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Synthesis and Properties of Disazo Dyes Derived from 4-Amino-2′-nitrodiphenylamine

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ABSTRACT

*A series of black and navy-blue disazo acid dyes, derived from 4-amino-2′-nitrodiphenylamine and 1-*N*-phenylaminonaphthalene-8-sulphonic acid, were synthesized. The dyes were suitable for dyeing polyamide fibres and wool from a weakly acidic dyebath without electrolytes. Spectroscopic data for these dyes were estimated. Their application properties are characterized by a high tinctorial power and a very high degree of exhaustion from the dyebath. Copyright © 1996 Elsevier Science Ltd*

INTRODUCTION

Acid dyes are the main group of dyes used for dyeing wool, silk and polyamide fibres and they have also found use in leather dyeing.[1,2] The requirements for acid dyes vary, depending on their end-use, but they are now mostly expected to show a high degree of exhaustion from the dyebath at a low or a very low concentration of electrolytes and at a relatively high pH (5–6).

This investigation concerns some disazo dyes in which derivatives of 4-amino-2′-nitrodiphenylamine were used as first components, *p*-cresidine (**I**) or 1-aminonaphthalene-7-sulphonic acid (**II**) as middle component, and 1-*N*-phenylamino-naphthalene-8-sulphonic acid as the final component, i.e. as exemplified by the general formula 1.

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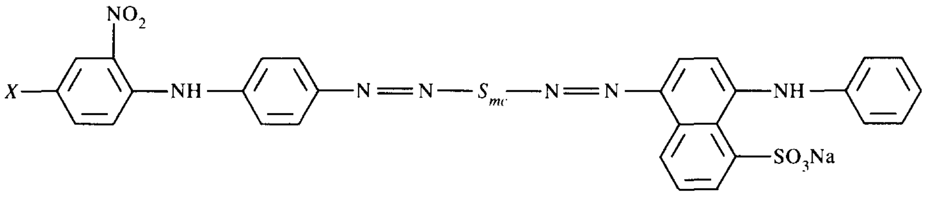
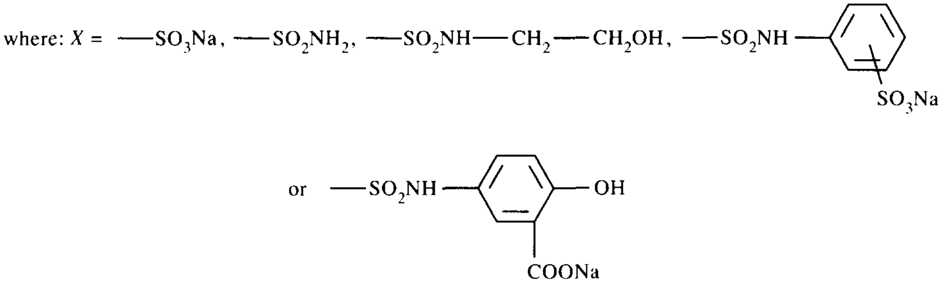


(1)



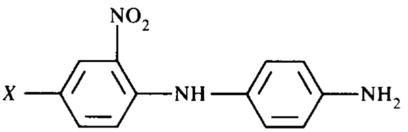
S_{mc} = p-cresidine or 1-aminonaphthalene-7-sulphonic acid

Taking into account the structural analogy between the dyes under investigation and dyes such as C.I. Acid Blue 116 or C.I. Acid Blue 113, and similar dyes in which as the S_{mc} component 1-naphthylamine, a strongly carcinogenic compound, is used,[3,4] it was expected that by using derivatives of 4-amino-2′-nitrodiphenylamine as diazo component (which have quite a high absorption in the range 420–450 nm) and 1-aminonaphthalene-7-sulphonic acid or *p*-cresidine as middle components, it would be possible to obtain acid dyes having black and navy blue hues and high tinctorial power. Additionally, by introducing sulphonamide groups in to the dye molecule, it was anticipated that the resultant dyes would dye polyamide fibres and wool from a weakly acidic bath, providing dyeings of relatively high fastness to wet treatments.[5]

EXPERIMENTAL

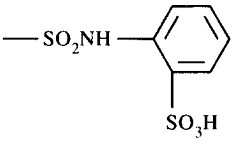
Synthesis of 4-aminodiphenylamine derivatives

The following derivatives of 4-amino-2-nitrophenylamine, as shown by the general formula 2, were used for the synthesis of dyes (**1**):

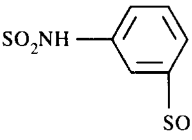


(2)

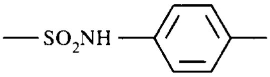
where: X = —SO_3H (A-1), —SO_2NH_2 (A-2), —$SO_2NHCH_2CH_2OH$ (A-3),



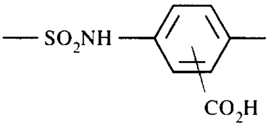
(A-4),



(A-5),

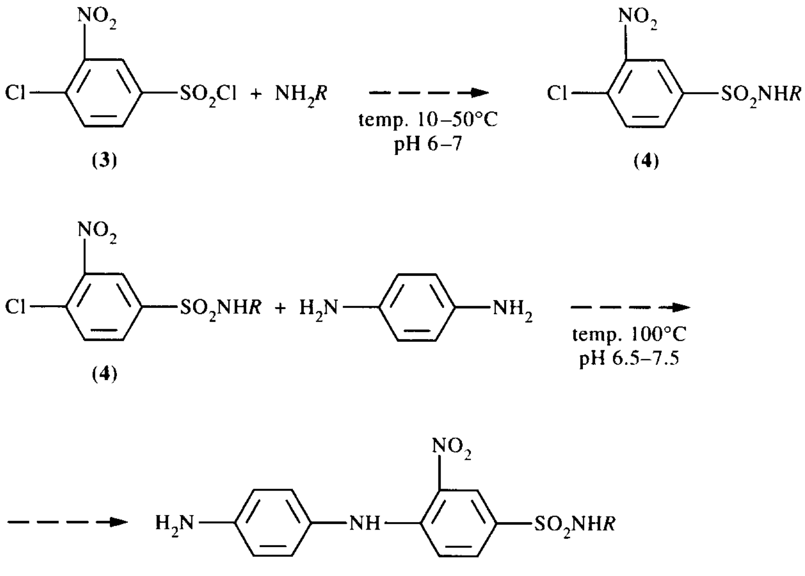


(A-6),



(A-7).

Amines (**2**) were prepared according to the following general reaction scheme:



(3) **(4)** **(4)** **(2)**

where: R is H or a residue of 2-, 3- or 4- p–anilinesulphonic acid, ethanoloamine or 3–aminosalicylic acid

The condensations between 1-chloro-2-nitrobenzene-4-sulphonyl-chloride and the anilinesulphonic acids or 3-aminosalicylic acid were carried out in aqueous solution at 30–50°C; when ethanolamine or ammonia were used, the condensation was carried out at 10–30°C and pH 6–7. The reaction was maintained at pH 8–8.5 only during the condensation between the sulphonylchloride (**3**) and ammonia.

Crude products (**4**) were crystallized from 80% aq. ethanol. The resulting derivatives were then condensed with 1,4-phenylenediamine (10% excess) in aqueous solution in the presence of sodium acetate at 100–102°C, except for the ethanolamine derivative, which was condensed with 1,4-diphenyleneamine in 80% aq. DMF at 80°C. The products obtained were separated from the reaction solution by salting out at pH 2–3.

Crude amines (**2**) were crystallized from 50% or 80% aq. ethanol. The properties of the prepared amines are listed in Table 1.

Synthesis of disazo dyes

Dyes (**1**) were synthesized according to methods reported in Ref. (6).

The diazotization of the derivatives of 4-aminodiphenylamine (**2**), was carried out by the 'inverse' procedure at 5–8°C, using 4.5 moles of hydrochloric acid and a diazotization time of 2–3 h. To the resulting diazonium compound, after removal of excess nitrous acid, a solution of *p*-cresidine hydrochloride or 1-aminonaphthalene-7-sulphonic acid at pH 4.5–5 was added dropwise. The initial pH of 2 was increased to pH 5 by dropwise addition of a solution of sodium acetate. The obtained monoazo dyes were separated, and after dissolving them in water, they were diazotized by the 'inverse' procedure at 8–10°C. After diazotization, a solution of 1-*N*-phenylaminonaphthalene-8-sulphonic acid was added at pH 5. After stirring for 2 h a solution of sodium acetate was added dropwise. Once the coupling process and neutralization to pH 8–8.5 were completed, the resultant dyes were separated by salting out with sodium chloride at 70°C. When impurities were found (chromatographic test), the dyes were recrystallized from water by salting out with sodium chloride.

Dye properties

The disazo dyes were spectroscopically evaluated using solutions in 50% aq. acetone; these solutions satisfied the Lambert–Beer's law within the range of the concentrations used viz. $1 \times 10^{-6} \div 2 \times 10^{-4}$ mol/dm^3. Measurements were carried on an M-40 spectrophotometer (Carl Zeiss, Jena).

The results are listed in Table 2 and are shown in Figs 1 and 2. The results of the measurements are given in relation to 100% dyes.

TABLE 1

Characterization Data for the Derivatives of 4-Amino-2′-nitrodiphenylamine

Amine	*Melting point (°C)*	*Elemental analysis (%)*				*Specific IR absorption (cm^{-1})*						*Electronic spectral data (50% aq. acetone)*	
		N		*S*		*NH_2*	*NH*	*CNO_2*	*$NHSO_2$*	*SO_3Na*	*CO_2H*	λ_{max} *nm*	ϵ_{max} *dm^3/mol cm*
		Calc.	*Found*	*Calc.*	*Found*								
A-1	320[a]	13.6	13.6	10.4	10.3	1600, 1240	1565, 1280	1495, 1340		1170, 1030		444.0	6800
A-2	247–250	18.2	18.3	10.4	10.4	1600, 1240	1560, 1275	1495, 1340	1310, 1165			430.0	6600
A-3	202–204	15.9	15.9	9.1	9.0	1590, 1240	1555, 1270	1490, 1340	1300, 1140			430.0	6600
A-4	270[a]	12.1	12.2	13.8	13.8	1595, 1230	1550, 1265	1490, 1330	1320, 1160	1180, 1020		428.1	6800
A-5	310[a]	12.1	12.2	13.8	13.8	1590, 1230	1550, 1265	1490, 1340	1320, 1160	1200, 1030		428.8	6800
A-6	320[a]	12.1	12.1	13.8	13.9	1595, 1230	1550, 1265	1495, 1340	1320, 1160	1170, 1030		428.8	6800
A-7	207–210	12.6	12.5	7.2	7.1	1595, 1230	1550, 1270	1490, 1340	1320, 1160		1580	430.3	6800

[a] Decompose.

TABLE 2
Structure, Paper Chromatography R_F, Spectrophotometric and Application Properties of the Dyes

Dye no.	*Structure of dye*		*Paper chromatography* $R_F{}^a$	*Spectrophotometry*				*Application dyebath exhaustion pH 5.0 (%)*
				Water		*50% aq Acetone*		
	Amine	*Middle coupling component*		λ_{max} *nm*	ϵ_{max} *dm*^{3}/*mol cm*	λ_{max} *nm*	ϵ_{max} *dm*^{3}/*mol cm*	
D-1	A-1	I	0.80	454.0	22 000	449.6	17 200	96.4
				574.7	34 400	578.7	41 600	
D-2	A-4	I	0.80	443.0	18 000	432.0	18 000	99.8
				573.4	29 800	576.0	35 400	
D-3	A-5	I	0.80	454.5	20 000	434.2	21 000	99.2
				570.0	24 000	579.3	40 600	
D-4	A-6	I	0.80	447.0	18 000	433.2	19 800	99.5
				573.4	23 000	578.0	38 000	
D-5	A-1	II	0.72	496.0	17 200	459.6	18 400	90.8
				582.8	23 250	601.0	37 200	
D-6	A-2	II	0.76	490.2	22 000	457.8	18 200	97.1
						591.0	28 600	
D-7	A-3	II	0.77	480.8	21 300	442.2	18 600	98.4
				591.0	26 200	608.2	36 400	
D-8	A-4	II	0.74	461.3	19 400	432.50	18 000	95.4
				591.0	20 800	603.9	29 800	
D-9	A-5	II	0.74	462.0	19 600	433.3	18 800	94.8
				592.2	21 400	603.9	30 900	
D-10	A-6	II	0.74	458.0	21 000	433.0	18 200	95.6
				585.2	22 500	603.6	31 600	
D-11	A-7	II	0.73	470.8	17 800	442.0	18 000	98.7
				555.6	21 000	603.6	27 400	

[a] R_F Whatman 3 paper, using pyridine: *n*-butanol:water 3:3:2 (by vol.) as eluent.

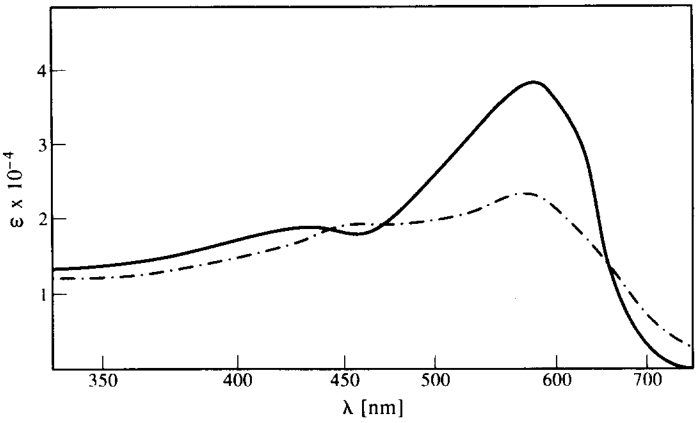


Fig. 1. Absorption spectra of dye D-4 in acetone:water, 50:50 by vol. (———) and water (-·-·-).

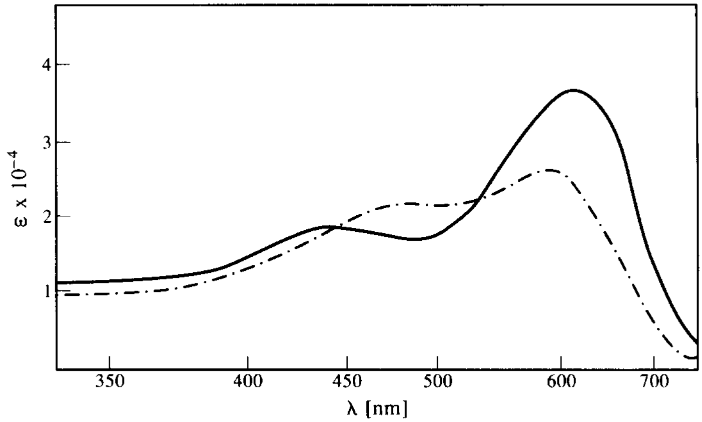


Fig. 2. Absorption spectra of dye D-7 in acetone:water, 50:50 by vol. (———) and water (-·-·-).

The dye performance properties were determined on the basis of dyeings on polyamide 6 fibres. The degree of dyebath exhaustion was determined at a liquor ratio of 1:40 and pH 5, using 3% of a 100% dye.

Light-fastness was determined using a Xenotest (Heraus-Hanau), using samples of polyamide fabrics dyed to a strength 1/3 and 1/1 of the standard sample. The fastnesses of the dyeings to water, acidic and alkaline perspiration, washing at 40°C, dry and wet rubbing were determined in accord with defined standards.[7] The results are listed in Table 3 and shown in Fig. 3.

TABLE 3
End-use Fastness of the Dyes

Dye no.	*Water*			*Washing*			*Acid perspiration*			*Alkaline perspiration*			*Rubbing*		*Light fastness*	
	1	*2*	*3*	*1*	*2*	*3*	*1*	*2*	*3*	*1*	*2*	*3*	*Dry*	*wet*	*1/3*	*1/1*
D-1	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4–5	5–6
D-2	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4–5	5–6
D-3	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4–5	5–6
D-4	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4–5	5–6
D-5	5	4	4–5	5	5	5	5	4	4–5	5	4	5	5	5	5–6	6–7
D-6	5	4–5	5	5	5	5	5	4–5	5	5	4–5	5	5	4–5	5–6	6–7
D-7	5	4–5	5	5	5	5	5	4–5	5	5	4–5	5	5	5	5–6	6–7
D-8	5	4–5	5	5	5	5	5	4–5	5	5	4–5	5	5	5	5–6	6–7
D-9	5	4–5	5	5	5	5	5	4–5	5	5	4–5	5	5	5	5–6	6–7
D-10	5	4–5	5	5	5	5	5	4–5	5	5	4–5	5	5	5	5–6	6–7
D-11	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5–6	6–7

1: change of shade of dyed fabric; 2: staining nylon; 3: staining wool.

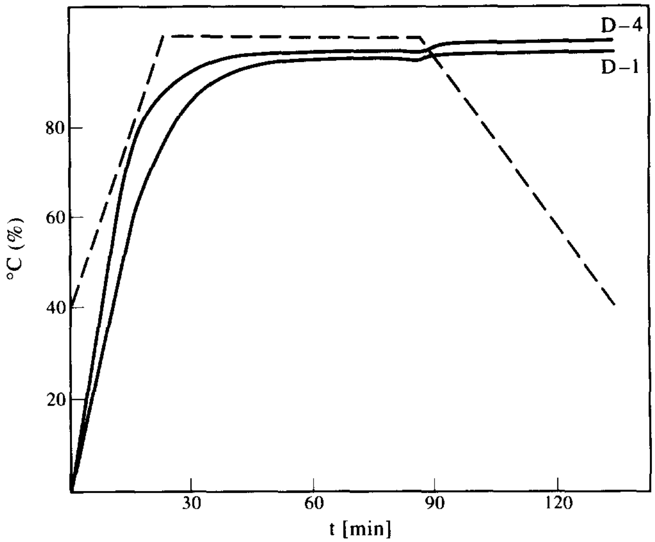


Fig. 3. Absorption curves of dyes D-1 and D-4 (———); dyeing temperature (– –).

Typical example of the syntheses

Synthesis of 1-chloro-2-nitrobenzene-4-sulphonanilido-3′-sulphonic acid

To a solution of 87 g (0.5 mole) of metanilic acid (sodium salt) in 500 cm^3 of water at pH 6.5–7 and 30–35°C, 128 g of 2-nitrochlorobenzene-4-sulphonylchloride was added over 2 h with vigorous stirring. The reaction was maintained at pH 6.5–7 by dropwise addition of 15% aq. NaOH. The end-point of the process was estimated by diazotization of samples of the reaction mixture; the reaction duration was about 4 h. The system was then heated to 50°C, stirred for 1 h at pH 7, and 50 g of sodium chloride was then added and the mixture slowly cooled to room temperature. The precipitated product was filtered and washed with 200 cm^3 of 10% brine. The press cake was dried at 60°C; yield 197 g.

The syntheses of the other derivatives were carried out under the same conditions.

Synthesis of 1-amino-2′-nitrodiphenylamino-4′-sulphonanilido-3-sulphonic acid

To a solution of 124.6 g (0.3 mole) of the sodium salt of the acid (**4**) and 24 g of sodium acetate in 500 cm^3 of water at 50°C, 35.7 g (0.33 mole) of 1,4-phenylenediamine were added. The reaction mixture was heated to 100°C and stirred for 4 h. After 2 h stirring the product began to precipitate. The process was complete when a chromatographic test confirmed the absence of **4**. After cooling to 70°C, 50 g of sodium chloride was added. The precipitated product was filtered off at room temperature, dispersed in 400 cm^3 of water, heated to 70°C and 30 cm^3 of hydrochloric acid was added to give an acid reaction to Congo Red. After stirring for 30 min, the product was filtered, washed with water at 50°C, and then dried at 60°C; yield 138 g of a dark-green product containing 97% of pure amine (A-5). Other amines were prepared in the same way, except for amine (A-3) which was prepared in 80% aq. DMF.

Synthesis of dye D-3

9.3 g (0.02 mole) of 1-amino-2'-nitrodiphenylamine-4'-sulphonanilido-3-sulphonic acid (A-5) was dissolved in 100 cm^3 of water and 2.5 cm^3 of 30% NaOH solution (alkaline reaction against Brilliant Yellow) and 1.38 g (0.02 mole) of sodium nitrite were added. The resulting solution was added dropwise at 20–25°C to 9 cm^3 of 30% HCl in 25 cm^3 of water and 40 g of ice with vigorous stirring. The diazotization process was carried out at 5–8°C for 2–3 h, maintaining a slight excess of nitrous acid. Once the diazotization process was completed, excess nitrous acid was removed using 10% aq. sulphamic acid. To the obtained diazonium compound, 5.1 g (0.02 mole) of the sodium salt of 1-aminonaphthalene-7-sulphonic acid dissolved in 100 cm^3 of water at pH 5 was added dropwise. Whilst maintaining a temperature of 6–8°C, 20% aq. sodium acetate was added dropwise over 2 h to ensure pH 4.5–5. The duration of the coupling process was 5–6 h. The liquor was then heated to 60°C, 27 g of sodium chloride added, and after cooling to room temperature, the product was filtered. The press cake was dissolved in 200 cm^3 of water, 2.5 cm^3 of 30% aq. NaOH added (to give an alkaline reaction with Brilliant Yellow), followed by 1.38 g of sodium nitrite in 5 cm^3 of water. The resultant solution was then added dropwise at 10°C over 0.5 h to 7 cm^3 of 30% HCl in 25 cm^3 of water and 30 of ice, keeping the reaction temperature at 8–10°C; the diazotization duration was 3–4 h. Excess nitrous acid was removed with 10% aq. sulphamic acid.

To the resulting suspension of the diazonium compound, 6.3 g (0.02 mole) of 95% 1-*N*-phenylaminonaphthalene-8-sulphonic acid dissolved in 100 cm^3 of water at pH 6 was added dropwise. After stirring the mixture for 2 h at 8–10°C, sodium acetate solution was added over 1 h to give pH 4.5–5; the coupling process proceeded over 5–6 h. The reaction mixture was then heated to 70°C, 30% aq. NaOH was added to give pH 8.5–9 and the dye was precipitated by addition of 30 g sodium chloride. After cooling to 25°C, the dye was filtered off and washed with 150 cm^3 of 10% brine. After drying at 70°C, 23.7 g of dye containing 15.4% of sodium chloride was obtained.

RESULTS AND DISCUSSION

Dyeing and fastness properties

Investigations of the synthesis of dyes (**1**) confirmed that the process proceeded satisfactorily both in the diazotization and coupling reactions, resulting in the formation of dyes with quite a high degree of purity, an important factor from a technological point of view.

The performance properties of the dyes showed that their dyeings were characterized by high or very high fastness.

Dyes in which *p*-cresidine was used as middle component showed wet fastness and rubbing of a maximum rating of 5. The light fastness of dyeings on polyamide 6 (Xenotest) was 4–5 for the dyeings corresponding to 1/3 of the standard sample, and 5–6 for 1/1 strength of standard sample. Dyes in which 1-aminonaphthalene-7-sulphonic acid was used as middle component also showed high or very high wet fastnesses. Their fastness to wet treatments and to acidic and alkaline perspiration were within the range 4–5, showing slight stains on concomitant polyamide fibres. On the other hand, these dyes showed, for azo dyes, a very high light fastness, viz. 5–6 for dyeings on polyamide fibres at a strength 1/3 of standard sample; dyes of this group can therefore be considered very good. Only dye D-5, containing no sulphonamide group, showed fastnesses to water, acidic and alkaline perspirations and wet rubbing at a level of 4 or 4–5. On the other hand, dye D-11, containing a residue of salicylic acid, had very high fastnesses to wet treatments and rubbing, similar to the dyes derived from *p*-cresidine, and a light fastness which was higher than that of the latter dyes.

The dyes were also characterized by advantageous properties from the point of view of their application, including a very high degree of dyebath exhaustion, e.g. from 94.8% for D-7 to 99.8% for D-2 (Table 3). Only dye D-5 was exhausted to a lower value of 90.8%, but this exhaustion could be increased to 95% when the pH of the dyebath was decreased to 4.

A further useful feature of the dyes is their very high degree of absorption from the dyebath at a temperature of 98°C, i.e. over 90–95% (Fig. 3). The increase of absorption whilst the dyebath was being cooled was only of a few percent. Very often in dyeing polyamide fibres it is not before the cooling stage that the dye absorption increases from 30 to 40%. This phenomenon is considered disadvantageous, as it often decreases the wet fastness and the degree of dye absorption. Therefore, the dyes could be considered to be pro-ecological products due to their practically quantitative exhaustion from the dyebath without the use of electrolytes, and with only a slight increase in the quantity of acid required in the dyeing process.

Spectroscopic examinations

The dyes have two absorption bands, the first within the range 432–459 nm (50% acetone) and the second within the range 576–603 nm (50% acetone). In 50% acetone, independent of the middle component, dyes D-2 to D-4 (derivatives of *p*-cresidine), when compared with dyes D-7 to D-10 (derivatives of 1-naphthylamine-7-sulphonic acid) showed the same λ_{max} (433 nm) as well as a very similar molar absorption. This band is related to the 2-nitrodiphenylamine moiety, while the remaining elements of the dye structure show only a slight effect on its character.

On the other hand, the long wavelength bands show considerable differences in λ_{max} and in molar absorption, depending on the type of the middle component.

For dyes D-1 to D-4, in which the middle component is *p*-cresidine, λ_{max} varied from 576 to 579 nm, and for dyes in which the middle component is 1-naphthylamine-7-sulphonic acid, λ_{max} was from 591 nm (D-6) to 608 nm (D-7). Thus, comparing pairs of dyes, such as D-1 and D-5, the latter shows a bathochromic effect equal to 22 nm, while for dyes D-2 and D-8 the bathochromic effect is 28 nm. Similar effects are shown by other pairs of dyes.

Spectroscopic measurements of the dyes in aqueous solutions indicate their high degree of aggregation, particularly in the dyes containing sulphonamide groups. This aggregation is mainly apparent in the long wavelength band, which shows high hypochromic effect and a slight hypsochromic effect.

On the other hand, no hypochromic effect was observed in the short wavelength band when compared with the measurements in 50% aq. acetone. There was only a bathochromic effect from 5 to 38 nm.

The observed spectroscopic effects show that the aggregation of these dyes is relatively complicated and that aggregates of the 'sandwich' type are superimposed over one another and arranged 'head to tail'. It can be assumed that the high capability of the dyes to aggregate advantageously effects the wet fastnesses of the dyeings on polyamide fibres. In addition, the short wavelength band is very broad, from 370 to 500 nm, and the λ_{max} is mostly apparent on a broad slight inflexion. Such a shape of the absorption curve is often characteristic of black dyes.

Dyes D-1 to D-4, containing *p*-cresidine as the middle component, in polyamide fibre dyeings over 3% are blacks with a slight red hue. On the other hand, dyes D-6 and D-11 in polyamide dyeings over 3% are deep natural blacks, giving uniform colours on this fibre. The remaining dyes dyed polyamide fibres to a dark navy-blue colour.

All the investigated dyes were characterized by a high tinctorial power and, as already mentioned, by a very high degree of exhaustion from the dyebath, essentially without the use of electrolytes (Na_2SO_4 or NaCl).

REFERENCES

1. Stead, C. V., Azodyes. In *The Chemistry of Synthetic Dyes* Vol. III, ed. K. Venkataraman. Academic Press, New York and London, 1970.
2. Feeman, J. F., Leather Dyes. In *The Chemistry of Synthetic Dyes* Vol VII, ed. K. Venkataraman. Academic Press, New York, 1978.
3. FIAT 764; Bayer Co., German Patent 118655; Fr. **5**, 958.
4. B. P. 24527/97; French Patent 271609; German Patent 101274; Fr. **5**, 514.
5. Kraska, J. & Blus, K., *J. S. D. C.*, **106** (1990) 110.
6. Kraska J. & Blus K., *Polish Patent* 146488 (1989).
7. Anon, *Standard Methods for the Determination of the Colour Fastness of Textiles and Leather*. Society of Dyers and Colourists, Bradford, 1978.