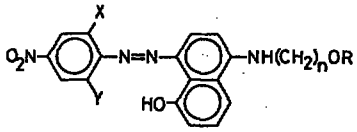
SPECIFICATION

Water-insoluble azo-dyes

This invention relates to a series of new water-insoluble monoazo-dyes free from hydrosolubilizing groups, to their synthesis, to their application to textile materials, and to the preparation of corresponding intermediates.

Specifically, the invention relates to new mono-azo dyes having the following general formula:



(I)

wherein:

Y is H; Cl; Br;

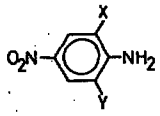
X is H; Cl; Br; lower alkyl; lower alkoxyl; CN; CF_3; NO_2; SO_2-lower alkyl; COO-lower alkyl

n is 2 or 3;

R is lower alkyl;

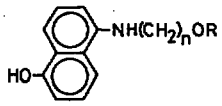
and wherein the expression 'lower' signifies having from 1 to 4 carbon atoms.

The dyes of general formula (I) may be prepared from corresponding starting materials by conventional techniques, i.e. by diazotizing in an acid medium an amine of the general formula:



(II)

and by coupling, in an aqueous medium, preferably at a pH of 4 - 5, the resulting diazo compound with a coupling compound of the general formula:



(III)

wherein:

X, Y, n and R have the meanings defined above.

The intermediates of the general formula (III) may be obtained under the conditions of the Bucherer reaction, as described in certain of the Examples that follow, by reacting 1,5-dihydroxy-napthalene with a lower alkoxy C_1 - C_3 alkylene amine.

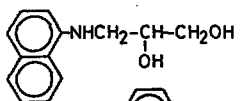
Usually the dyes of general formula (I) are obtained at a high degree of purity, and no purification is required.

The monoazo-dyes of the present invention are particularly suitable for the dyeing and printing of synthetic polymeric materials, for example, polyesters, polyamides, polyacrylonitrile and esters of cellulose in any form. When applied by conventional dyeing methods, for example from an aqueous bath under pressure at 130°C or by padding-steaming or by padding and heating with dry air (Thermosol), or by printing the above-said dyes provide, on these materials, intense and bright dyeings and printings having reddish blue to green-blue shades, and they exhibit a good affinity and good stabilities to sunlight, washing and sublimation.

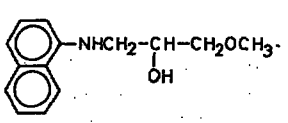
Because of the excellent stability exhibited to variation of the pH value of the dyeing bath, the monoazo-dyes of the general formula (I) are particularly suitable for dyeing polyesters at high temperatures.

Azo-dyes are known having shades ranging from reddish blue to greenish blue and having a structure somewhat similar to that of the dyes of the present invention, for example dyes described in the following patents:

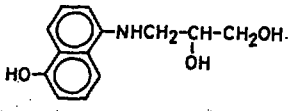
German patents Nos. 659,147 and 658,124, in which 6-chloro-2.4-dinitroaniline or 6-bromo-2.4-dinitroaniline are diazotized and coupled respectively with:



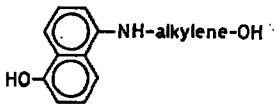
and



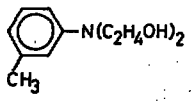
U.S. patent No. 2,434,150 in which 2-alkylsulphonyl-4-nitro-anilines are diazotized and coupled with:

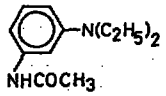


German patent No. 639,727, in which 2-amino-benzothiazoles are diazotized and coupled with:

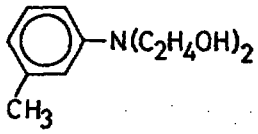


Furthermore, there are known other blue shade azo-dyes derived, for example, from substituted 2-amino-5-nitrothiazoles or from 2-amino-benzothiazoles diazotized and coupled with substituted N,N-dialkyl-anilines, such as:





or dyes derived from 6-bromo- or from 6-chloro-2.4-dinitro-aniline diazotized and coupled with substituted N,N-dialkyl-anilines, such as:



All these dyes, however, have the drawback of being little stable to the pH variations which occur during the dyeing process, or of undergoing degradation during dyeing, or even of having very low values of fastness to sunlight.

It has now surprisingly been found that the dyes of general formula (I) obtained according to this invention exhibit, in comparison with those already known, improved general stabilities, in particular to sunlight and sublimation, and a considerable improvement in tinctorial properties, in particular a high stability to pH variations of the dyeing bath: in practice no substantial differences of shade can be noticed among dyeings effected at pH values between 7 and 3.

For the above-mentioned applications, the dyes in the dry state or in the mass are suitably ground in the presence of appropriate dispersing agents, such as, for example, sodium ligninsulphonate, down to a particle size of 0.5 - 1 microns, and are applied to the fibres by the above-indicated techniques.

According to one preferred aspect of the invention, in the monoazo-dyes according to the invention, Y may be H, and X may be CH_3, Br, Cl, OCH_3 or CF_3.

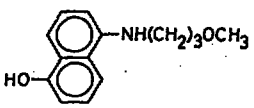
In another preferred aspect of the invention, in the monoazo-dyes according to the invention, R may be CH_3 and n may be 3.

The following examples illustrate how the invention may be carried into effect without being however a limitation of the broader aspects thereof. Unless otherwise specified, the term 'parts' is to be understood as being by weight, related to parts by volume as grams to millilitres.

Example 1

1.52 parts of 2-methyl-4-nitro-aniline were treated at an elevated temperature with 4.0 parts by volume of aqueous of HC1 of density 1.18, and 30 parts by volume of water. After cooling the solution to 5 - 10°C, 0.69 parts of sodium nitrite in 10 parts by volume of water were gradually added.

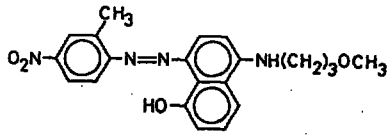
The resulting diazo solution was then clarified and poured, at 5 - 10°C, into a solution of 2.31 parts of the coupling compound:



in 20 parts by volume of acetic acid and 50 parts by volume of water.

During the coupling reaction the pH was maintained at 4 - 5 by the addition of sodium acetate crystals. Then, after stirring for 30 minutes the product was filtered, and the precipitate was washed with water and

dried. There were obtained 3.8 parts of the dye:



which imparts to artificial fibres, in particular to polyester fibres, an intense and bright reddish navy-blue shade having good fastnesses to sunlight, moisture and sublimation; also the stability of the dye to variations in the dye bath pH value from 3 to 7 was excellent.

The coupling compound used in Example 1 was synthesised as follows:

2.0 parts of 3-methoxy-propylamine were treated with 27.4 parts by volume of aqueous $NaHSO_3$, density 1.309, and 100 parts by volume of water. The solution was stirred for 10 minutes at room temperature, whereupon 20.3 parts of 1,5-dihydroxy-naphthalene and 14.7 parts of 3-methoxy-propylamine were charged, the temperature was raised to 106°C and was maintained at this level for 27 hours. Finally, the solution was cooled to 20°C, and the pH brought to 14 by the addition of aqueous sodium hydroxide of density 1.18.

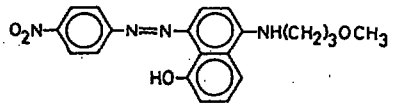
The suspension was then stirred for 1 hour, and filtered to separate 1,5-bis-(3-methoxy-propylamino)-naphthalene, the filtrate being acidified with aqueous HCl, of density 1.09, to pH 1. The acidified filtrate was then treated with activated carbon and kept stirred for about 1 hour, whereupon it was filtered to remove unreacted 1,5-dihydroxy-naphthalene.

The filtrate was now treated again with aqueous sodium hydroxide as above to bring it to a pH of 7. At this pH, 1-(3-methoxy-propylamino)-5-hydroxy-naphthalene precipitated, initially in the form of a thick oil and then as a crystalline solid that was separated by filtration. After washing and drying the filter-cake, 17.7 parts (yield 58.8%) of a product having a melting point of 78 - 80°C and the following elemental analysis were obtained:

	C	H	N
calculated %	72.73	7.36	6.06
found %	72.15	7.29	6.03

Example 2

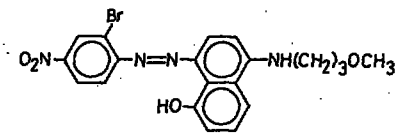
1.38 parts of p-nitro-aniline were dissolved in 4.0 parts by volume of aqueous HCl, of density 1.18, and 20 parts by volume of water. The nitro-aniline was diazotized at 5 - 10°C by gradually adding a solution of 0.69 parts of sodium nitrite in 10 parts by volume of water. The diazo solution, after clarification, was poured at 5 - 10°C into a solution of 2.31 parts of the coupling compound of example 1 in 20 parts by volume of acetic acid and 50 parts by volume of water. By working up as described in Example 1, there were obtained 3.65 parts of the dye:



which imparts to the above-said fibres a very reddish navy blue shade having good general stabilities and an excellent stability to variation in pH.

Example 3

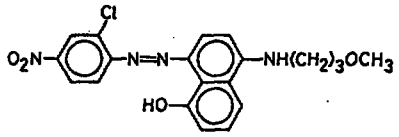
2.17 parts of 2-bromo-4-nitro-aniline were diazotized and coupled with 2.31 parts of the coupling compound of Example 1, according to the procedure illustrated in Example 1, 4.4 parts of the dye:



were obtained, which imparts to the above-said fibres a very greenish blue shade having good general stabilities and an excellent stability to variation in pH.

Example 4

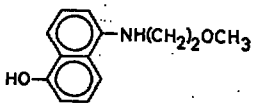
1.73 parts of 2-chloro-4-nitro-aniline were diazotized and coupled with 2.31 parts of the coupling compound of Example 1 according to the procedure described in Example 1. 3.89 parts of the dye:



were obtained, which imparts to the above-mentioned fibres a greenish dark blue shade having good general stabilities and an excellent stability to variation in pH.

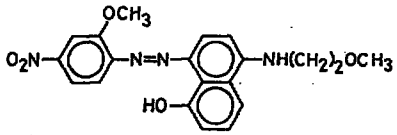
Example 5

1.68 parts of 2-methoxy-4-nitro-aniline were diazotized according to the procedure described in Example 1 and were coupled with 2.17 parts of the coupling compound:



in 20 parts by volume of acetic acid and 50 parts by volume of water.

By working up according to Example 1 there was obtained 3.75 parts of the dye:

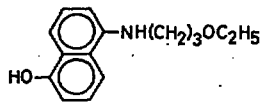


which dyes the above-said fibres reddish navy blue with good general stabilities and an excellent stability to variation in pH.

The coupling compound was synthetised by following a method analogous with that described in Example 1.

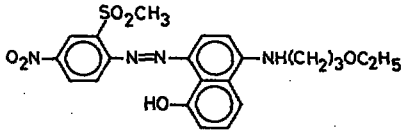
Example 6

2.16 parts of 2-methylsulphonyl-4-nitroaniline were added, at 0 - 5°C and during 1 hour, to a solution of 0.69 parts of sodium nitrite in 20 parts by volume of aqueous H_2SO_4 of density 1.84. After a further 30-minute stirring the diazo solution was poured at 5 - 10°C into a solution of 2.45 parts of the coupling compound:



in 15 parts by volume of acetic acid and 40 parts by volume of water. During the coupling reaction the pH was maintained at 4 - 5 by addition of sodium acetate crystals.

After stirring for 1 hour, the reaction mixture was filtered and the precipitate was washed with water. By drying the cake there were obtained 4.4 parts of the dye:

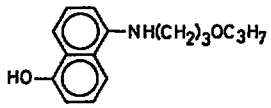


which imparts to the above-mentioned fibres a greenish blue shade having good general stabilities and an excellent stability to variation in pH.

The coupling compound was synthetised in the same manner as for that of Example 1.

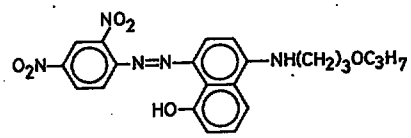
Example 7

1.83 parts of 2,4-dinitro-aniline were diazotized following the procedure of Example 6 and were coupled with 2.59 parts of the coupling compound:



in 20 parts by volume of acetic acid and 40 parts by volume of water.

By working up as in Example 6, there were obtained 4.35 parts of the dye:



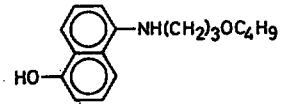
which dies the above-mentioned fibres greenish blue with good general stabilities and an excellent stability to variation in pH.

The coupling compound was synthetised by a method analogous with that described in Example 1.

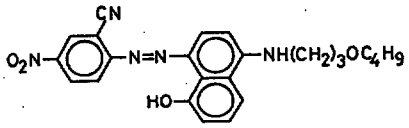
Example 8

A solution of 1.63 parts of 2-cyano-4-nitroaniline in 20 parts of acetic acid, 4 parts of propionic acid and 2 parts by volume of water was cooled to 5 - 10°C, whereupon 10 parts by volume of 1-N nitrosylsulphuric acid were gradually added.

After stirring for about 1 hour at 5 - 10°C, the diazo solution was slowly poured into a solution of 2.73 parts of the coupling compound:



in 20 parts by volume of acetic acid and 40 parts by volume of water. By working up as described in Example 6, there were obtained 4.2 parts of the dye:



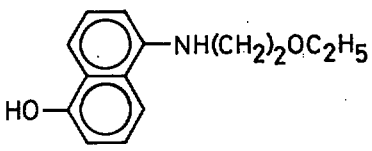
which dyes the above-said fibres green-blue with good general stabilities and an excellent stability to variation in pH.

The coupling compound was synthetised by a method analogous with that described in Example 1.

Example 9

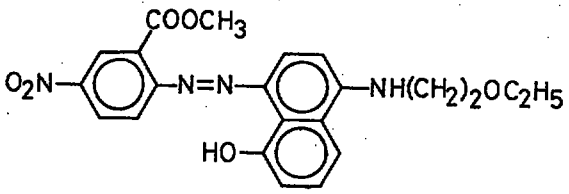
A solution of 0.69 parts of sodium nitrite in 10 parts by volume of aqueous sulphuric acid of density 1.84, was added in the course of 1 hour to a solution of 1.96 parts of the methyl ester of 2-amino-5-nitro-benzoic acid in 10 parts by volume of and cooled to 0 - 5°C.

After stirring for 1 hour, the diazo solution was poured at 5 - 10°C into a solution of 2.31 parts of the coupling compound:



in 20 parts by volume of acetic acid and 50 parts by volume of water.

By working up generally as described in Example 6 there were obtained 4.1 parts of the dye:

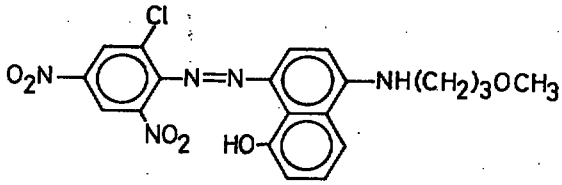


which imparts to the above-mentioned fibres a green-blue shade having good general stabilities and an excellent stability to variation in pH.

The coupling compound was synthetised by a method analogous with that described in Example 1.

Example 10

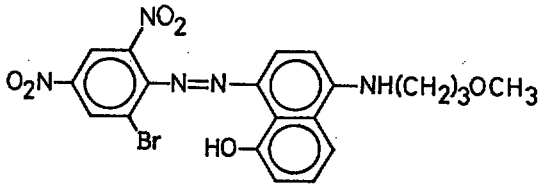
2.18 parts of 2,4-dinitro-6-chloro-aniline were diazotized by the procedure of Example 9 and coupled with 2.31 parts of the coupling compound of Example 1, again by the procedure of Example 1. 4.35 parts of the dye:



were obtained, which imparts to the above-said fibres a very green-blue shade having good general stabilities and an excellent stability to variation in pH.

Example 11

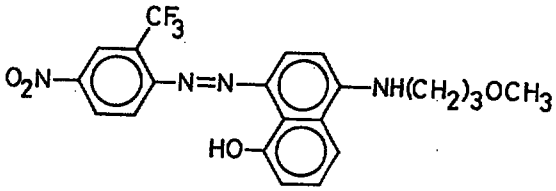
2.62 parts of 2,4-dinitro-6-bromo-aniline were diazotized and coupled with 2.17 parts of the coupling compound of Example 5 by the process described in Example 9. 4.8 parts of the dye:



were obtained, which imparted to the above-mentioned fibres a very green-blue shade having good general stabilities and an excellent stability to variation in pH.

Example 12

2.06 parts of 2-trifluoro-methyl-4-nitroaniline were diazotized and coupled with 2.31 parts of the coupling compound of Example 1 according to the procedure of Example 1. 4.25 parts of the dye:



were obtained, which dyes the above-said fibres greenish blue with good general stabilities and an excellent stability to variation in pH.

Example 13

0.6 parts of the dye of Example 1, previously microfined, were added to a dyeing bath at 40°C containing 100 parts of a polyester yarn.

The pH was brought to 5 with acetic acid, whereupon, by operating at a bath ratio of 1 : 15, the bath was gradually heated to 130 - 135°C: dyeing was carried out for 1 hour at this temperature.

After cooling, the bath was discharged and the dyed material was subjected to the usual alkaline reducing washing treatment.

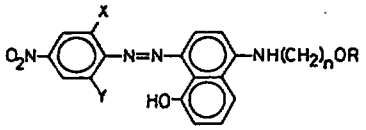
There was obtained an intense and bright reddish navy blue dyeing having good stabilities to sunlight, moisture and sublimation, and an excellent stability to variation of the dyeing pH from 7 to 3: the shade remained practically unaltered within this range.

By operating as described in the foregoing Examples, the following monoazo-dyes of general formula (I) were obtained.

Ex No.	X	Y	n	R	Dye shade on
14	$SO_2C_2H_5$	H	3	CH_3	Green blue
15	NO_2	H	3	CH_3	Green blue
16	CN	H	3	CH_3	Green blue
17	Br	H	2	CH_3	Greenish blue
18	CH_3	H	2	C_2H_5	Reddish navy blue
19	OCH_3	H	2	C_3H_7	Reddish navy blue
20	NO_2	Cl	2	C_4H_9	Very green blue
21	NO_2	Br	2	CH_3	Very green blue
22	Cl	Cl	3	C_4H_9	Green blue
23	Br	Br	3	C_3H_7	Green blue
24	CN	Br	3	C_2H_5	Very green blue
25	CF_3	H	3	C_3H_7	Greenish blue

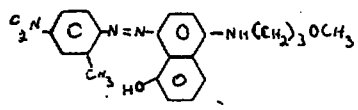
CLAIMS

1. Monoazo-dyes of the general formula:

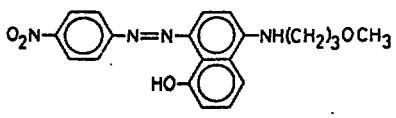


wherein:
Y is H, Cl or Br;
X is H, Cl, Br, lower alkyl, lower alkoxyl, CN, CF_3, NO_2, SO_2-lower alkyl, or COO-lower alkyl;
n is 2 or 3, and
R is a lower alkyl group, and wherein the expression 'lower' signifies having from 1 to 4 carbon atoms.

2. The monoazo-dyes according to claim 1, in which Y is H, and X is CH_3, Br, Cl, OCH_3 or CF_3.
3. The monoazo-dyes according to claim 1, in which R is CH_3 and n is 3.
4. The dye:



5. The dye:



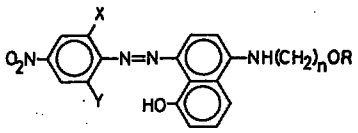
There was obtained an intense and bright reddish navy blue dyeing having good stabilities to sunlight, moisture and sublimation, and an excellent stability to variation of the dyeing pH from 7 to 3: the shade remained practically unaltered within this range.

By operating as described in the foregoing Examples, the following monoazo-dyes of general formula (I) were obtained.

Ex No.	X	Y	n	R	Dye shade on
14	$SO_2C_2H_5$	H	3	CH_3	Green blue
15	NO_2	H	3	CH_3	Green blue
16	CN	H	3	CH_3	Green blue
17	Br	H	2	CH_3	Greenish blue
18	CH_3	H	2	C_2H_5	Reddish navy blue
19	OCH_3	H	2	C_3H_7	Reddish navy blue
20	NO_2	Cl	2	C_4H_9	Very green blue
21	NO_2	Br	2	CH_3	Very green blue
22	Cl	Cl	3	C_4H_9	Green blue
23	Br	Br	3	C_3H_7	Green blue
24	CN	Br	3	C_2H_5	Very green blue
25	CF_3	H	3	C_3H_7	Greenish blue

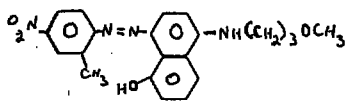
CLAIMS

1. Monoazo-dyes of the general formula:

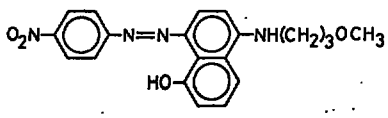


wherein:
Y is H, Cl or Br;
X is H, Cl, Br, lower alkyl, lower alkoxyl, CN, CF_3, NO_2, SO_2-lower alkyl, or COO-lower alkyl;
n is 2 or 3, and
R is a lower alkyl group, and wherein the expression 'lower' signifies having from 1 to 4 carbon atoms.

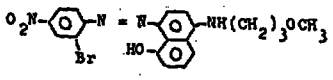
2. The monoazo-dyes according to claim 1, in which Y is H, and X is CH_3, Br, Cl, OCH_3 or CF_3.
3. The monoazo-dyes according to claim 1, in which R is CH_3 and n is 3.
4. The dye:



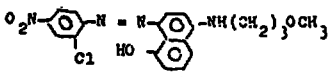
5. The dye:



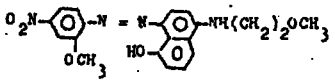
6. The dye:



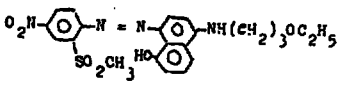
7. The dye:



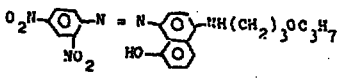
8. The dye:



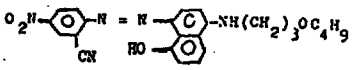
9. The dye:



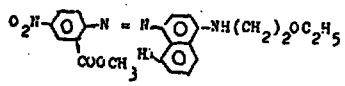
10. The dye:



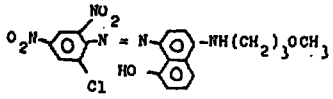
11. The dye:



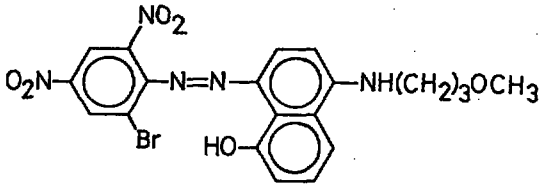
12. The dye:



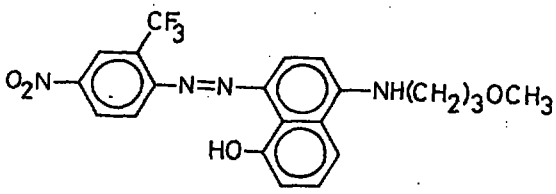
13. The dye:



14. The dye:



15. The dye:



16. Synthetic polymeric materials dyed or printed with any of the dyes of Claims 1 to 15.

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