

PATENT SPECIFICATION

(11) 1 330 784

NO DRAWINGS

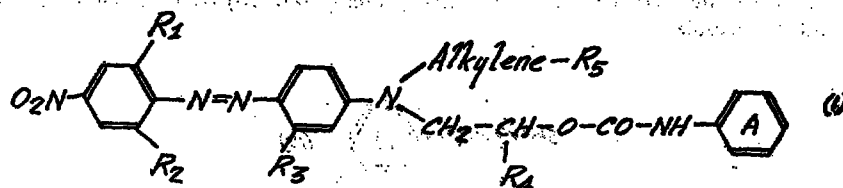
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 (72) Inventors DR. WOLFGANG GROEBKE and DR. ROSWITHA WIRZ



(54) AZO COMPOUNDS, THEIR PRODUCTION AND USE AS DISPERSE 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 the formula



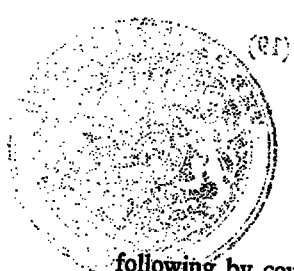
where R_1 and R_2 , independently of each other, stand for chlorine or bromine atoms, R_3 and R_4 , independently of each other, for hydrogen atoms or methyl groups, and R_5 for a hydrogen atom or a cyano group, and where the benzene nucleus A may bear one or more further substituents, with the exception of sulphonic acid groups.

Examples of suitable substituents on the nucleus A are halogen atoms, alkyl, alkoxy, acyl, acylamino, acyloxy, nitro and cyano groups. Chlorine and bromine atoms are the preferred halogen atoms. The alkyl and alkoxy groups may be further substituted; generally they contain 1, 2, 3 or 4 carbon atoms. The alkylene group in formula (I) contains preferably 1 to 4 carbon atoms.

Preferred compounds of formula (I) are those in which R_1 is a hydrogen atom, Alkylene represents an alkylene group containing 1 to 4 carbon atoms and in which the benzene nucleus A may be substituted by a methyl or methoxy group, particularly those in which the benzene nucleus A is unsubstituted.

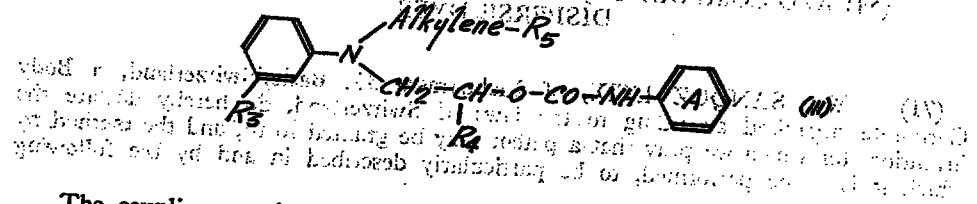
The acyl groups correspond to the formula $R-Y$ or $R'-Z$, where R stands for a hydrocarbon radical which may bear one or more of the aforementioned substituents and/or may be interrupted by one or more hetero atoms, preferably for an alkyl or phenyl radical which may bear one or more substituents, Y for a radical $-O-CO-$ or $-SO_2-$, R' for a hydrogen atom or R, Z for a radical $-CO-$, $-NR''CO-$ or $-NR''SO_2-$ and R'' for a hydrogen atom or R.

A preferred process for the production of the new compounds comprises diazotization of an amine of formula

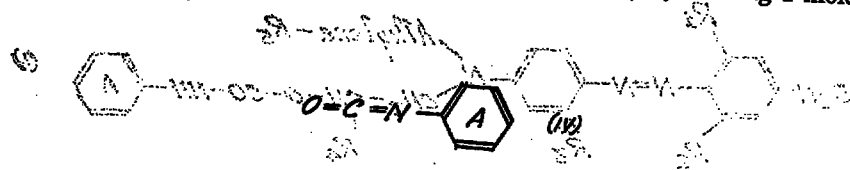


following by coupling of the diazonium compound thus produced with a compound of formula

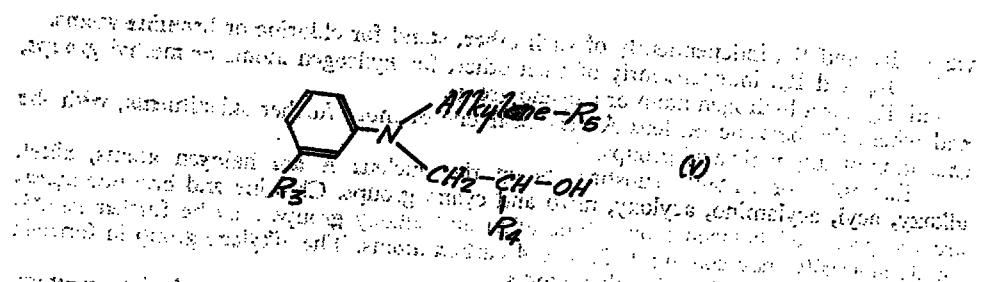
2A HSD UHA MOTOUCOYH NITR 20XKOUHLS UHA 02;



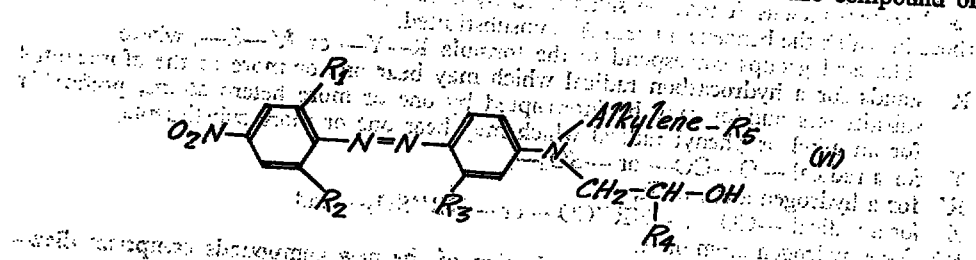
The coupling reaction is normally carried out in an acid, if necessary buffered medium, with cooling.
The compounds of formula (III) can be produced in the known manner (in analogy with the method described in British Patent 845,220) by reacting 1 mole of a



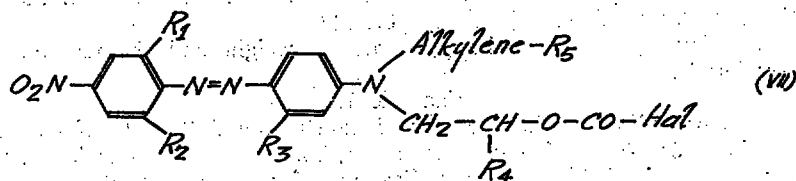
with 1 mole of a tertiary amine of formula



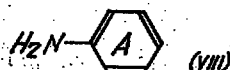
In analogy with this method the dyes of formula (I) can also be produced by the reacting 1 mole of a compound of formula (IV) with 1 mole of an azo compound of formula



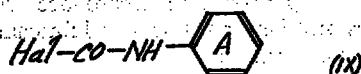
It is preferable to carry out these addition reactions in an inert, aprotic organic solvent such as benzene, toluene, xylene, nitrobenzene, chlorobenzene, acetone, dioxan or dimethyl formamide, at temperatures in the range of about 70°C to 180°C.
Alternatively, the dyes of formula (I) can be formed by the condensation of 1 mole of a compound of formula



where Hal represents a chlorine or bromine atom, with 1 mole of an amine of formula



or again by the condensation of 1 mole of a compound of formula (VI) with 1 mole of a compound of formula



where Hal represents a chlorine or bromine atom.

These condensation reactions are generally carried out in an inert solvent, e.g. one of those named above, at temperatures up to about 130°C and preferably in the presence of an acid-binding agent such as an alkali metal carbonate, bicarbonate or acetate, magnesium oxide, or pyridine.

Of the dyes of formula (I), preference is given to those in which the benzene nucleus A is not substituted or contains as substituent a methyl or methoxy group. Of these dyes, those in especial are preferred in which R₅ represents hydrogen and the alkylene radical contains 1, 2, 3 or 4, or more especially 2, carbon atoms.

The new compounds of formula (I) can be processed by the known methods to give commercial dyeing preparations, for example by grinding, in the presence of dispersing agents and/or fillers. The resulting pastes are dried in a vacuum or injection drier if powder preparations are desired. After being dispersed in a suitable volume of water, the new dyes can be applied by exhaust dyeing, pad dyeing or printing methods at a long or short liquor to good ratio.

From aqueous dispersion the dyes build up powerfully on textiles made of synthetic or semi-synthetic, high molecular-weight organic materials of hydrophobic character, giving dyeings and prints of the full depth. They are especially suitable for dyeing and printing polyester, cellulose acetate, cellulose triacetate and synthetic polyamide fibres in the various textile forms. They are also dyeable on polyolefins. The known dyeing and printing methods are employed, for instance the process described in British Patent 1,114,433.

The dyeings and prints show excellent colour fastness in a comprehensive range of properties; the fastness to light and to dry and wet heat (thermo-fixation, sublimation, steaming, pleating) being outstanding. They are very fast to wet treatments, including water, sea water, washing, perspiration, solvents, and in particular dry cleaning, and to lubricants, rubbing, cross dyeing, ozone, gas fumes and chlorine. They are stable to the pre-cure and post-cure permanent press finishing processes and to soil release finishes. Other good features are the dischargeability, the stability to reduction (in dyeing with wool), and the reserve of wool, cotton, viscose and silk. On direct exposure to light over a long period of time the originally bright dyeings fade tone-in-tone.

In the dyeing of polyester textiles at room temperature, for which carriers are used, the dyes of this invention are adsorbed in approximately equal amounts on set fibre and on fibre that has not been previously set. Goods which have been set under conditions producing variations in the degree of setting are therefore dyed to uniform depth. Applied to polyester textiles under high temperature conditions, the dyes are unaffected by variations in the bath pH between pH 5 and 9. The stability of the

dispersions in long dyeing times at high temperature is fully satisfactory. On polyester fibres the dyes of the present invention show better wash fastness than the nearest comparable dyes described in British Patent 824,443.

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

Example 1.

7.5 Parts of sodium nitrite are entered slowly into 200 parts of concentrated sulphuric acid at 65—70°. After cooling to 15°, 20.7 parts of 2,6-dichloro-4-nitro-1-aminobenzene are added. The amine is diazotized for 3 hours at 10—15°, then the dark solution is run with stirring into a mixture of 350 parts of ice and 160 parts of water. After excess sodium nitrite has been decomposed with 2 parts of aminosulphonic acid, the diazo solution is filtered clear from a small amount of residual matter. A solution of 28.4 parts of the phenylcarbamic acid ester of N-ethyl-N-(2'-hydroxyethyl)-aminobenzene in a mixture of 60 parts of glacial acetic acid and 36 parts of concentrated hydrochloric acid is allowed to flow into the clarified diazo solution at 0—3°. The coupling reaction is brought to an end by the addition of a solution of 130 parts of crystallized sodium acetate in 200 parts of water. The red-brown dye is filtered and dried. It dyes polyester fibres in brown shades which are very fast to thermofixation.

In relation to the next comparable dye which is disclosed in British Patent 824,443 the polyester dyeing of this dye is faster to light, washing and lubricants. In comparison with the nearest comparable dye described in the published Japanese patent application No. 3009/67, the above dye produced in accordance with this invention has higher affinity for polyester fibres and better fastness to lubricants on these fibres, along with better wash fastness on cellulose triacetate.

Example 2.

A diazonium salt solution is prepared from 2,6-dichloro-4-nitro-1-aminobenzene as described in the foregoing Example. 100 parts of urea are added, followed at 0—3° by a solution of 29.8 parts of the phenylcarbamic acid ester of 1-N-ethyl-N-(2'-hydroxyethyl)-3-methylaminobenzene in 100 parts of glacial acetic acid. After 2 hours the brown dye formed is filtered and dried. It gives brown-red dyeings on polyester fabrics which are fast to thermofixation. Compared with the nearest comparable dye of British Patent 824,443 it is faster to light, washing and lubricants on polyester fibres.

Example 3.

At 65—70° 7.5 parts of sodium nitrite are entered slowly into 200 parts of concentrated sulphuric acid. After cooling to 15° 29.6 parts of 2,6-dibromo-4-nitro-1-aminobenzene are added. The amine is diazotized for 3 hours at 10—15°, then the dark solution is added with stirring to a mixture of 350 parts of ice and 160 parts of water. The excess sodium nitrite is decomposed with 2 parts of aminosulphonic acid and the diazo solution filtered free from a small amount of residue. A solution of 16.5 parts of N-ethyl-N-(2'-hydroxyethyl)-aminobenzene in 40 parts of glacial acetic acid is allowed to flow into the clarified diazo solution at 0—3°. Coupling is completed by the addition of 130 parts of sodium acetate in 200 parts of water. The red-brown dye is filtered, washed and dried.

47.2 Parts of the dry dye are dissolved in 70 parts of anhydrous dioxan and 14.3 parts of phenyl iso-cyanate are slowly added to the solution. The mixture is reacted at the boil for 24 hours with reflux. On cooling to 50° it is diluted with 70 parts of methyl alcohol and allowed to run very slowly with good stirring into a mixture of 100 parts of water and 7 parts of concentrated hydrochloric acid. After 3 hours the dye, having settled out, is filtered, washed free of acid and dried. It dyes polyester fibres in brown shades showing high thermofixation fastness.

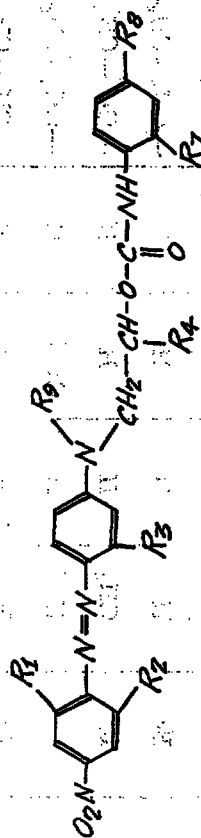
Example 4.

38.3 Parts of dry 2,6-dichloro-4-nitro-4'-[N-ethyl-N-(2''-hydroxy-ethyl)-amino]-1,1'-azobenzene (prepared by diazotization of 2,6-dichloro-4-nitro-1-aminobenzene and coupling with N-ethyl-N-(2'-hydroxyethyl)-aminobenzene) are dissolved in 120 parts of toluene. After the dropwise addition of 14.3 parts of phenyl iso-cyanate the mixture is reacted for 12 hours at the boil with reflux, after which the excess toluene is removed by evaporation in vacuum. As the concentrated solution cools the dye settles out in crystalline form. It is isolated by filtration and dried. The dye of this Example is identical with that of Example 1.

Example 5.

44.2 Parts of 2-chloro-6-bromo-4-nitro-4'-[N-ethyl-N-(2'-hydroxyethyl)-amino]-2'-methyl-1,1'-azobenzene (produced by diazotization of 2-chloro-6-bromo-4-nitro-1-aminobenzene and coupling with 1-N-ethyl-N-(2'-hydroxyethyl)-3-methylamino-benzene) are dissolved in 100 parts of dimethyl formamide. 14.3 Parts of phenyl isocyanate are added to the solution with stirring. After 3 hours at 100° the reaction is complete. The cooled reaction mixture is run into 200 parts of water to precipitate the dye, which is isolated by filtration, washed and dried. On polyester fibres it gives brown-red dyeings which are fast to thermofixation.

Table 1 below specifies further dyes conforming to the present invention which are of formula



The dyeings obtained on polyester fibres with these dyes range in shade from yellow-brown to brown-red.

TABLE 1

Expt. No.	R ₁	R ₂	R ₃	R ₄	R ₇	R ₈	R ₉
6	Cl	Cl	H	H	H	H	-CH ₂ -CH ₂ -CN
7	Cl	Cl	H	CH ₃	H	H	-CH ₂ -CH ₃
8	Cl	Cl	CH ₃	H	H	H	-CH ₂ -CH ₂ -CN
9	Cl	Cl	H	H	H	H	-CH ₃
10	Cl	Cl	H	H	H	H	-CH ₂ -CH ₂ -CH ₃
11	Cl	Cl	CH ₃	H	H	H	-CH ₂ -CH ₂ -CH ₂ -CH ₃
12	Cl	Cl	H	H	H	H	-CH ₂ -CH(CN)-CH ₃

TABLE I (Continued)

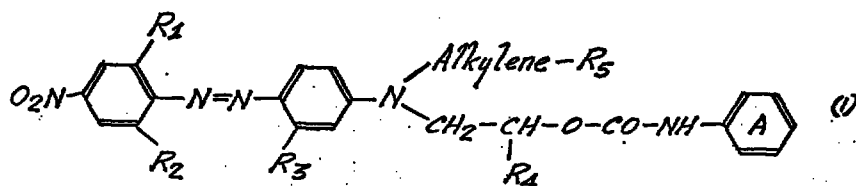
Expt. No.	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈	R ₉
13	Cl	Cl	CH ₃	H	H	H	H	OCH ₃	—CH ₃
14	Cl	Cl	CH ₃	H	H	CH ₃	CH ₃	H	—CH ₂ —CH ₃
15	Br	Br	H	CH ₃	H	H	H	H	—CH ₂ —CH ₃
16	Br	Br	H	H	H	H	H	H	—CH ₂ —CH ₂ —CH ₃
17	Br	Br	H	CH ₃	H	H	H	H	—CH ₂ —CH ₃
18	Br	Br	CH ₃	H	H	H	H	H	—CH ₃
19	Br	Br	H	H	H	H	H	CH ₃	—CH ₃
20	Br	Br	H	H	H	H	H	H	—CH ₂ —CH ₂ —CH ₂ —CH ₃
21	Br	Br	CH ₃	H	H	H	H	H	—CH ₂ —CH ₃
22	Br	Br	H	H	H	OCH ₃	OCH ₃	H	—CH ₂ —CH ₂ —CN
23	Cl	Br	H	H	H	H	H	H	—CH ₂ —CH ₂ —CH ₂ —CH ₃
24	Cl	Br	CH ₃	H	H	H	H	H	—CH ₂ —CH ₂ —CH ₃
25	Cl	Br	H	H	H	H	H	H	—CH ₂ —CH—CN CH ₃

Application Examples

- 5 A. A mixture of 4 parts of the dye produced as in Example 1, 6 parts of sodium ligninsulphonate and 100 parts of water is ground in a ball mill and the resulting paste dried in an injection drier. With 3 parts of the dry paste and 3000 parts of water at 40—50° a dyebath is prepared, into which 100 parts of a scoured polyester fabric are entered. The bath is raised slowly to 130° and the fabric dyed for about 1 hour at this temperature under static pressure. On removal it is rinsed, soaped, rinsed again and dried. A level red-brown dyeing of good depth is obtained which has excellent fastness to light, washing, water, sea water, perspiration, sublimation, thermofixation, pleating, cross dyeing, solvents, gas fumes and rubbing. The dyeing is stable to pre-cure and post-cure permanent press finishing and to soil release finishes.
- 10 B. A fine aqueous dispersion is prepared with 8 parts of the dye produced as in Example 1, 6 parts of sodium dinaphthylmethane-disulphonate, 6 parts of sodium ligninsulphonate and 3 parts of sodium alginate. The dispersion is made up to 1000 parts with water and well stirred to give a padding liquor. A polyester fabric is padded with the liquor at 25°, dried in dry air at 100—130° and exposed to dry heat at 230° for fixation of the dyeing. Subsequently the fabric is rinsed, soaped, rinsed again and dried. A red-brown dyeing is obtained with the good fastness properties enumerated in Application Example A.
- 15 C. A mixture of 25 parts of the dye produced according to Example 2, 55 parts of sodium ligninsulphonate and 800 parts of water is ground in a ball mill until the dye particles are smaller than 1 micron in size. The colloidal solution thus formed is mixed with 25 parts of 2-n-butoxy-ethanol and 400 parts of 10% sodium alginate solution to give a printing paste. This paste is very suitable for printing woven and knitted polyester fabrics on machines with two rollers. Without intermediate drying, the prints are steamed at 120° for fixation. Prints of red-brown shade with good fastness properties are obtained.

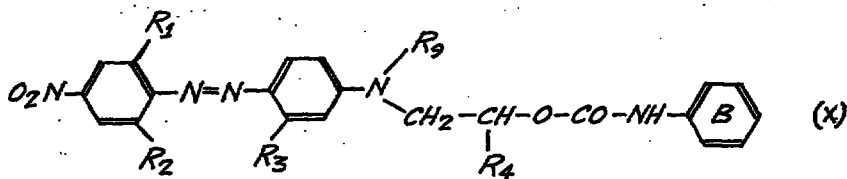
WHAT WE CLAIM IS:—

- 30 1. Azo compounds of low solubility in water which are of formula



where R_1 and R_2 , independently of each other, stand for chlorine or bromine atoms, R_3 and R_4 , independently of each other, for hydrogen atoms or methyl groups, and R_5 for a hydrogen atom or a cyano group, and where the benzene nucleus A may bear one or more further substituents with the exception of sulphonic acid groups.

- 35 2. Azo compounds according to Claim 1 and of formula



40 where R_1 and R_2 , independently of each other, stand for chlorine or bromine atoms, R_3 and R_4 , independently of each other, for hydrogen atoms or methyl groups, and R_5 for an alkyl radical having 1 to 4 carbon atoms which may bear a cyano group as substituent

and where the benzene nucleus B may bear a methyl or methoxy group.

- 45 3. Azo compounds according to claim 2, in which R_5 represents an unsubstituted alkyl group and the benzene nucleus B is also unsubstituted.

4. The particular azo compounds as herein described and as illustrated in any of Examples 1 to 25.

Application Examples

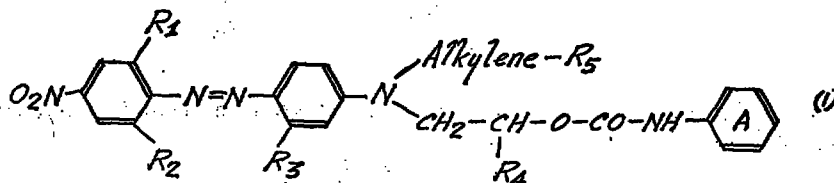
A. A mixture of 4 parts of the dye produced as in Example 1, 6 parts of sodium ligninsulphonate and 100 parts of water is ground in a ball mill and the resulting paste dried in an injection drier. With 3 parts of the dry paste and 3000 parts of water at 40—50° a dyebath is prepared, into which 100 parts of a scoured polyester fabric are entered. The bath is raised slowly to 130° and the fabric dyed for about 1 hour at this temperature under static pressure. On removal it is rinsed, soaped, rinsed again and dried. A level red-brown dyeing of good depth is obtained which has excellent fastness to light, washing, water, sea water, perspiration, sublimation, thermofixation, pleating, cross dyeing, solvents, gas fumes and rubbing. The dyeing is stable to pre-cure and post-cure permanent press finishing and to soil release finishes.

B. A fine aqueous dispersion is prepared with 8 parts of the dye produced as in Example 1, 6 parts of sodium dinaphthylmethane-disulphonate, 6 parts of sodium ligninsulphonate and 3 parts of sodium alginate. The dispersion is made up to 1000 parts with water and well stirred to give a padding liquor. A polyester fabric is padded with the liquor at 25°, dried in dry air at 100—130° and exposed to dry heat at 230° for fixation of the dyeing. Subsequently the fabric is rinsed, soaped, rinsed again and dried. A red-brown dyeing is obtained with the good fastness properties enumerated in Application Example A.

C. A mixture of 25 parts of the dye produced according to Example 2, 55 parts of sodium ligninsulphonate and 800 parts of water is ground in a ball mill until the dye particles are smaller than 1 micron in size. The colloidal solution thus formed is mixed with 25 parts of 2-n-butoxy-ethanol and 400 parts of 10% sodium alginate solution to give a printing paste. This paste is very suitable for printing woven and knitted polyester fabrics on machines with two rollers. Without intermediate drying, the prints are steamed at 120° for fixation. Prints of red-brown shade with good fastness properties are obtained.

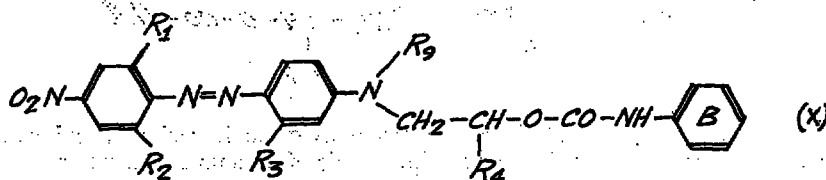
WHAT WE CLAIM IS:—

1. Azo compounds of low solubility in water which are of formula



where R_1 and R_2 , independently of each other, stand for chlorine or bromine atoms,
 R_3 and R_4 , independently of each other, for hydrogen atoms or methyl groups,
 and R_5 for a hydrogen atom or a cyano group,
 and where the benzene nucleus A may bear one or more further substituents with the exception of sulphonic acid groups.

2. Azo compounds according to Claim 1 and of formula



where R_1 and R_2 , independently of each other, stand for chlorine or bromine atoms,
 R_3 and R_4 , independently of each other, for hydrogen atoms or methyl groups,
 and R_9 for an alkyl radical having 1 to 4 carbon atoms which may bear a cyano group as substituent

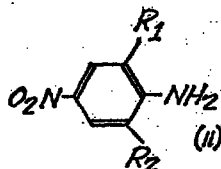
and where the benzene nucleus B may bear a methyl or methoxy group.

3. Azo compounds according to claim 2, in which R_9 represents an unsubstituted alkyl group and the benzene nucleus B is also unsubstituted.

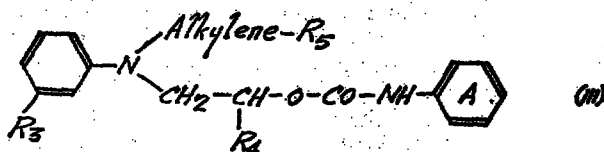
4. The particular azo compounds as herein described and as illustrated in any of Examples 1 to 25.



5. A process for the production of an azo compound of formula (I) according to claim 1, which comprises diazotization of an amine of formula

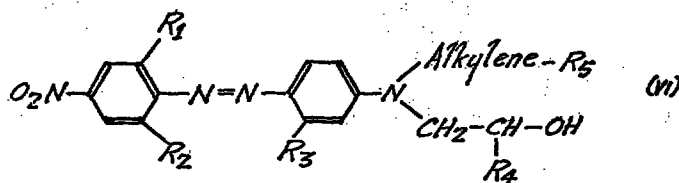


and coupling of the diazonium compound thus produced with a compound of formula

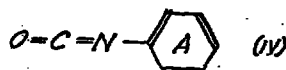


where R_1 , R_2 , R_3 , R_4 and R_5 have the meanings given in claim 1.

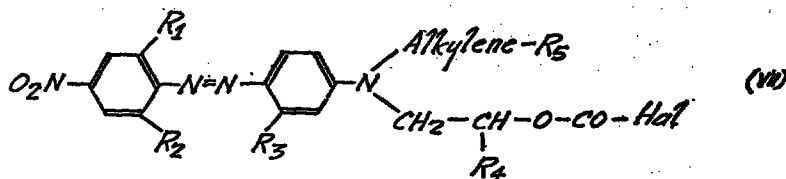
6. A process for the production of an azo compound of formula (I) according to claim 1, which comprises condensing 1 mole of a compound of formula



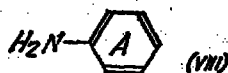
where R_1 , R_2 , R_3 , R_4 and R_5 have the meanings given in claim 1 with 1 mole of a compound of formula



7. A process for the production of an azo compound of formula (I) according to claim 1, which comprises condensing 1 mole of a compound of formula

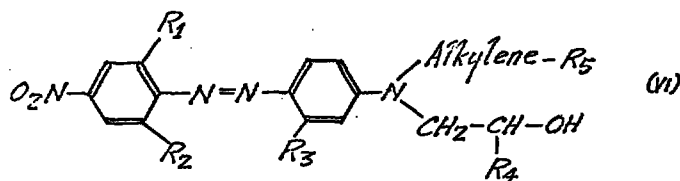


where R_1 , R_2 , R_3 , R_4 and R_5 have the meanings given in claim 1, and where Hal represents a chlorine or bromine atom, with 1 mole of an amine of formula

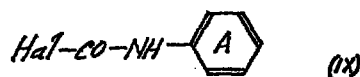


8. A process for the production of an azo compound of formula (I) according to claim 1, which comprises condensing 1 mole of a compound of formula





where R_1 , R_2 , R_3 , R_4 and R_5 have the meanings given in claim 1 with 1 mole of a compound of formula



- 5 9. A process for the production of an azo compound of formula (I) substantially as herein described and as illustrated in any of Examples 1 to 5. 5
- 10 10. Azo compounds of formula (I) whenever produced by a process according to any one of claims 5 to 9.
- 10 11. A dyeing or printing process in which fibres, yarns or textiles made thereof, which consist of or contains a synthetic or semi-synthetic high molecular weight organic material of hydrophobic character, are dyed or printed with a dye of formula (I) according to claim 1. 10
- 15 12. A dyeing or printing process using a dye of formula (I) according to claim 1 conducted substantially as herein described and as illustrated in any of Application Examples A to C. 15
- 15 13. Fibres, yarns and textiles which consist of or contain a synthetic or semi-synthetic high molecular weight organic material of hydrophobic character dyed or printed by a process according to claim 11 or claim 12.

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* C L M S *