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HYDRAZINE SULPHONATES OF THE
DIARYLAMINE SERIES

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Our present invention relates to hydrazine sulphonates of the diarylamine series, more particularly to those corresponding to the probable general formula.

5 $X-NH-R-NH-NH-SO_3$ -alkali-metal

wherein X means a naphthalene nucleus or a radical of the benzene series which may contain in the para-position to the NH-group a further
10 $-NH-NH-SO_3$ -alkali-metal group and R means a radical of the benzene series.

As substituents of the benzene radicals may be specifically named: alkyl, alkoxy, aryloxy, alkylmerkapto, aroylamino, halogen, nitro, arylsulphonyl, arylaminocarbonyl.

15 These compounds are produced by treating the corresponding diazo- or bis-diazo-diarylamine sulphonates with a suitable reducing agent or by reducing the corresponding diazo- or bis-diazo-diarylaminines in the manner described in Journal of the Society of Dyers and Colorists, 1921, page 7.

20 They are of a great value for the production of azo-dyestuffs. For this purpose they are advantageously first mixed with combining components containing a hydroxy or an O-alkali-metal group whereof the adjacent position is capable of attaching an aryl-azo-group. The compositions of matter thus produced are then brought onto the fibers in the presence of an
25 alkali and the goods thus treated are thereafter subjected to a steaming operation.

As combining components of the aforesaid kind may be named: 2-hydroxynaphthalene, its nuclear substitution products as, for instance, aroylamino-hydroxynaphthalenes, (2-hydroxy-naphthalene-3-carbonyl)-amino-aryls (as described in U. S. Patents No. 1,101,111 and No. 1,140,747), (6-halogen or 6-arylamino-2-hydroxy-naphthalene-3-carbonyl)-amino-aryls (see German Patent No. 396,519 and British Patent No. 330,349), derivatives of 1-hydroxy-naphthalene-4-carboxylic acid (see U. S. Patent No. 1,453,660), as, for instance, 1-hydroxy-naphthalene-4-phenyl-ketone, compounds containing an acidic methylene group capable of being combined with diazocompounds, as, for instance, pyrazolones and derivatives of β -ketonaldehyde, for instance, aceto-acetyl-amino-aryls and di-(aceto-acetyl-amino)-aryls (see U. S. Patents No. 1,594,864, No. 1,594,866, No. 1,594,867, No. 1,580,709, No. 1,634,090), dihydroxy-quinolines (see U. S. Patents No. 1,820,039, No. 1,846,073 and No. 1,846,074, British Patent No. 332,940), (2-hydroxy-carbazole-3-carbonyl)-amino-aryls, (2-hydroxy-ben-

zo-carbazole-3-carbonyl)-amino-aryls, (2-hydroxy-anthracene-3-carbonyl)-amino-aryls.

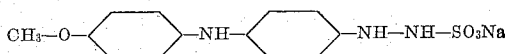
These dyeing preparations yield, when applied in an alkaline medium to fibers, by steaming only, insoluble azo-dyestuffs on the fibers.

Such applying to the fibers consists in dyeing according to the one-bath-method or in printing. The dyebath or the printing paste or also the powdery dyeing preparations themselves are advantageously mixed with dyeing assistants having wetting, emulsifying or solvent properties, or also with the additional agents customary in using nitrosamine-printing colors, as, for instance, chromate. Furthermore, sulphur is advantageously added to the printing paste. Thereby, in some cases, the quickness and the evenness of the dyestuff formation is favorably influenced.

In order to further illustrate our invention the following examples are given, the parts being by weight and all temperatures in centigrade degrees; but we wish it, however, to be understood that we are not limited to the particular conditions or specific products mentioned therein.

Example 1

32.9 parts of the sodium salt of 4'-methoxydiphenylamine-4-diazosulphonic acid (obtained according to U. S. Patent No. 1,897,410) are suspended in a solution of 14 parts of calcined sodium carbonate in 500 parts of water and reduced by introducing slowly at 60–65° 20 parts of sodiumhydrosulphite. The reduction is finished when the reaction mass is dissolved and decolorized. Then the mass is filtered warm and the sodium salt of the 4'-methoxy-diphenylamine-4-hydrazine-sulphonic acid precipitated from the filtrate by salting in form of colorless needles. It is worked up as usual. It corresponds to the probable formula:

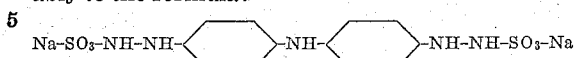


43.4 parts of a nearly colorless filtering cake of a content of pure substance of 59.9% are thus obtained.

Example 2

42.9 parts of the sodium salt of diphenylamine-4,4'-tetrazosulphonic acid are suspended in a mixture of 400 parts of water and 30 parts of glacial acetic acid; at 55–60° 50 parts of zinc dust are added whereby the reaction mass is dissolved with decolorization. The solution is rendered weakly alkaline by means of sodium carbonate, filtered warm and the sodium salt of the diphe-

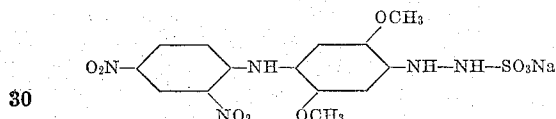
nylamine-4,4'-dihydrazine-sulphonic acid is precipitated from the filtrate by salting in form of fine feebly colored needles. It corresponds probably to the formula:



After working up as usual 104 parts of a feebly colored paste containing 21.5% of pure substance are obtained.

Example 3

To a diazosolution, prepared as usual from 16.7 parts of 4-amino-2,5-dimethoxy-2',4'-dinitrodiphenylamine, 25 parts of hydrochloric acid of 20° Bé., 300 parts of water and 4 parts of sodium nitrite, 15 parts of hydrochloric acid of 20° Bé. are added, and the mass is cooled down to 0° and mixed at 0 to +2° with a solution of 7 parts of sodium hydrosulphite in 20 parts of water. Thereby the color of the solution which is at first yellow turns to light red-brown, sulphurous acid is disengaged and the sodium salt of the 2,5-dimethoxy-2',4'-dinitrodiphenylamine-4-hydrazine-sulphonic acid partially precipitates. It corresponds to the probable formula



The precipitation is completed by salting and the sodium salt of the hydrazine sulphonic acid is worked up as usual. 22 parts of a light red-brown paste containing 50.2% of pure substance are thus obtained.

In an analogous manner the corresponding hydrazine-sulphonates are obtained by starting from other 4-amino-diarylamines of the above mentioned kind, as for instance:

4-amino-3'-chloro-diphenylamine, 4-amino-2'-methyl-diphenylamine, 4-amino-4'-methylmerkapto-diphenylamine, 4-amino-4'-benzoylamino-diphenylamine, 4-amino-3-(4'-methyl-benzene-sulphonyl)-diphenylamine, 4-amino-3'-(phenyl amino-carbonyl)-diphenylamine, 4-amino-4'-nitro-diphenylamine, 4-amino-2,5-dimethoxy-2'-nitro-4'-chloro-diphenylamine, 2-(4'-amino-phenyl-amino)-naphthalene.

All the dyestuffs described in the table of U. S. Patent No. 1,920,542, may also be prepared according to our present invention if the diazo-sulphonates mentioned in the said table are replaced by the corresponding hydrazine sulphonates claimed in the present application.

Since an object of the present invention is to prepare intermediates for the production of dyestuffs of good fastness properties which dyestuffs

are insoluble in water and alkalies, it is to be understood that the aromatic nuclei of the general formulæ appearing in the appended claims contain no substituents as are known to render organic compounds soluble in water or alkalies and to tend to depreciate the fastness of the dyestuff to alkalies. Substituents of this kind are the sulphonic acid, the carboxylic acid and the hydroxy group.

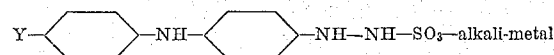
We claim:

1. The hydrazine-sulphonates of the diarylamine series corresponding to the probable general formula:

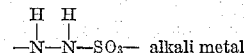


wherein X means a naphthalene nucleus or a radical of the benzene series which may contain in the para-position to the NH-group a further $\text{-NH-NH-SO}_3\text{-alkali-metal}$ group and R means a radical of the benzene series, which compounds represent when dry yellowish to brownish powders and are valuable intermediates for the production of azodyestuffs.

2. The hydrazine-sulphonates of the diarylamine series corresponding to the probable general formula:

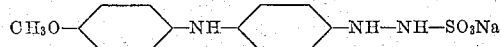


wherein the benzene nuclei may contain alkyl, alkoxy, aryloxy, halogen or nitro substituents and Y means hydrogen or one of the aforesaid substituents or a second



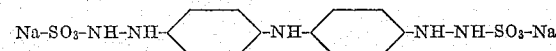
group, which compounds represent when dry yellowish to brownish powders and are valuable intermediates for the production of azo-dyestuffs.

3. The 4'-methoxy-diphenylamine-4-hydrazine-sulphonate of the probable formula



which compound represents nearly colorless crystals and is a valuable intermediate for the production of azo-dyestuffs.

4. The diphenylamine-4,4'-dihydrazine-sulphonate of the probable formula



which compound represents feebly colored needles and is a valuable intermediate for the production of azo-dyestuffs.

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