicals i.e. alkyl radicals having 1 to 4 carbon atoms. If they are substituted they usually contain one or more substituents selected from halogen atoms, cyano, hydroxyl and amino groups and aryl radicals such as a phenyl radical. Thus the term "alkyl" includes aralkyl radicals, e.g. a benzyl radical.

Chromic fluoride, chromic sulphate, chromic formate, chromic acetate, chromic potassium sulphate and chromic ammonium sulphate may be instanced as suitable chromium donating compounds. The chromates and bichromates too, e.g. sodium and potassium chromate and bichromate, are highly suitable for the metallization on the fibre of the monoazo compounds of formula (I). 1:1- or 2:1-dye:metal complexes or mixtures thereof may be formed.

The principal natural polyamides are wool and silk. The synthetic polyamides include types of different chemical constitution, as named in SVF—Fachorgan 15, p. 8—9 (1960); examples are the products produced by condensation of a dibasic acid such as adipic acid and hexamethylene diamine (nylon 6.6), of caprolactam (nylon 6) and of aminoundecanoic acid (nylon 11).

Any of the known dyeing methods can be employed. Thus the polyamide fibre can be dyed with a compound of formula (I) and simultaneously treated with a chromium donating agent in the same bath, or the compound of formula (I) can be applied first and metallized on the fibre with the chromium donor, either in the dyebath or in a fresh bath.

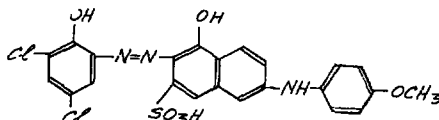
It is best to carry out the process in an aqueous acid medium at temperatures up to 100°C with the addition of an organic acid such as acetic acid or formic acid and in the presence of sodium sulphate or ammonium sulphate.

It is surprising that polyamide fibres dyed by the process of this invention have better fastness properties, such as fastness to potting, than the dyeings given by preformed chromium complexes of the monoazo compounds of formula (I). The dyeings are also of more brilliant shade.

In the following Examples the parts and percentages are by weight and the temperatures in degrees centigrade.

Example 1.

0.7 Parts of the dye of formula



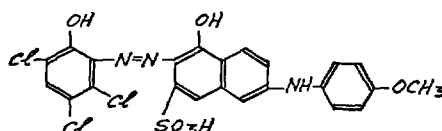
are dissolved in 6000 parts of water at $40-50^{\circ}$. To this solution are added 5 parts of sodium sulphate, 2 parts of glacial acetic acid and 2 parts of 85% formic acid. 100 Parts of wool gaberdine are entered into this dyebath and the temperature is then increased to the boil in 45 minutes, dyeing being continued at this temperature for 30 minutes. After this time a further 2 parts of 55% formic acid are added and dyeing is continued for 30 minutes at the boil. The bath is then cooled to 70° , set with 0.75 parts of potassium bichromate and raised to the boil again. The fabric is treated for 30 minutes and on removal is treated further under the normal conditions. A navy blue dyeing is obtained on the wool gaberdine which has good light and yet fastness properties.

Example 2.

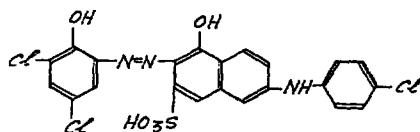
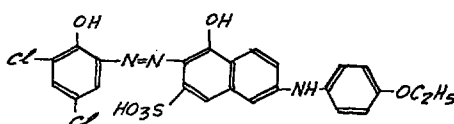
A dyebath is prepared by dissolving 1.5 parts of the dye of Example 1, 10 parts of sodium sulphate, 5 parts of ammonium sulphate and 1.5 parts of potassium dichromate in 6000 parts of water. 100 Parts of wool gaberdine are entered into the bath at 40°, the bath is brought to the boil in 60 minutes and the fabric dyed for 1 hour 30 minutes at this temperature. It is then treated further by the normal method. A navy blue dyeing of the same quality as that of Example 1 is obtained.

The unmetallized dye specified in Example 1 can be produced by coupling the diazo compound of 1-hydroxy-2-amino-4,6-dichlorobenzene with 2-(4'-methoxyphenylamino)-5-hydroxy-naphthalene-7-sulphonic acid.

Comparably good dyeings on natural and synthetic polyamide fibres are obtained when the navy blue dye of formula

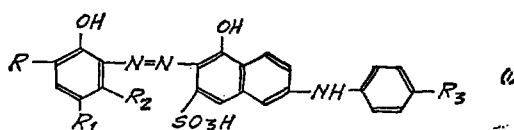


is applied by one of the procedures of Examples 1 or 2. The dyes of the following formulae, which also give dyeings of navy blue shade using the procedure of Example 1 or Example 2, can be produced in an analogous manner to that used for the production of the unmetallized dye of Example 1.



WHAT WE CLAIM IS:—

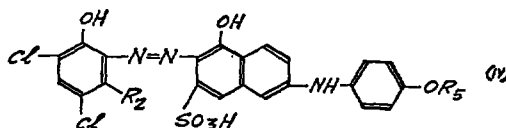
1. A process for dyeing natural or synthetic polyamide fibres or textiles consisting of or containing such fibres comprising applying to the fibre a monoazo dye of formula I,



where each of R and R₁ signifies halogen, R₂ signifies hydrogen or halogen, R₃ signifies halogen or —OR₄, and R₄ signifies an unsubstituted or substituted alkyl radical, and a chromium donating compound, thereby forming a 1:1 or 2:1 dye:chromium complex or a mixture thereof on the fibre.

2. A process according to Claim 1, in which R₄ signifies an unsubstituted lower alkyl radical or a lower alkyl radical substituted by one of more substituents selected from halogen atoms, cyano, hydroxy, amino and phenyl groups.

where R₅ signifies an unsubstituted lower alkyl radical, and R₂ signifies a hydrogen or monoazo compound of formula IV,

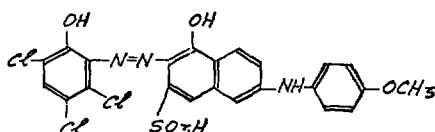


Example 2.

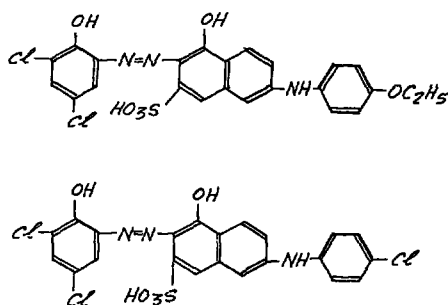
A dye bath is prepared by dissolving 1.5 parts of the dye of Example 1, 10 parts of sodium sulphate, 5 parts of ammonium sulphate and 1.5 parts of potassium dichromate in 6000 parts of water. 100 Parts of wool gaberdine are entered into the bath at 40°, the bath is brought to the boil in 60 minutes and the fabric dyed for 1 hour 30 minutes at this temperature. It is then treated further by the normal method. A navy blue dyeing of the same quality as that of Example 1 is obtained.

The unmetallized dye specified in Example 1 can be produced by coupling the diazo compound of 1-hydroxy-2-amino-4,6-dichlorobenzene with 2-(4'-methoxyphenylamino)-5-hydroxy-naphthalene-7-sulphonic acid.

Comparably good dyeings on natural and synthetic polyamide fibres are obtained when the navy blue dye of formula

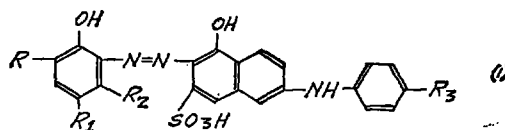


is applied by one of the procedures of Examples 1 or 2. The dyes of the following formulae, which also give dyeings of navy blue shade using the procedure of Example 1 or Example 2, can be produced in an analogous manner to that used for the production of the unmetallized dye of Example 1.



WHAT WE CLAIM IS:—

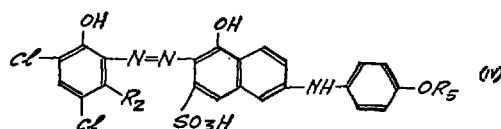
1. A process for dyeing natural or synthetic polyamide fibres or textiles consisting of or containing such fibres comprising applying to the fibre a monoazo dye of formula I,



where each of R and R₁ signifies halogen, R₂ signifies hydrogen or halogen, R₃ signifies halogen or —OR₄ and R₄ signifies an unsubstituted or substituted alkyl radical, and a chromium donating compound, thereby forming a 1:1 or 2:1 dye:chromium complex or a mixture thereof on the fibre.

2. A process according to Claim 1, in which R₄ signifies an unsubstituted lower alkyl radical or a lower alkyl radical substituted by one of more substituents selected from halogen atoms, cyano, hydroxy, amino and phenyl groups.

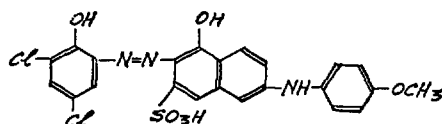
where R₃ signifies an unsubstituted lower alkyl radical, and R₂ signifies a hydrogen or monoazo compound of formula IV,



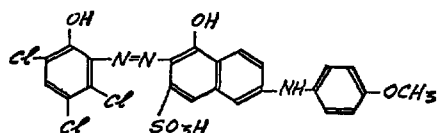
where R_3 signifies an unsubstituted lower alkyl radical, and R_3 signifies a hydrogen or halogen atom.

4. A process according to Claim 3, in which R_2 represents a hydrogen atom.

5. A process according to any one of Claims 1 to 4, which is characterized by the use of a monoazo compound of formula (V),



6. A process according to any one of Claims 1 to 3, which is characterized by the use of a monoazo compound of formula (VI),



7. A dyeing process conducted substantially as herein described with particular reference to Example 1 or Example 2.

8. Natural and synthetic polyamide fibres and textiles consisting of or containing such fibres dyed by a process according to any one of Claims 1 to 7.

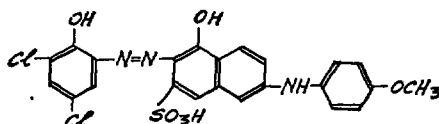
9. A compound of formula (I), as defined in Claim 1.

10. A compound according to Claim 9, in which R_4 signifies an unsubstituted lower alkyl radical or a lower alkyl radical substituted by one or more substituents selected from halogen atoms, cyano, hydroxy, amino and phenyl groups.

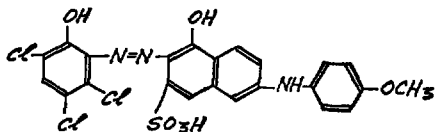
11. A compound according to Claim 9, of formula (IV), as defined in Claim 3.

12. A compound according to Claim 11, in which R_2 signifies a hydrogen atom.

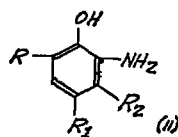
13. A compound of formula



14. A compound of formula

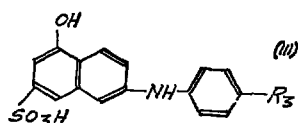


15. A process for the production of a compound of formula (I), as defined in Claim 1, characterized by coupling the diazo derivative of an amine of formula (II),



in which R_1 , R_2 and R_3 are as defined in Claim 1, with a coupling component of formula III,





in which R_3 is as defined in Claim 1.

16. A process for the production of a compound of formula (I) as defined in Claim 1, substantially as described hereinbefore.

17. A compound of formula (I), whenever obtained by a process according to Claim 15 or Claim 16.

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