

PATENT SPECIFICATION

(11) 1349 003

1349 003

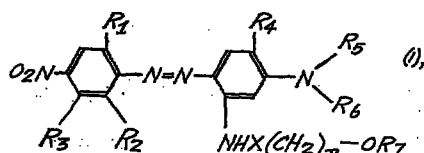
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 (72) Inventor WOLFGANG GROEBKE



(54) MONOAZO COMPOUNDS OF LOW SOLUBILITY IN WATER, THEIR PRODUCTION AND USE AS DYES

(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 compounds of formula



where R_1 stands for chlorine, bromine, cyano, nitro, or unsubstituted or substituted alkylsulphonyl or phenylsulphonyl,

R_2 for hydrogen, chlorine or bromine,

R_3 for hydrogen, chlorine, bromine or acylamino, provided that at least one of R_2 and R_3 stands for hydrogen,

R_4 for hydrogen or unsubstituted or substituted alkyl or alkoxy,

R_5 and R_6 , independently of each other, for alkyl which is unsubstituted or is substituted by one or more substituents selected from chlorine, bromine, cyano, hydroxyl, alkoxy, chloroalkoxy, bromoalkoxy, cyanoalkoxy, and unsubstituted and substituted alkylcarbonyloxy, benzoyloxy, alkoxy carbonyl, phenoxy carbonyl, alkoxy carbonyloxy and phenoxy carbonyloxy,

R_7 for unsubstituted or substituted alkyl,

X for a group of formula $-\text{CO}-$, $-\text{COO}-$ or $-\text{SO}_2-$

and n for 2, 3 or 4.

and where the molecule is free from sulphonic acid groups.

All the afore-named alkyl, alkylene and alkoxy groups contain preferably 1 to 4 carbon atoms. The preferred substituents on any alkyl or alkoxy group present (if substituted) include halogen atoms, notably chlorine and bromine atoms, hydroxyl and cyano groups.

Any phenyl radical present, including the phenyl nucleus of the benzoyl radical, may bear one or more substituents such as chlorine, bromine, cyano, nitro, acyl, alkyl and alkoxy.

Any acyl group present is of formula $\text{R}-\text{Y}-$ or $\text{R}'-\text{Z}-$,

where R stands for a hydrocarbon radical which may bear one or more substituents and/or may contain one or more hetero atoms, preferably for an alkyl or phenyl radical,

Y for a radical of formula $-\text{O}-\text{CO}-$ or $-\text{SO}_2-$,

R' for a hydrogen atom or R ,

Z for a radical of formula $-\text{CO}-$, $-\text{NR}''\text{CO}-$ or $-\text{NR}''\text{SO}_2-$

and R'' for a hydrogen atom or R .

Price 75p

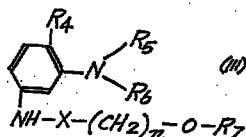
[Price 25p]

SPECIFICATION AMENDED - SEE ATTACHED SLIP

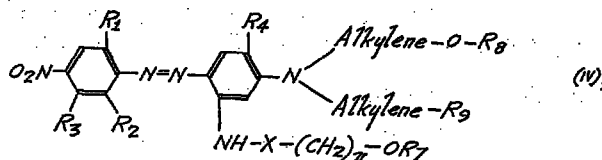
The compounds of formula (I) may be produced by diazotizing an amine of formula



and coupling the resulting diazonium compound with a compound of formula

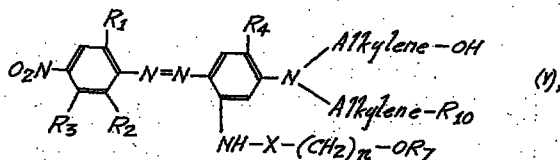


The compounds of the general formula (I) which have the specific formula



where R_8 represents optionally substituted alkylcarbonyl, alkoxy carbonyl, benzoyl or phenoxy carbonyl

and R_9 cyano, or optionally substituted alkoxy carbonyl, phenoxy carbonyl, alkylcarbonyloxy, alkoxy carbonyloxy, benzoyloxy or phenoxy carbonyloxy, can be produced by acylation of an azo compound of formula



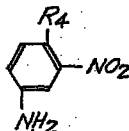
where R_{10} represents optionally substituted alkoxy carbonyl or phenoxy carbonyl, cyano or hydroxyl, with an acid of formula



or with a functional derivative of such an acid. Suitable functional derivatives are, for example, the anhydrides and acid halides, in particular the acid chlorides of these acids.

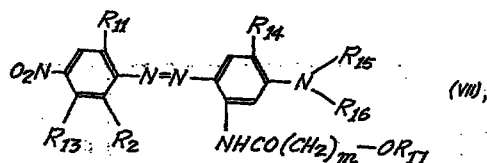
The diazotizing and coupling reactions can be carried out in accordance with the standard methods, which have been known for over a century.

The coupling components of formula (III) can be produced by the known methods, e.g. by reaction of an amine of formula



with an acid of formula $HOOC(CH_2)_n-O-R_7$ at temperatures in the range of about 150°C to 200°C with cleavage of water, followed by reduction of the nitro group and introduction of the radicals R_5 and R_6 either by condensation or addition.

Preferred compounds of formula (I) have the formula



where R_2 stands for hydrogen, chlorine or bromine,

R_{11} for chlorine, bromine, cyano, nitro, methylsulphonyl, phenylsulphonyl or toluylsulphonyl,

R_{13} for hydrogen, chlorine or bromine or for alkylcarbonylamino which has 1 or 2 carbon atoms in the alkyl radical and may bear one or more substituents selected from chlorine and bromine atoms, provided that at least one of R_2 and R_{13} stands for hydrogen,

R_{14} for hydrogen, methoxy or ethoxy,

R_{15} and R_{16} , independently of each other, for alkyl which has 1 to 4 carbon atoms and may bear one or more substituents selected from hydroxyl, cyano, methoxy, ethoxy, acetoxy, propionyloxy, butyryloxy, benzoyloxy, methoxycarbonyl, ethoxycarbonyl, methoxycarbonyloxy and ethoxycarbonyloxy,

R_{17} for methyl, ethyl or propyl

and m for 2 or 3.

The new compounds of formula (I) can be worked up as dyeing preparations by the known methods, for example by grinding in the presence of a dispersing agent and/or a filler. The ground mixtures may be vacuum or injection dried if dry preparations are desired. The preparations may be added to a suitable volume of water for exhaust dyeing, pad dyeing or printing at long or short liquor ratio.

From aqueous dispersion the dyes build up powerfully on synthetic and regenerated organic fibres, both in the loose form and as yarn or textiles. They are especially suitable for dyeing and printing polyester, cellulose acetate, cellulose triacetate and polyamide fibres and textiles, and can also be applied to polyolefin fibres. The known dyeing and printing methods may be used, for instance the process described in French Patent 1,445,311.

The dyeings obtained have good fastness in a comprehensive range of properties, the fastness to light and to thermofixation, sublimation and pleating being notably good. They are very fast to wet treatments such as washing, water, sea water, perspiration, solvents, especially conventional dry cleaning liquors, lubricants, and to rubbing, cross dyeings, ozone, gas fumes and chlorine. The dyeings are stable to pre-cure and post-cure permanent press finishing and to soil release finishes. They show good stability to reducing action in the dyeing of textiles containing wool and reserve wool and cotton. The dyeings are dischargeable.

In relation to the nearest comparable dyes disclosed in French Patents 1,382,654 and 1,382,655, the new dyes of this invention show higher fastness to sublimation. This invention therefore serves the purpose, inter alia, of supplying the textile industry with new, superior dyes for dyeing the synthetic fibre and regenerated fibre textiles which are being produced on an ever growing scale, and with which a prime consideration is to have dyes which are applicable by the rationalized continuous and high-temperature dyeing processes in use today.

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

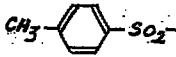
Example 1.

At a temperature not higher than 70° 7 parts of sodium nitrite are added to 155 parts of concentrated sulphuric acid, followed at 15° by 24.2 parts of 2-amino-3-bromo-5-nitrobenzonitrile. The solution is stirred for 2 hours at $15-20^\circ$ and the diazonium salt solution thus formed is combined with a solution of 2 parts of urea and 25 parts of 1-N,N-diethylamino-3-(3'-methoxypropionyl)-anilide in 100 parts of glacial acetic acid. After the addition of 500 parts of ice-water the reaction solution is stirred for a further 2 hours, on which the dye settles out. It is filtered, washed with water until free of acid, and dried.

Applied to polyester fibres or textiles, this dye gives brilliant blue shades of great depth which have very good fastness properties.

Further dyes of formula (I) which can be produced in analogy with the foregoing Example are specified in the table below.

TABLE

Ex. No.	R ₁	R ₂	R ₃	R ₄	R ₅
2	—CN	—Br	H	H	—C ₂ H ₅
3	Cl	H	H	H	—CH ₂ CH ₂ OCOCH ₃
4	—CN	H	H	H	do
5	—CN	H	H	H	—CH ₂ CH ₂ CN
6	—SO ₂ CH ₃	H	H	H	do
7	—NO ₂	Br	H	H	—C ₂ H ₅
8	do	do	H	—OC ₂ H ₅	—CH ₂ CH ₂ CN
9	do	do	H	do	—CH ₂ CH ₂ OCOC ₂ H ₅
10	do	do	H	do	do
11	do	Cl	H	do	—CH ₂ CH ₂ OCH ₃
12	do	H	Cl	H	—C ₂ H ₅
13	do	H	—NHCOCH ₃	H	do
14	do	H	—NHCOCH ₂ CH ₂ Cl	H	do
15	—CN	Br	H	H	—C ₂ H ₅
16	H ₅ C ₆ —SO ₂ —	Cl	H	—OC ₂ H ₅	—CH ₂ CH ₂ OCOCH ₃
17		do	H	do	do
18	do	Cl	H	do	do
19	do	Cl	H	do	do
20	do	do	H	do	do
21	—NO ₂	Br	H	—OCH ₃	—CH ₂ CH ₂ CN
22	do	Br	H	do	do
23	do	H	—NHCOCH ₂ CH ₂ Br	H	—C ₂ H ₅
24	do	Br	H	—OCH ₃	—CH ₂ CH ₂ COOCH ₃
25	do	Cl	H	—OC ₂ H ₅	—CH ₂ CH ₂ COOC ₂ H ₅
26	do	Br	H	do	—CH ₂ CH ₂ OC ₂ H ₅
27	do	Br	H	do	—CH ₂ CH ₂ CH ₃

1

R_6	R_7	n	X	Shade on polyester fibre
$-\text{C}_2\text{H}_5$	$-\text{CH}_3$	2	$-\text{CO}-$	reddish blue
$-\text{CH}_2\text{CH}_2\text{OCOCH}_3$	do	2	do	red
do	$-\text{C}_2\text{H}_5$	2	do	bluish red
do	do	2	do	do
do	$-\text{CH}_3$	2	do	red
$-\text{C}_2\text{H}_5$	do	2	do	violet
$-\text{CH}_2\text{CH}_2\text{OH}$	do	2	do	blue
$-\text{CH}_2\text{CH}_2\text{OCOC}_2\text{H}_5$	do	2	do	do
do	do	3	do	do
$-\text{CH}_2\text{CH}_2\text{CN}$	do	2	do	do
$-\text{C}_2\text{H}_5$	do	2	do	violet
do	do	2	do	reddish blue
do	do	2	do	do
$-\text{C}_2\text{H}_5$	$-\text{CH}(\text{CH}_3)_2$	2	$-\text{CO}-$	blue
$-\text{CH}_2\text{CH}_2\text{OCOCH}_3$	$-\text{CH}_3$	2	do	do
do	do	2	do	do
do	$-\text{CH}(\text{CH}_3)_2$	2	do	do
do	$-\text{C}_2\text{H}_5$	2	do	do
do	do	3	do	do
$-\text{C}_2\text{H}_5$	do	2	$-\text{COO}-$	do
do	do	2	$-\text{SO}_2-$	do
do	do	2	$-\text{CO}-$	reddish blue
$-\text{CH}_3$	do	2	do	do
$-\text{C}_2\text{H}_5$	do	2	do	do
$-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$	do	2	do	do
$-\text{CH}_2\text{CH}_2\text{CN}$	do	2	do	do

TABLE 1

Ex. No.	R ₁	R ₂	R ₃	R ₄	R ₅
28	—NO ₂	Br	H	—OC ₂ H ₅	—CH ₂ CH ₂ CH ₂ CH ₃
29	do	Br	H	do	—CH ₂ CH ₂ OCOOCH ₃
30	do	Br	H	do	—CH ₂ CH ₂ OCOOCC ₂ H ₅
31	do	Br	H	do	—CH ₂ CH ₂ OCOC ₆ H ₅
32	—CN	H	H	H	—C ₂ H ₅

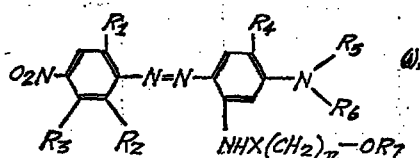
Application Example.

A mixture of 7 parts of the dye produced as in the foregoing Example 1, 4 parts of sodium dinaphthylmethane disulphonate, 4 parts of sodium cetyl sulphate and 5 parts of anhydrous sodium sulphate is ground in a ball mill for 48 hours to give a fine powder. One part of the powder is dispersed in a little water and the dispersion run through a sieve into a bath of 4000 parts of water containing 2 parts of sodium lauryl sulphate.

100 Parts of a scoured polyester fabric are entered into this dye bath (goods to liquor ratio 1:40) at 40—50°, after which 20 parts of an emulsion of a chlorinated benzene in water are added. The bath is raised slowly to 100° and the fabric dyed for 1—2 hours at 95—100°. On removal it is rinsed, soaped, rinsed and dried. A level blue dyeing of good depth is obtained which is outstandingly fast to light, washing, water, sea water, perspiration, sublimation, gas fumes, thermofixation, pleating, cross dyeing and permanent press finishing.

WHAT WE CLAIM IS:—

1. A monoazo compound of low solubility in water of the formula



where R₁ stands for chlorine, bromine, cyano, nitro, or unsubstituted or substituted alkylsulphonyl or phenylsulphonyl,

R₂ for hydrogen, chlorine or bromine,

R₃ for hydrogen, chlorine, bromine or acylamino, provided that at least one of R₂ and R₃ stands for hydrogen,

R₄ for hydrogen or unsubstituted or substituted alkyl or alkoxy,

R₅ and R₆, independently of each other, for alkyl which is unsubstituted or is substituted by one or more substituents selected from chlorine, bromine, cyano, hydroxyl, alkoxy, chloroalkoxy, bromoalkoxy, cyanoalkoxy, and unsubstituted and substituted alkylcarbonyloxy, benzoyloxy, alkoxycarbonyl, phenoxycarbonyl, alkoxycarbonyloxy and phenoxycarbonyloxy,

R₇ for unsubstituted or substituted alkyl,

X for a group of formula —CO—, —COO— or —SO₂—

and n for 2, 3 or 4,

and where the molecule is free from sulphonic acid groups.

TABLE 1

Ex. No.	R ₁	R ₂	R ₃	R ₄	R ₅
28	—NO ₂	Br	H	—OC ₂ H ₅	—CH ₂ CH ₂ CH ₂ CH ₃
29	do	Br	H	do	—CH ₂ CH ₂ OCOOCH ₃
30	do	Br	H	do	—CH ₂ CH ₂ OCOCOC ₂ H ₅
31	do	Br	H	do	—CH ₂ CH ₂ OCOC ₆ H ₅
32	—CN	H	H	H	—C ₂ H ₅

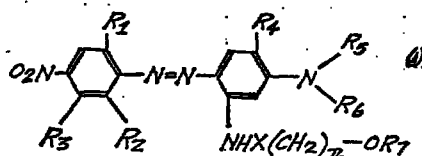
Application Example.

A mixture of 7 parts of the dye produced as in the foregoing Example 1, 4 parts of sodium dinaphthylmethane disulphonate, 4 parts of sodium cetyl sulphate and 5 parts of anhydrous sodium sulphate is ground in a ball mill for 48 hours to give a fine powder. One part of the powder is dispersed in a little water and the dispersion run through a sieve into a bath of 4000 parts of water containing 2 parts of sodium lauryl sulphate.

100 Parts of a scoured polyester fabric are entered into this dyebath (goods to liquor ratio 1:40) at 40—50°, after which 20 parts of an emulsion of a chlorinated benzene in water are added. The bath is raised slowly to 100° and the fabric dyed for 1—2 hours at 95—100°. On removal it is rinsed, soaped, rinsed and dried. A level blue dyeing of good depth is obtained which is outstandingly fast to light, washing, water, sea water, perspiration, sublimation, gas fumes, thermofixation, pleating, cross dyeing and permanent press finishing.

WHAT WE CLAIM IS:—

1. A monoazo compound of low solubility in water of the formula



where R₁ stands for chlorine, bromine, cyano, nitro, or unsubstituted or substituted alkylsulphonyl or phenylsulphonyl,

R₂ for hydrogen, chlorine or bromine,

R₃ for hydrogen, chlorine, bromine or acylamino, provided that at least one of R₂ and R₃ stands for hydrogen,

R₄ for hydrogen or unsubstituted or substituted alkyl or alkoxy,

R₅ and R₆, independently of each other, for alkyl which is unsubstituted or is substituted by one or more substituents selected from chlorine, bromine, cyano, hydroxyl, alkoxy, chloroalkoxy, bromoalkoxy, cyanoalkoxy, and unsubstituted and substituted alkylcarbonyloxy, benzoyloxy, alkoxy carbonyl, phenoxycarbonyl, alkoxy carbonyloxy and phenoxycarbonyloxy,

R₇ for unsubstituted or substituted alkyl,

X for a group of formula —CO—, —COO— or —SO₂—

and n for 2, 3 or 4,

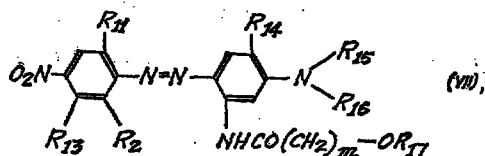
and where the molecule is free from sulphonic acid groups.



(continued)

R_6	R^7	n	X	Shade on polyester fibre
$-\text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5$	$-\text{C}_2\text{H}_5$	2	$-\text{CO}-$	reddish blue
$-\text{CH}_2\text{CH}_2\text{CN}$	do	2	do	do
$-\text{CH}_2\text{CH}_2\text{OCOOC}_2\text{H}_5$	do	2	do	do
$-\text{CH}_3$	do	2	do	do
$-\text{C}_2\text{H}_5$	$-\text{CH}_3$	2	do	red

2. A monoazo compound according to Claim 1 of the formula



where R_2 stands for hydrogen, chlorine or bromine,

R_{11} for chlorine, bromine, cyano, nitro, methylsulphonyl, phenylsulphonyl or toluylsulphonyl,

R_{13} for hydrogen, chlorine, bromine or for alkylcarbonylamino, which has 1 or 2 carbon atoms in the alkyl radical and may bear one or more substituents selected from chlorine and bromine atoms provided that at least one of R_2 and R_{13} stands for hydrogen,

R_{14} for hydrogen, methoxy or ethoxy,

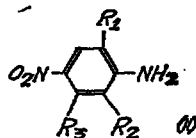
R_{15} and R_{16} , independently of each other, for alkyl which has 1 to 4 carbon atoms and may bear one or more substituents selected from hydroxyl, cyano, methoxy, ethoxy, acetoxy, propionyloxy, butyryloxy, benzoyloxy, methoxycarbonyl, ethoxycarbonyl, methoxycarbonyloxy or ethoxycarbonyloxy,

R_{17} for methyl, ethyl or propyl

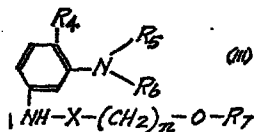
and m for 2 or 3.

3. The particular monoazo compounds of formula (I) according to Claim 1 herein described and exemplified.

4. A process for the production of a monoazo compound of formula (I) according to Claim 1, which comprises diazotizing an amine of formula



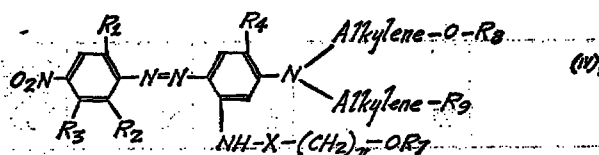
and coupling of the resulting diazonium compound with a compound of formula



where R_1 to R_7 , X and n have the meanings given in claim 1.



5. A process for the production of a monoazo compound of formula

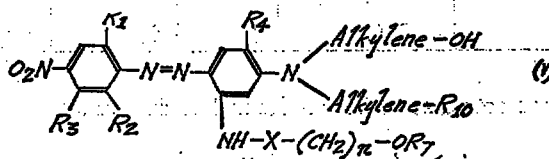


where $R_1, R_2, R_3, R_4, R_5, X$ and n have the meanings given in claim 1,

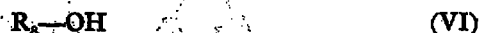
R_8 stands for optionally substituted alkylcarbonyl, alkoxy carbonyl, benzoyl or phenoxy carbonyl,

R_9 for cyano or optionally substituted alkoxy carbonyl, phenoxy carbonyl, alkylcarbonyloxy, alkoxy carbonyloxy, benzoyloxy or phenoxy carbonyloxy;

which comprises condensing an azo compound of formula



where R_{10} stands for optionally substituted alkoxy carbonyl or phenoxy carbonyl, cyano or hydroxyl, with an acid of formula



or with a functional derivative of such an acid.

6. A process for the production of a monoazo compound of formula (I) according to Claim 1 conducted substantially as herein described and exemplified.

7. Monoazo compound of formula (I) according to Claim 1 whenever prepared by a process according to any one of Claims 4 to 6.

8. A dyeing or printing process in which high molecular weight synthetic or regenerated organic fibres are dyed or printed with a monoazo compound according to any one of Claims 1 to 3 and 7.

9. High molecular weight synthetic or regenerated organic fibres dyed or printed by a process according to Claim 8.

MEWBURN ELLIS & CO.,
Chartered Patent Agents,
70/72 Chancery Lane,
London WC2A 1AD.
Agents for the Applicants.

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