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Disperse and Cationic Dyes Derived from 2-(*meta*- and *para*-Aminophenyl)imidazo[4,5-*b*]pyridine

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ABSTRACT

A series of monoazo disperse dyes has been obtained using N,N-*disubstituted anilines as coupling components and diazotized 2-(*m- *and* p-*aminophenyl)imidazo[4,5-*b*]pyridines as diazo components. The dyes were suitable for the dyeing of polyamide and polyester.*

By quaternization of the pyridine nitrogen with methyl iodide, cationic azo dyes, suitable for the dyeing of polyacrilic fibres, were obtained.

NMR and electronic absorption spectra of the dyes, dyeings, fastness properties, and colour parameters of dyed fabrics were measured and correlated with the structure of the dyes.

1 INTRODUCTION

The synthesis and properties of azo dyes obtained by coupling the diazonium salts of 2-(*meta*- and *para*-aminophenyl)imidazo[4,5-*b*]pyridines (**III**) to acyl derivatives of 4-amino-2-hydroxybenzoic acid have been described in a previous paper.[1] This present work deals with the coupling of the above salts to a series of *N*,*N*-disubstituted anilines (**IV**). The pathway of the synthesis is outlined in Scheme 1.

The dyes **V** were suitable for application to polyester and polyamide and the presence of quaternizable sites in the dyes enabled a series of cationic dyes (**VI**), suitable for the dyeing of polyacrylic fibres to be prepared.

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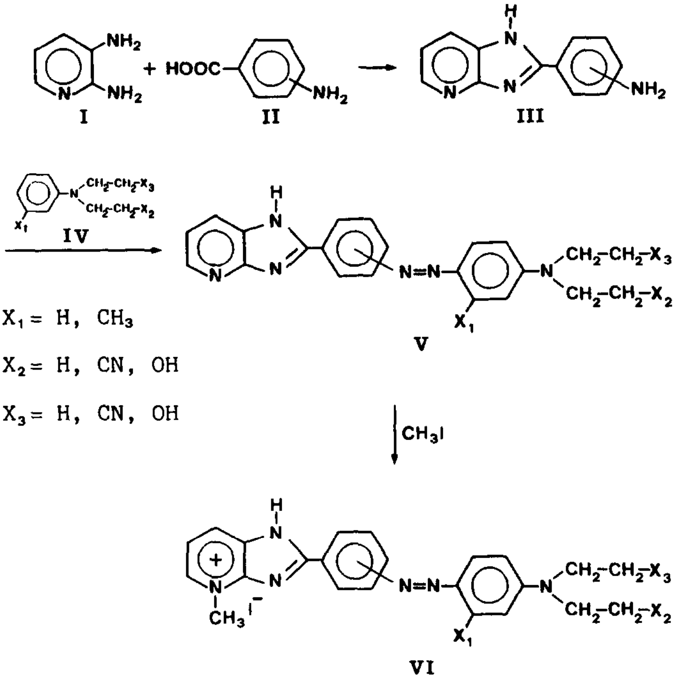


Scheme 1

2 EXPERIMENTAL

2.1 Dyes and intermediates

Commercial 2,3-diaminopyridine, *m*- and *p*-aminobenzoic acids, *N*,*N*-diethylaniline, *N*-ethyl-*N*-(2-cyanoethyl)aniline, *N*-ethyl-*N*-(2-hydroxyethyl)aniline, *N*,*N*-bis(2-cyanoethyl)aniline, *N*,*N*-bis(2-hydroxyethyl)aniline, *N*,*N*-diethyl-*m*-toluidine and *N*-ethyl-*N*-(2-cyanoethyl)-*m*-toluidine were employed for the synthesis of dyes.

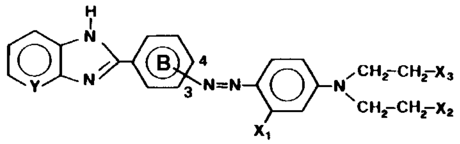
The synthesis and the diazotization of the amines were carried out as indicated in Ref. 1.

The coupling was performed in glacial acetic acid at a temperature of 18°C. After 2 h a solution of sodium acetate was added to give pH 4·5 and the dye was then filtered, washed and recrystallized from ethanol/water.

The cationic dyes were obtained by refluxing the corresponding disperse dye with an excess of methyl iodide for the period indicated in Table 1. The crude material was washed with ether and recrystallized.

The purity of the dyes was confirmed by chromatography and the characterization data for them are reported in Table 1.

TABLE 1
Characterization Data for Dyes



Dye no.	*Position in the B ring*	X_1	X_2	X_3	*Y*	*Reaction time (h)*	*Crystallization solvent*	*M.p. (°C)*	λ_{max} *(nm)*	*log ε*	R_f
1	4	H	H	H	N	—	Ethanol/water	264–266	470	4·49	0·95
2	4	H	H	CN	N	—	Ethanol/water	245–246	437	4·51	0·90
3	4	H	H	OH	N	—	Ethanol/water	231–233	464	4·47	0·89
4	4	H	CN	CN	N	—	Ethanol/water	279–281	420	4·30	0·82
5	4	H	OH	OH	N	—	Ethanol/water	249–251	450	4·60	0·84
6	4	CH_3	H	H	N	—	Ethanol/water	278–279	480	4·60	0·90
7	4	CH_3	H	CN	N	—	Ethanol/water	236–239	442	4·52	0·88
8	3	H	H	H	N	—	Ethanol/water	233–235	430	4·43	0·90
9	3	H	CN	CN	N	—	Ethanol/water	209–211	400	4·00	0·81
10	3	H	OH	OH	N	—	Ethanol/water	235–236	423	4·45	0·82
11	4	H	H	H	$^+NCH_3I^-$	2	Isopropanol	244–245	480	4·50	0·42
12	4	H	H	CN	$^+NCH_3I^-$	3	Butanol	228–230	438	4·60	0·40
13	4	H	H	OH	$^+NCH_3I^-$	20	Ethanol/water	239–241	465	4·41	0·40
14	4	H	CN	CN	$^+NCH_3I^-$	8	Ethanol/isopropanol	231–232	421	4·58	0·38
15	4	H	OH	OH	$^+NCH_3I^-$	3	Ethanol	236–238	466	4·56	0·38
16	4	CH_3	H	H	$^+NCH_3I^-$	8	Ethanol/isopropanol	258–259	486	4·59	0·40
17	4	CH_3	H	CN	$^+NCH_3I^-$	4	Ethanol/isopropanol	247–249	450	4·57	0·40
18	3	H	H	H	$^+NCH_3I^-$	20	Ethanol/water	165–167	430	4·36	0·43
19	3	H	CN	CN	$^+NCH_3I^-$	9	Ethanol/isopropanol	156–158	400	4·30	0·37
20	3	H	OH	OH	$^+NCH_3I^-$	35	Ethanol/isopropanol	160–162	420	4·40	0·38

2.2 Chromatography

R_f values were determined on silica gel 60 F-254 TLC plates (Merck), using butanol/acetic acid/water (BAW), 4:1:5 by vol., as eluent.

2.3 Spectra

The electronic spectra were determined on a Pye–Unicam SP 8-100 spectrophotometer in methanol (molarity of the dye 1×10^{-5}).

In view of phototropic *trans–cis* isomerization of 4-aminoazobenzene and its derivatives,[2] the neutral solutions were retained in cells in the spectrophotometer until maximum ε values were reached. Relevant data are reported in Table 1.

^{1}H-NMR spectra were obtained with a JEOL G X 270 spectrometer using DMSO-d_6 (3%) as solvent for the dyes.

2.4 Dyeings and fastness determinations

The baths for the dyeing of polyamide 6 (Snia Viscosa) and polyester (Terital) fabrics were prepared by milling the dye (0·5% depth) with the same weight of sodium sulphate and of Dispersogen-A (Hoechst Italia Spa, Turin) and diluting with an aqueous (1%) solution of Lenol O (Hoechst Italia Spa, Turin) to a final liquor ratio of 40:1 w/w. The patterns, previously wetted, were introduced into the dispersion at 30°C and dyed following the dyeing cycle reported in Fig. 1. The dyed fabrics were removed, well rinsed and dried in hot air.

For the dyeing of polyacrylic fibres the baths were prepared by milling the dye (0·25% depth) with acetic acid (1%) and diluting with distilled water to a final liquor ratio of 20:1, w/w. The patterns, previously wetted, were placed in the dye solutions at 30°C and dyed as indicated in Fig. 1. The dyed fabrics were removed, well rinsed and aftertreated for 15 min at 95°C in 1‰ acetic acid solution.

All the dyeings were carried out on a Linitest apparatus. The fastness properties were assessed by standard procedures.[3] Lightfastness was determined on a Xenotest 150.

2.5 Colour measurements

The colour parameters of dyed fabrics were determined on a Cary 210 spectrophotometer, equipped with integrating sphere and connected to an Apple II computer, using the D65 source and barium sulphate as standard blank.

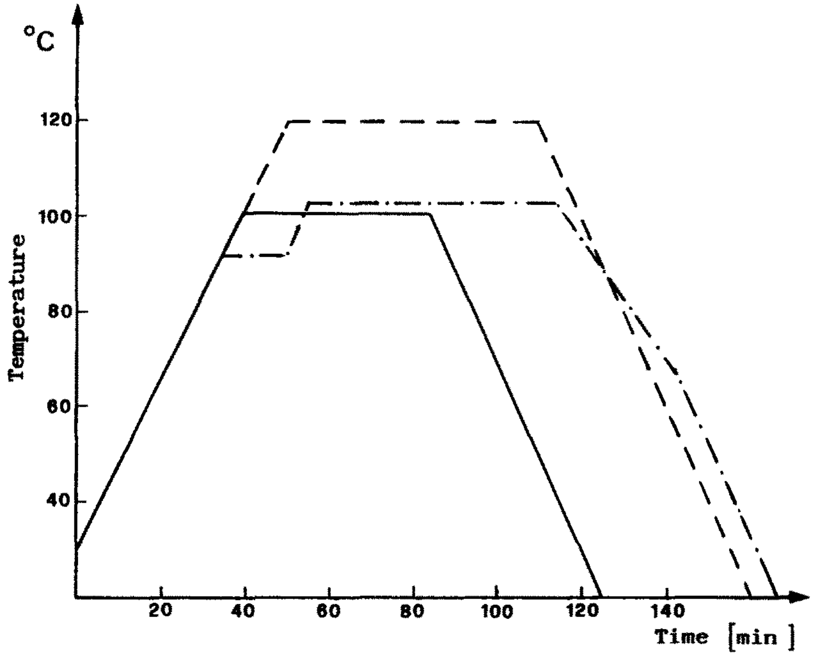


Fig. 1. Dyeing cycle: ——, polyamide; – – –, polyester; – · – ·, polyacrylonitrile.

3 RESULTS AND DISCUSSION

3.1 Chromatographic behaviour

The R_f values fall into two groups. Disperse dyes, due to their hydrophobicity, show a lower interaction with the polar substrate (range 0·81–0·95), whereas cationic dyes are more efficiently retained (range 0·37–0·42).

3.2 ^{1}H-NMR spectra

The determination of the structure of cationic dyes obtained by quaternization is, in most cases, superfluous since the reaction pathway to them is unambiguous. Our previous experience, however, on the behaviour of heterocycles containing pyridine and imidazole moieties with quaternizing agents[4,5] indicates the necessity of particular accuracy in the assignment of the structures of quaternary salts. NMR spectroscopy, including selective spin decoupling experiments, was particularly useful in this respect. Figures 2 and 3 show the spectra of dye **6**, taken as an example, and of its cationic counterpart, dye **16**.

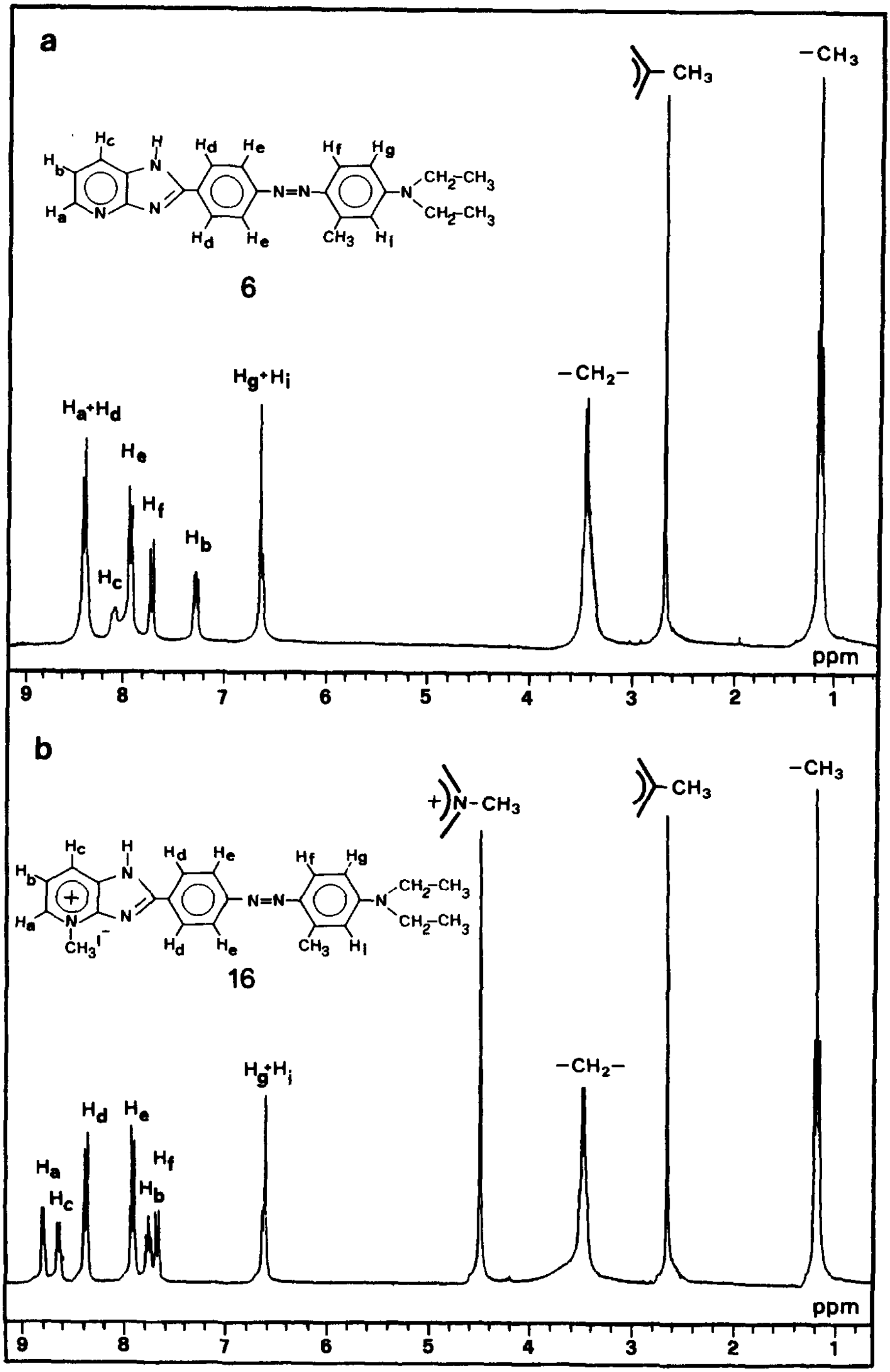


Fig. 2. ^{1}H-NMR spectra of (a) dye **6** and (b) dye **7**.

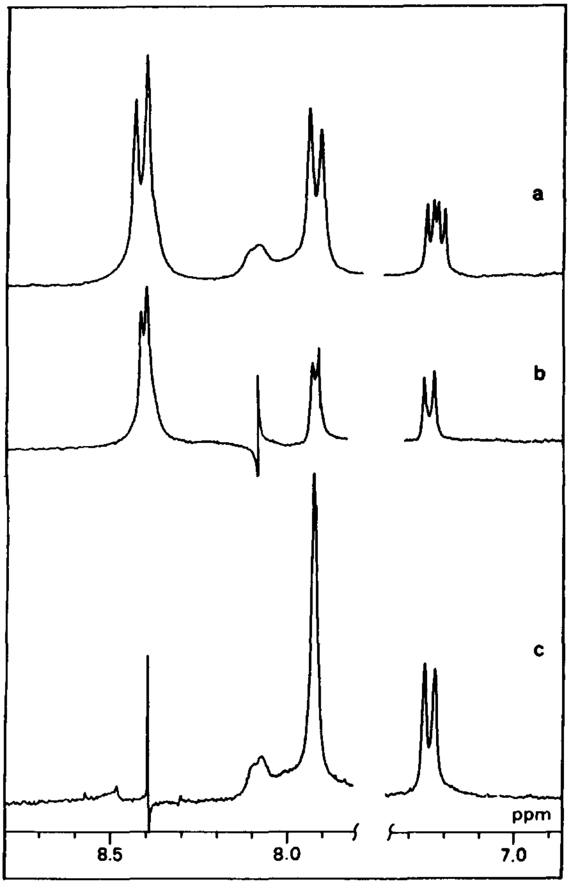


Fig. 3. Selective spin decoupling of dye **6**: (a) without decoupling; (b) irradiated at 8·08 ppm; (c) irradiated at 8·38 ppm.

The signal at 7·27 ppm (1H, doublet of doublets) in Fig. 2(a) is ascribed to the H_b proton for its upfield position and this is confirmed by the results of irradiation at 8·08 ppm (Fig. 3b) and 8·38 ppm (Fig. 3c) respectively. The downfield signal at 8·38 ppm (3H, apparent doublet) has been assigned to the H_a proton (on the basis of the simplification of the signal at 7·27 ppm in the selective decoupling) superimposed on the aromatic protons H_d.

The broad signal at 8·08 (1H) is due to the H_c proton on the basis of the above-mentioned irradiation. The decoupling at 8·38 ppm simplifies the signal at 7·92 ppm (2H, doublet) which is therefore attributed to H_e. As far as the remaining aromatic protons H_f, H_g, H_i are concerned, the first is found at 7·72 ppm (1H, doublet) whereas the others give superimposed signals at 6·63 ppm. Irradiation at 6·63 ppm (Fig. not reported), exclusively leads to the simplification of the doublet at 7·72 ppm. In the aliphatic region, the methyl linked to the aromatic ring appears as a singlet at 2·67 ppm, whereas the triplet at 1·15 ppm and the quartet at 3·45 ppm are due to the diethylamino group.

The spectrum of the cationic dye **16** (Fig. 2b) remains unchanged as far as the aliphatic and aromatic (benzo) signals are concerned. Only a further singlet (3H) at 4·48 ppm due to the methyl group introduced by quaternization appears; its position is typical for an *N*-methylpyridinium salt. This attribution is sustained by the general downfield shifts of the heteroaromatic protons H_a (8·80 ppm, 1H, doublet), H_b (7·76 ppm, 1H, apparent triplet) and H_c (8·64 ppm, 1H, doublet), which are consistent with those observed for α, β and γ positions in pyridinium salts.[6]

3.3 Electronic absorption spectra

In the visible region of the spectrum all the dyes showed an intense, broad peak. Taking into account the data given in Ref. 5, the following general conclusions can be made.

On the basis that the dyes **V** and **VI** can be considered as diethylaminoazobenzenes having a hetaryl substituent which behaves as an electron-withdrawing group, a batho-hyperchromic shift is generally observed as a consequence of such a substitution. The shifts of the absorption maxima for analogous compounds of type **V** and **VI** are higher in the pyrido-oxazole series (range 19–62 nm, see Ref. 5) than in the pyridoimidazole series (range 14–54 nm, present work) thus indicating, in agreement with other observations,[7] the stronger electron-withdrawing nature of the oxazole moiety. The above conclusions are also sustained when a given dye is compared with its cationic counterpart. Thus, considering *para* isomers (*meta* isomers are obviously less sensitive to this effect) the bathochromic shift ranges from 1 to 16 nm in consequence of the enhanced attracting ability of hetarylium groups. The *para* isomers show well-defined shifts to longer wavelengths compared with their *meta* counterparts (in the range 20–50 nm).

3.4 Dyeing properties

The disperse dyes were found to be very suitable for the dyeing of polyamide and polyester fabrics, giving satisfactory dyebath exhaustion, levelling and colour yields. Some dyeings showed a slight tendency to phototropic changes. Table 2 gives the fastness data of the dyeings and in view of the maximum fastness (5) shown in most tests the table has been drawn up, for clarity, using a star (*) to indicate the maximum rating of '5' (lightfastness is excluded, this being measured on a 1–8 scale).

Dyes **16** and **17** are of especial interest, but taking the series as a whole the following generalizations can be drawn.

(i) all dyes show excellent fastness to tetrachloroethylene and to acetic acid on both substrates, and to sodium carbonate, to dry and wet rubbing on polyamide, to washing (40 and 60°C), and to acid and basic perspiration on polyester;
(ii) the disperse dyes have, on polyamide, low fastness to severe washing (the worst dye, **5**, contains two hydroxyl groups) and have poor rubbing fastness on polyester.
(iii) the lightfastness is generally moderate, being slightly better on polyamide; the presence of cyano substituents is beneficial.

The cationic dyes coloured polyacrylic with satisfactory exhaustion of dye liquors, colour yields and levelling without use of a retarder. The properties of the cationic dyes (Table 2) are of a generally good order, although lower than analogous unquaternized disperse dye types.

3.5 Colour assessment

The colour of dyed fabrics was assessed in terms of tristimulus colorimetry. Table 3 shows the values obtained for the chromaticity coordinates, luminance factor, Helmholtz coordinates (λ_D, λ_C, $P\%$), and also the positions of the colours in the CIELAB colour solid (coordinates L^*, a^* and b^*).

The parameters connected with the lightness of colours (Y, L) indicate the decreasing sequence polyester > polyamide > polyacrylic, relatable to the different reflectances of the undyed patterns. Structural factors improving lightness are the presence of substituents such as —OH and —CN in X_2 and X_3, and the absence of a methyl group in X_1, The percentage purity, $P\%$, shows, as a general trend, the order polyamide > polyester > polyacrylic. Allowing for λ_D as a representative parameter of the colour on the fibre (λ_C is directly dependent on λ_D, and a and b give the relative amounts of redness and yellowness in a set of orange-hue colours), the shift towards longer wavelengths is promoted by (i) quaternization, (ii) *para* substitution, (iii) the presence of a methyl group in X_1, and (iv) the absence of substituents in X_2 and X_3.

4 CONCLUSIONS

The monoazo disperse dyes obtained by reacting *N*,*N*-disubstituted anilines with diazotized 2-(*m*- and *p*-aminophenyl)imidazo[4,5-*b*]pyridines, gave satisfactory results on polyamide and polyester with respect to dyeing

TABLE 2
Fastness Properties of Dyes[a]

Dye no.	*Washing*[b]			*Perspiration*[b]		*Acid/Alkali*	*Tetrachloro-ethylene*[b]	*Rubbing*		*Light*
	40°C	*60°C*	*95°C*	*pH 5*	*pH 8*			*Dry*	*Wet*	
Polyamide										
1	* 4–5 *	* 3–4 *	3 2–3 3	* 4–5 *	* 4–5 *	* *	* * *	*	*	4
2	* 4–5 *	* 4 *	2–3 2 3–4	* 4 *	* 4 *	* *	* * *	*	*	6
3	* 4–5 *	* 3–4 *	3–4 3 3	* 4 *	* 4 *	* *	* * *	*	*	4
4	* * *	* 4 *	2 3 4	* 4 *	* 3 *	* *	* * *	*	*	5–6
5	* 4 *	4–5 3 *	2 1–2 2	* 3 4–5	* 3 4–5	* *	* * *	*	*	4
6	* 4–5 *	* 3 *	4 1–2 2–3	* 4–5 *	* 4–5 *	* *	* * *	*	*	5
7	* 4–5 *	4–5 3–4 *	2–3 1–2 3	* 4 *	* 4 *	* *	* * *	*	*	5–6
8	* 4–5 *	* 4 *	3 2–3 4–5	* 4 *	* 4 4–5	* *	* * *	*	*	5
9	* * *	* 4–5 *	3 3–4 *	* 4–5 *	* 4–5 *	* *	* * *	*	*	4
10	* 4 *	* 4 *	2 2–3 4–5	* 3 4	* 3 4–5	* *	* * *	*	*	4
Polyester										
1	* * *	* * *	* * 4–5	* * *	* * *	* 4	* * *	4	4	3
2	* * *	* * *	* * 4–5	* * *	* * *	* *	* * *	3–4	4–5	3–4
3	* * *	* * *	* * 4–5	* * *	* * *	* *	* * *	3–4	4	3–4
4	* * *	* * *	* * 4–5	* * *	* * *	* *	* * *	3	3–4	3–4
5	* * *	* * *	* * 4–5	* * *	* * *	* 4–5	* * *	3–4	4–5	3

6	*	*	*	*	*	*	*	*	3–4	*	*	*	*	*	*	*	4–5	*	*	*	2	3	3
7	*	*	*	*	*	*	*	*	4–5	*	*	*	*	*	*	*	4	*	*	*	3–4	4–5	4
8	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4	*	3–4
9	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4	*	*	*	4	4–5	2–3
10	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4–5	*	3
Polyacrylonitrile																							
11	*	*	*	*	*	*	3–4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4
12	*	*	*	*	*	*	4–5	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	2
13	*	*	*	*	*	*	4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4
14	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4
15	*	*	*	*	*	*	3–4	*	4–5	*	*	*	*	*	*	*	*	*	*	*	*	*	3–4
16	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	5
17	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4–5
18	*	*	*	*	*	*	3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	2
19	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	3
20	*	*	*	*	*	*	3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	4–5	2

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[a] Except for light fastness values, * indicates a rating of 5.

[b] Values in the first column refer to the change of colour, in the second column to the staining of wool or cotton, in the third column to the staining of the same kind of fibre as the specimen.

TABLE 3
Colour of Dyed Fibres

Dye no.	*Chromaticity coordinates*		*Luminance factor, Y (%)*	*Helmholtz coordinates*			*CIELAB coordinates*		
	x	*y*		*Dominant wavelength, λ_D (nm)*	*Complementary dominant wavelength, λ_c (nm)*	*Purity P (%)*	*L**	*a**	*b**
Polyamide									
1	0·53	0·39	33·53	592	488	81·0	64·6	42·5	64·0
2	0·52	0·42	44·91	587	486	84·8	72·8	34·5	77·9
3	0·54	0·39	38·82	592	488	83·8	68·6	47·0	71·2
4	0·48	0·45	61·29	581	482	81·9	82·5	15·4	83·5
5	0·54	0·40	35·22	592	488	85·9	65·9	45·7	72·3
6	0·55	0·38	34·45	596	484	82·5	65·3	53·7	65·5
7	0·54	0·40	39·90	592	488	84·5	69·4	45·9	73·1
8	0·48	0·46	58·83	581	482	86·1	81·2	16·7	89·7
9	0·42	0·45	60·28	575	475	63·6	82·0	−4·1	60·4
10	0·49	0·46	61·83	580	482	86·3	82·8	15·0	91·7

Polyester									
1	0·51	0·72	46·80	587	486	80·1	74·1	32·8	71·6
2	0·48	0·44	56·42	582	483	78·7	79·9	19·7	75·8
3	0·48	0·43	54·28	584	484	74·3	78·6	24·7	68·0
4	0·42	0·44	74·73	576	477	59·5	89·3	0·3	59·5
5	0·45	0·43	63·66	581	482	76·3	83·8	13·4	62·6
6	0·52	0·40	41·35	591	487	76·1	70·4	41·1	62·2
7	0·51	0·42	48·93	586	486	80·2	75·4	31·8	73·0
8	0·45	0·45	60·79	578	480	74·7	82·3	7·4	73·1
9	0·37	0·40	73·04	573	472	35·2	88·8	−5·6	34·6
10	0·38	0·42	78·85	574	474	44·8	91·2	−4·7	45·0
Polyacrylonitrile									
11	0·45	0·29	15·05	—	495	40·0	45·7	47·7	6·0
12	0·50	0·36	25·05	599	490	62·2	57·1	43·9	37·7
13	0·46	0·30	14·86	—	494	38·7	45·4	47·0	9·7
14	0·48	0·40	34·23	587	486	67·3	65·1	27·1	49·9
15	0·48	0·32	16·46	617	492	45·8	47·6	45·0	19·8
16	0·42	0·24	10·13	—	502	54·0	38·1	53·2	−9·4
17	0·48	0·32	17·21	622	492	42·4	48·5	45·3	17·9
18	0·47	0·37	36·66	593	488	56·3	67·0	35·2	39·2
19	0·41	0·43	53·90	576	477	56·0	78·4	−1·0	49·9
20	0·48	0·40	38·97	588	486	66·6	68·7	29·4	51·2

properties and fastness properties. The cationic dyes derived by quaternization of the disperse dyes showed similar good behaviour on polyacrylonitrile.

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