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DISAZO DYES

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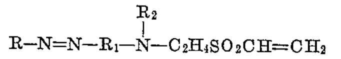
8 Claims. (Cl. 260—186)

This invention relates to new water insoluble disazo compounds useful as dyes for textile fibers, yarns and fabrics. In particular, the invention is directed to dyestuffs wherein the disazo component is preferably free of the vinylsulfonyl group.

The disazo compounds of the invention have the following general formula

(I)



$$R-N=N-R_1-\overset{R_2}{\overset{|}{N}}-C_2H_4SO_2CH=CH_2$$

wherein R represents an azobenzene group preferably free of the vinylsulfonyl group, wherein the aromatic groups of the azobenzene radical include phenyl and substituted phenyl such as alkylphenyl, e.g. o,m,p-tolyl; alkoxyphenyl, e.g. o,m,p-methoxyphenyl; halophenyl, e.g. o,m,p-chlorophenyl; nitrophenyl, e.g. o,m,p-nitrophenyl; alkylsulfonylphenyl, e.g. o,m,p-methylsulfonylphenyl; alkylsulfonamidophenyl, e.g. o,m,p-methylsulfonamidophenyl; di(alkylsulfonyl)phenyl, e.g. 2,5-di(methylsulfonyl)phenyl; dicarboxylicacidimidophenyl, e.g. o,m-succinimidophenyl; fluoroalkylphenyl, e.g. trifluoromethylphenyl; acylamidophenyl; e.g. o,m,p-acetamidophenyl; cyanophenyl, e.g. o,m,p-thiocyanophenyl; alkylthiophenyl, e.g. o,m,p-carboxamidophenyl; benzamidophenyl; thiocyanophenyl, e.g. o,m,p-thiocyanophenyl;; alkylthiophenyl, e.g. o,m,p-methylthiophenyl; benzoxyphenyl, e.g. o,m,p-benzoxyphenyl; benzaminophenyl, e.g. o,m,p-benzaminophenyl; benzylaminophenyl, e.g. o,m,p-benzylaminophenyl; N-alkylbenzaminophenyl, e.g. N-phenylmethylaminophenyl; formylphenyl, e.g. o,m,p-formylphenyl; carbalkoxyphenyl, e.g. o,m,p-carbethoxyphenyl; benzoylphenyl, e.g. o,m,p-benzoylphenyl;

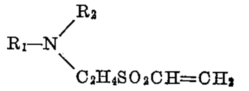
R_1 represents a monocyclic carbocyclic aromatic group of the benzene series including phenylene and substituted phenylene such as phenylene; alkylphenylene, e.g. o,m,-tolylene; alkoxyphenylene, e.g. o,m-methoxyphenylene, halophenylene, e.g. o,m-chlorophenylene; alkylsulfonylphenylene, e.g. o,m-methylsulfonylphenylene; alkylsulfonamidophenylene, e.g. o,m-methylsulfonamidophenylene; di(alkylsulfonyl)phenylene, e.g. 2,5-di(methylsulfonyl)-phenylene; dicarboxylicacidimidophenylene, e.g. o,m-succinimidophenylene; acylamidophenylene, e.g. o,m-acetamidophenylene; benzamidophenylene; thiocyanophenylene, e.g. o,m-thiocyanophenylene; alkylthiophenylene, e.g. o,m-methylthiophenylene; benzoxyphenylene, e.g. o,m-benzoxyphenylene; benzaminophenylene, e.g. o,m-benzaminophenylene; benzylaminophenylene, e.g. o,m-benzylaminophenylene; N-alkylbenzaminophenylene, e.g. o,m-N-phenylmethylaminophenylene; carbalkoxyphenylene, e.g. o,m-carbethoxyphenylene; benzoylphenylene, e.g. o,m-benzoylphenylene;

R_2 represents hydrogen or an alkyl radical including unsubstituted alkyl, preferably lower alkyl, i.e. from 1 to 4 carbon atoms, and substituted alkyl such as hydroxyalkyl, e.g. hydroxyethyl; polyhydroxyalkyl, e.g. glyceryl [—$CH(OH)CH(OH)CH_2OH$]; alkoxyalkyl, e.g. methoxyethyl; cyanoalkyl, e.g. cyanoethyl; cyanoalkoxyalkyl, e.g. β-cyanoethoxyethyl; acyloxyalkyl, e.g. acetoxyethyl; carbalkoxyalkyl, e.g. carbethoxyethyl; halogenoalkyl, e.g. chloroethyl; hydroxyhalogenoalkyl, e.g. β-hydroxy-γ-chloropropyl; alksulfonylalkyl, e.g. methylsulfonylethyl; alkyl-$OCOOCH_2CH_2$—, e.g. $CH_3OCOOCH_2CH_2$; carboxamidoalkyl, e.g. carboxamidoethyl, benzyl, phenoxyalkyl, e.g. β-phenoxyethyl; cyanoalkyl, e.g. β-cyanoethyl; alkylsulfonamidoalky, e.g. methylsulfonamidoethyl; alkylcarbonamidoalkyl, e.g. ethylcarbonamidoethyl; dicarboxamidoalkyl, e.g. β-dicarboxamidoethyl, etc. or R_2 represents a monocyclic carbocyclic aromatic radical of the benzene series, e.g. unsubstituted phenyl and substituted phenyl such as represented by R and R_1 above, e.g. alkylphenyl, alkoxyphenyl, etc. As can be seen from the examples given below, the substituents attached to the R, R_1 and R_2 groups serve primarily as auxochrome groups to control the color of the disazo compound.

The Heyna et al. U.S. Patent 2,784,204 granted Mar. 5, 1957 discloses monoazo compounds containing the vinylsulfone group, however such group, in all instances, is attached to the azo component of the dyestuff. Similarly, the Heyna et al. U.S. Patent 2,657,205 granted Oct. 27, 1953 claims azo compounds containing the vinylsulfone group, however such group is, in all instances, attached to the azo component of the dyestuff and, additionally, the azo component must contain a sulfonic acid group. As described above, the present disazo compounds contain a vinylsulfonylethyl group which is attached to the coupling component and the disazo component is preferably free of such group. This distinctive structure imparts unexpected properties to the present disazo compounds, especially when the disazo compounds are used for dyeing textiles, including improved fastness to light and improved affinity for polyester fibers. Thus, the disazo compounds in general can be expected to be superior to similar dyes containing the vinylsulfonyl or vinylsulfonylethyl group when tested by methods such as described in the A.A.T.C.C. Technical Manual, 1964 edition, depending in part upon the particular dye used and the fiber being dyed.

The disazo compounds of the invention are prepared by coupling well-known diazonium salts with the vinylsulfonylethyl-containing coupling components of the invention having the formula

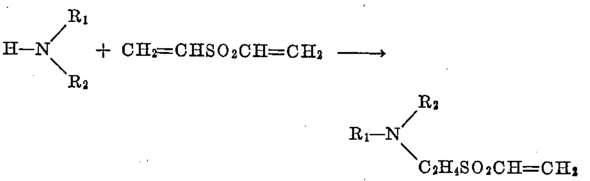
(II)



$$R_1-N\begin{array}{l}\diagup R_2\\ \diagdown C_2H_4SO_2CH=CH_2\end{array}$$

wherein R_1 and R_2 have the meaning given above.

The coupling components having the Formula II are prepared by the following method:



$$H-N\begin{array}{l}\diagup R_1\\ \diagdown R_2\end{array} + CH_2=CHSO_2CH=CH_2 \longrightarrow R_1-N\begin{array}{l}\diagup R_2\\ \diagdown C_2H_4SO_2CH=CH_2\end{array}$$

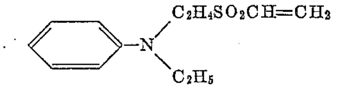
The disazo compounds can be used for dyeing textile materials including synthetic polymer fibers, yarns and fabrics giving a variety of fast shades including red, orange, yellow and violet when applied thereto by conventional dye methods. The disazo compounds have moderate to good affinity for cellulose ester and polyamide fibers. When the disazo compounds are used for dyeing such hydrophobic materials, they should be free of water-solublizing groups such as sulfo and carboxyl. In general, the dyes have good fastness, for example, to light, washing, gas (atmospheric fumes) and sublimation.

The following examples will serve to illustrate the preparation of representative intermediates and disazo compounds of our invention.

EXAMPLES OF VINYLSULFONYLETHYL-ANILINE COUPLERS

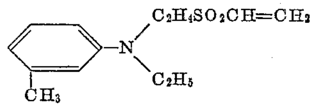
Preparation of N-ethyl-N-β-vinylsulfonyl-ethylaniline

23.6 g. divinylsulfone, 24.2 g. N-ethylaniline and 105 ml. toluene were refluxed for 24 hours. The toluene was removed under reduced pressure and the product distilled at 167–183° C./0.75 mm. had the structure:



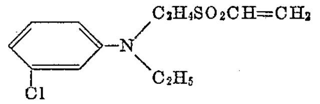
Preparation of N-ethyl-N-β-vinylsulfonylethyl-m-toluidine

27 g. of N-ethyl-m-toluidine, 23.6 g. divinylsulfone, 5 ml. acetic acid and 100 ml. toluene were mixed together and refluxed with stirring for 12 hours. The solvent was removed under reduced pressure and the product distilled under vacuum at 157–159° C./0.35 mm. The product has the structure:



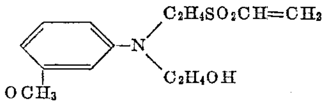
Preparation of N-ethyl-N-vinylsulfonylethyl-m-chloroaniline

In accordance with the method of preparation previously set forth, a solution of divinylsulfone, N-ethyl-m-chloroaniline and toluene was refluxed to prepare the product which has the structure:



Preparation of N-β-hydroxyethyl-N-β-vinyl-sulfonylethyl-m-anisidine

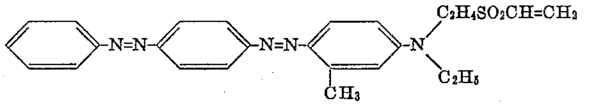
In accordance with the method of preparation previously set forth, a solution of divinylsulfone, N-β-hydroxyethyl-m-anisidine and toluene was refluxed to prepare the product which had the structure:



EXAMPLES OF THE DYES

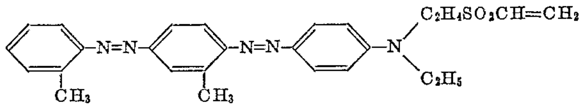
Example 1

To a solution of 1.44 g. sodium nitrite in 10 ml. conc. sulfuric acid was added 20 ml. acid (1 part propionic acid: 5 parts acetic acid). 3.94 g. p-phenylazoaniline was added to the solution followed by 20 ml. of 1:5 acid. This solution was stirred for two hours and then added to a solution of 5.06 g. N-ethyl-N-β-vinylsulfonylethyl-m-toluidine in 200 ml. 1:5 acid. The coupling solution was neutralized to brown on Congo Red paper with ammonium acetate and allowed to couple for two hours and was then washed, filtered and dried. The product dyes nylon, cellulose acetate, and polyester fibers bright orange shades of excellent fastness. The dye has the structure:



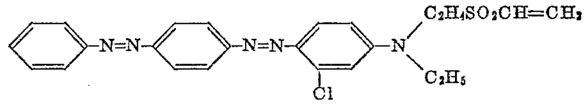
Example 2

To a solution of 0.72 g. sodium nitrite in 5 ml. conc. sulfuric acid was added 10 ml. 1:5 acid (1 part propionic acid: 5 parts acetic acid). 2.25 g. 4-amino-2′,3-dimethylazobenzene was added to the solution followed by 10 ml. 1:5 acid. The solution was stirred for two hours and then added to a solution of 2.39 g. N-ethyl-N-β-vinylsulfonylethylaniline in 75 ml. 1:5 acid. The coupling solution was neutralized to brown on Congo Red paper with ammonium acetate and allowed to couple for two hours and was then washed, filtered and dried. The product dyes nylon, cellulose acetate and polyester fibers bright shades of orange. The product has the structure:



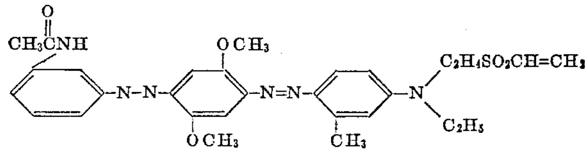
Example 3

The diazonium solution of Example 1 was added to a solution of 5.46 g. N-ethyl-N-vinylsulfonylethyl-m-chloroaniline in 150 ml. 1:5 acid. The coupling solution was neutralized to brown on Congo Red paper with ammonium acetate and allowed to couple for two hours. The coupling solution was then washed, filtered and dried. The product obtained dyes nylon, cellulose acetate and polyester fibers deep shades of orange. The dye has the structure:



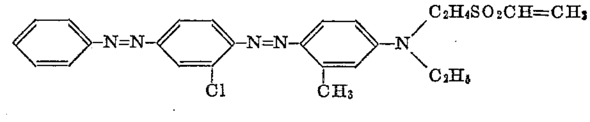
Example 4

3.14 g. 3′-acetamido-4-amino-2,5-dimethoxyazobenzene were diazotized using the same procedure and quantities of sodium nitrite, conc. sulfuric acid and 1:5 acid as in Example 2. The diazonium solution was added to a solution of 2.53 g. N-ethyl-N-β-vinylsulfonylethyl-m-toluidine in 100 ml. 1:5 acid. The solution was neutralized to brown on Congo Red paper with ammonium acetate and allowed to couple for two hours. The coupling solution was then washed, filtered and dried. The product obtained dyes nylon and polyester fibers deep shades of red. The dye has the structure:



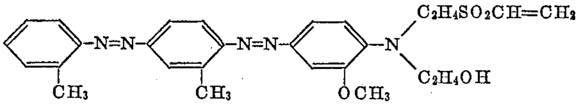
Example 5

4.62 g. 4-amino-3-chloroazobenzene were diazotized using the same procedure and quantities of reagents as described in Example 1. The resulting diazonium solution was added to a solution of 5.06 g. N-ethyl-N-β-vinylsulfonylethyl-m-toluidine in 200 ml. 1:5 acid. The solution was neutralized to brown on Congo Red paper with ammonium acetate and allowed to couple for two hours. The coupling solution was then washed, filtered and dried. The product dyes nylon a bright red shade with good fastness properties. The product has the structure:

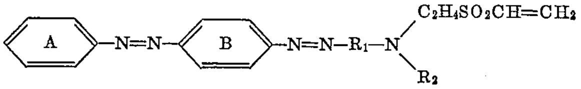


Example 6

2.25 g. 4-amino-2′,3-dimethylazobenzene were diazotized using the procedure described in Example 2 and the resulting solution was added to a solution of 2.86 g. N-β-hydroxyethyl-N-β-vinylsulfonylethyl-m-anisidine in 50 ml. 1:5 acid. The solution was neutralized to brown on Congo Red paper with ammonium acetate and allowed to couple for two hours. The coupling solution was washed, filtered and dried. The product dyes cellulose acetate and nylon red shades. The dye has the structure:



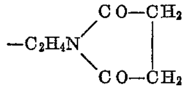
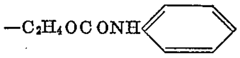
The disazo compounds of the following table are made by the method illustrated by Examples 1 through 6. Thus, the diazonium salts are coupled with the vinylsulfonylethylaniline couplers of Formula II to obtain dyes having the general structure:



wherein A and B are optionally substituted as described in the table.

have varying utility as dyes. The degree of utility varies, for example, depending upon the material being dyed and the formula of the disazo compound. Thus, for example, all the dyes will not have the same degree of utility for the same material. As mentioned above, the substituents on the R, R_1 and R_2 radicals serve primarily as auxochrome groups to control the color of the disazo compound.

Polymeric linear polyester materials of the terephthalate type are illustrative of the linear aromatic polyester textile materials that can be dyed with the new diazo compounds of our invention. The terephthalate fibers sold under the trademarks "Kodel," "Dacron," and "Terylene," for example, in the form of filaments, yarn and fabric, for example, are illustrative of the polyester textile materials that can be dyed. Kodel polyester fibers are more particularly described in U.S. Patent 2,901,446. Dacron and Terylene polyester fibers are described, for example, in U.S. Patent 2,465,319. The polymeric linear polyester materials disclosed in U.S. Patents 2,945,010, 2,957,745 and 2,989,363 for example, can be dyed. The linear aromatic polyester materials specifically named have a melting point of at least 200° C.

Example No.	Azobenzene Component		Vinylsulfonylethylaniline Coupler		
	Substituents on Ring A	Substituents on Ring B	Radical R_1	Radical R_2	Color Nylon Dyeing
7	2-CH_3	2-CH_3	m-tolylene	—C_2H_5	Orange.
8	3-acetamido	2,5-di-OCH_3	m-tolylene	—C_2H_5	Red.
9	3-hydroxymethyl	2,5-di-OCH_3	m-tolylene	—C_2H_5	Violet.
10	4-CH_3	2,5-di-OCH_3	m-tolylene	—CH_3	Do.
11	4-CH_3	2,5-di-CH_3	phenylene	—C_2H_4OH	Orange.
12	None	2-chloro	m-tolylene	—C_2H_5	Red.
13	4-CH_3	None	m-tolylene	—C_2H_4CN	Orange.
14	4-$NHCOCH_3$	None	m-tolylene	—C_2H_4CN	Do.
15	4-NO_2	2,5-di-OCH_3	m-tolylene	—C_2H_4CN	Violet.
16	4N-$(C_2H_4OH)_2$	None	m-tolylene	—C_2H_4CN	Red.
17	4-$COCH_3$	3-CH_3	m-Cl-phenylene	—C_2H_5	Red.
18	4-Cl	2-CH_3	phenylene	—CH_3	Yellow.
19	4-OCH_3	2,5-di-CH_3	m-tolylene	—C_2H_4Cl	Red.
20	4-CH_3	2,5-di-CH_3	m-OCH_3 phenylene	—C_2H_5	Reddish-orange.
21	None	None	m-tolylene	—$C_2H_4OCOCH_3$	Orange.
22	None	None	m-tolylene	—$C_2H_4OCH_3$	Do.
23	None	None	m-tolylene	—$C_2H_4SO_2CH_3$	Do.
24	None	None	m-tolylene		Do.
25	None	None	m-tolylene		Do.
6	None	None	o-tolylene	hydrogen	Yellow.

The disazo compounds of the invention may be used for dyeing hydrophobic fibers such as linear polyester, cellulose ester, acrylic, polyamide, etc., fibers in the manner described in U.S. Patents 2,880,050, 2,757,064, 2,782,187 and 2,043,827. The following examples illustrate methods by which the disazo compounds of the invention can be used to dye polyester textile materials.

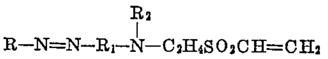
0.1 g. of the dye is dissolved in the dye pot by warming in 5 cc. of ethylene glycol monomethyl ether. A 2% sodium-N-methyl-N-oleyl taurate and 0.5% sodium lignin sulfonate aqueous solution is added, with stirring, until a fine emulsion is obtained. Water is then slowly added to a total volume of 200 cc. 3 cc. of Dacronyx (a chlorinated benzene emulsion) are added and 10 grams of a textile fabric made of Kodel polyester fibers are entered. The fabric is worked 10 minutes without heat and then for 10 minutes at 80° C. The dye bath is then brought to the boil and held at the boil for one hour. Following this, the fabric is rinsed in warm water, then scoured in aqueous 0.2% soap, 0.2% soda ash solution. After scouring, the fabric is rinsed with water and dried. Accordingly, since the disazo compounds of the invention are water-insoluble, they can be applied from aqueous dispersions in the manner of the so-called "dispersed dyes." However, coloration can be effected, for example, by incorporating the disazo compounds into the spinning dope and spinning the fiber as usual. The disazo compounds of our invention

Nylon, in fiber, yarn and fabric form, is representative of polyamides which can be dyed with the disazo compounds.

The invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended claims.

What we claim is:

1. A disazo compound of the general formula



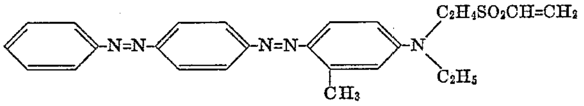
$$R{-}N{=}N{-}R_1{-}\overset{R_2}{\overset{|}{N}}{-}C_2H_4SO_2CH{=}CH_2$$

wherein

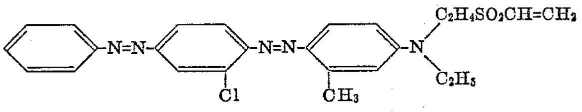
R=an azobenzene radical free of a vinylsulfonyl group,
R_1=a monocyclic aromatic radical, and
R_2=a member of the group consisting of hydrogen and a lower alkyl radical.

2. A disazo compound designated by claim 1 wherein R_2 represents a lower alkyl radical.

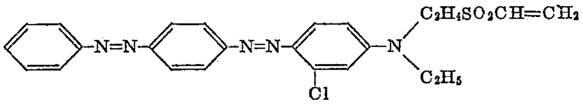
3. The compound



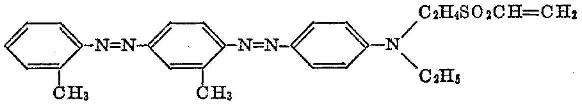
4. The compound



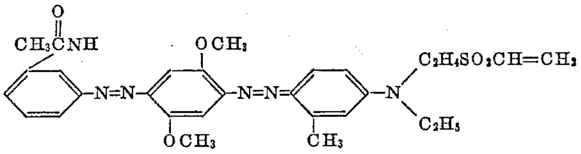
5. The compound



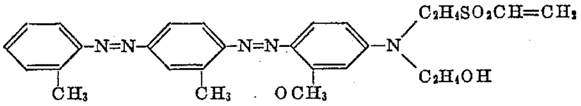
6. The compound



7. The compound



8. The compound



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779,781 7/1957 Great Britain.

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