

Water Soluble Fluorine Containing Reactive Dyes: Their Synthesis and Application on Various Fibres

P.C. PATEL, U.N. RANA, K.C. PATEL and S.K. PATEL*

Department of Chemistry, South Gujarat University, Surat-395 007, India

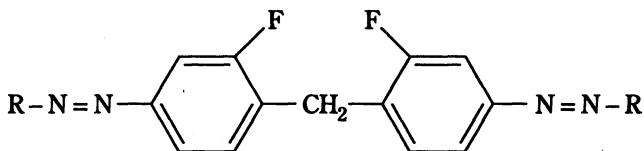
Various cold brand reactive dyes have been prepared by coupling diazotised 4,4'-methylene bis-*m*-fluoro aniline with various cyanurated coupling components and their dyeing performance as reactive has been assessed on silk, wool and viscose rayon. These dyes have been found to give a wide range of yellow to maroon shades with very good depth and levelness on each fibre. The purity of all dyes has been checked by thin-layer chromatography. The IR spectra showed all characteristic bands present in the dye molecules and PMR spectra of a representative dye showed all the characteristic signals of the dye. The percentage dye bath exhaustion and fixation on different fibres have been found to be reasonably good and acceptable. The dyed fibres show fair to very good fastness to light, washing and rubbing.

Key words: 4,4'-Methylene bis-*m*-fluoro aniline, cold brand bis-azo reactive dyes, dyeing silk, wool and viscose rayon.

INTRODUCTION

Reactive dyes are the only textile colouring products designed to form covalent bonds between the dye and the substrate during dyeing. Reactive dyes are becoming increasingly popular for dyeing cellulosic fibres because of their wide shade range, ease of application and excellent wet-fastness properties. Improvements in the structure of reactive dye chromogens and in the structure, selection and number of reactive groups have led to an increased use of reactive dyes¹⁻³. Patel *et al.*⁴⁻⁶ have synthesized fibre reactive dyes for silk, wool and viscose rayon.

The purpose of the present investigation was to obtain cold brand reactive dyes with a higher degree of activity. We report here the synthesis and study of the dyeing properties of the cold brand reactive dyes based on 4,4'-methylene bis-*m*-fluoro aniline. The cold brand reactive dyes of the following structure were prepared.



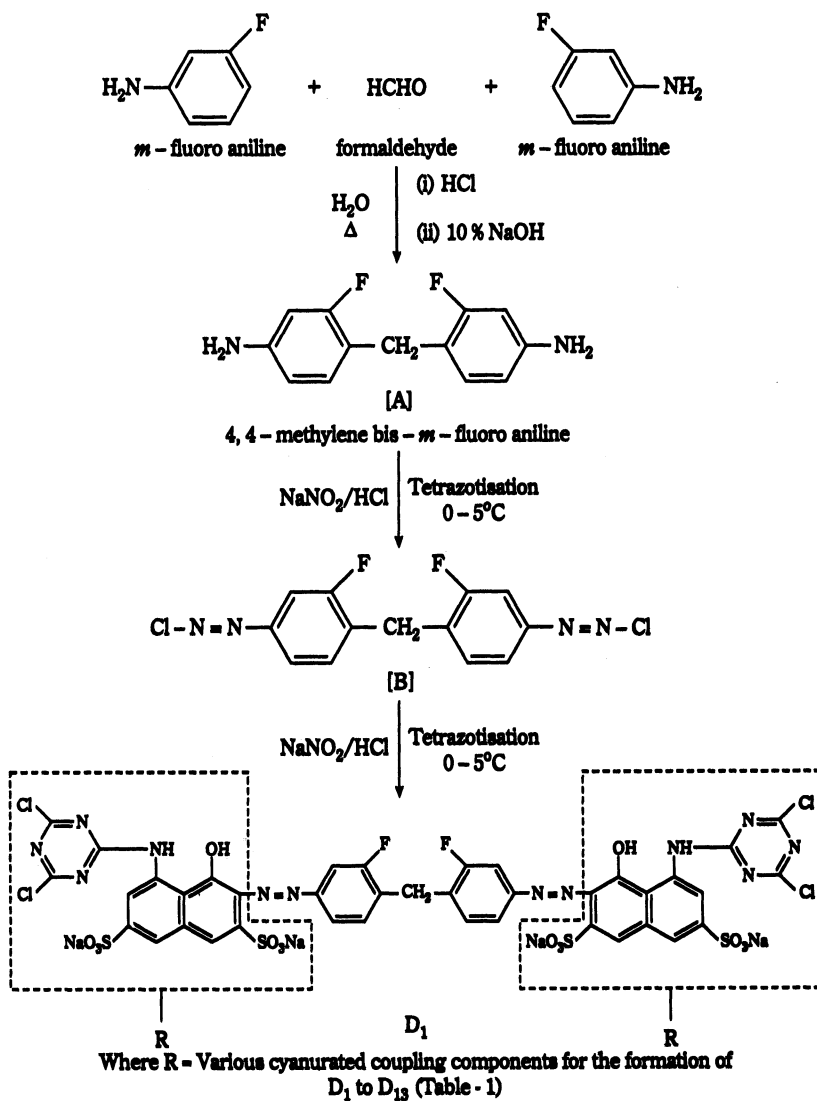
where R = cyanurated coupling components such as cyanurated H-acid, Chicago acid, K-acid, Koach acid, sulpho-Tobias acid, gamma acid, J-acid, N-phenyl-J-acid, N-methyl-J-acid, Tobias acid, Laurent's acid, Peri acid and Bronner's acid.

EXPERIMENTAL

Synthesis of 4,4'-methylene bis-*m*-fluoro aniline (A)

m-Fluoro aniline (4.1 g, 0.1 mol) was dissolved in water (125 mL) and 36.5% hydrochloric acid (25 mL) at 500°C. The reaction mixture was then treated with 3% aqueous formaldehyde (35 mL) solution at 15–20°C with stirring for 1 h and neutralized with 10% sodium hydroxide; the yellow precipitate obtained was filtered, washed with hot water, dried and recrystallized from acetic acid. Yield 86%, m.p. 154°C, m.f. C₁₃H₁₂N₂F₂. Found (required): N, 11.83 (11.99)%.

REACTION SCHEME



Tetrazotization of 4,4'-methylene bis-*m*-fluoro aniline (B)

4,4'-Methylene bis-*m*-fluoro aniline (A) (2.34 g, 0.01 mol) was suspended in H₂O (60 mL). Hydrochloric acid (10 mL) was added dropwise to this well stirred suspension. The mixture was gradually heated up to 70°C till clear solution was obtained. The solution was cooled to 0–5°C in an ice-bath. A solution of NaNO₂ (1.2 g, 0.02 mol) in H₂O (8 mL) previously cooled to 0°C was then added over a period of 5 min with stirring. The stirring was continued for 1 h, maintaining the same temperature, with positive test for nitrous acid on starch iodide paper. After just destroying excess of nitrous acid with required amount of a solution of sulphamic acid, the clear tetrazo solution (13 mL) at 0–5°C obtained was used for subsequent coupling reaction.

Cyanuration of coupling components (R)

Cyanuric chloride (3.7 g, 0.02 mol) was stirred in acetone (25 mL) at a temperature below 5°C for a period of 1 h. A neutral solution of coupling component (0.02 mol) in aqueous sodium carbonate solution (10% w/v) was then added in small lots in about 1 h. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1% w/v). The temperature was maintained below 5°C throughout this reaction. The reaction was then stirred at 0–5°C for further 4 h; then a clear solution was obtained. The cyanurated coupling component solution (R) thus formed was used for subsequent coupling reaction.

Coupling of tetrazo solution (B) with cyanurated coupling component (R)

Formation of dyes (D₁ to D₁₃): To an ice-cold and well stirred solution of cyanurated coupling component (R) a freshly prepared solution of tetrazo solution (B) was added dropwise over a period of 10–15 min. The pH was maintained at 7.5 to 8.5 during addition; stirring was continued for 4 h, maintaining the temperature below 5°C; sodium chloride (12 g) was then added and the mixture was stirred for 1 h.

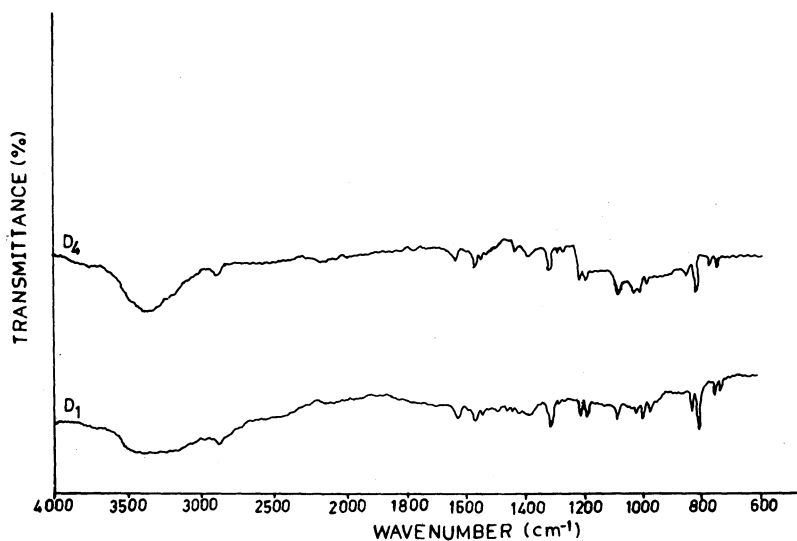
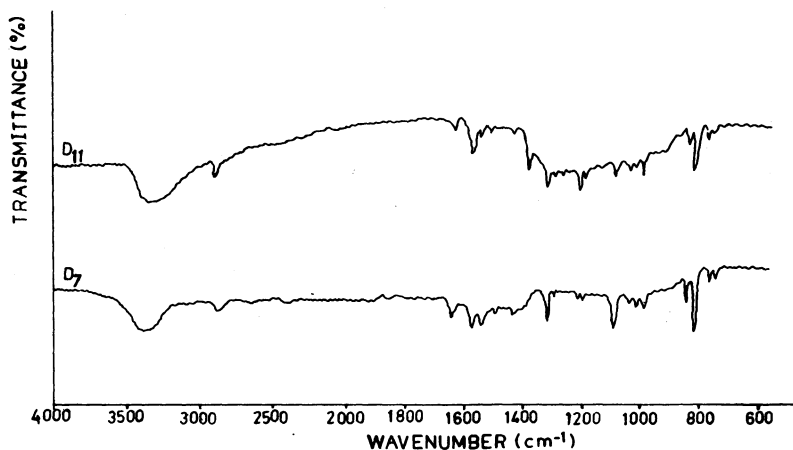
The solid dye separated out was filtered, washed with minimum amount of acetone and dried at room temperature. The same procedure was used to prepare other dyes using different cyanurated coupling components.

Dyeing of fibres: All the dyes D₁ to D₁₃ were applied on silk, wool and viscose rayon using the reported procedure⁷.

Fastness test: Fastness to light was assessed in accordance with BS: 1006–1978. The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC-1961, and the wash-fastness test in accordance with IS: 765–1979.

RESULTS AND DISCUSSION

All the dyes were of yellow to maroon colour obtained in excellent yield (74 to 88%). The purity of all dyes has been checked by thin-layer chromatography⁸. The absorption spectra of all the dyes were recorded on Beckmann DB-GT Grafting spectrophotometer. The characterisation data of the dyes are given in Table-1.

Fig. 1. Infrared spectra of D_1 and D_4 dyesFig. 2. Infrared spectra of D_7 and D_{11} dyes

The IR spectra of dyes D_1 to D_{13} were recorded on Perkin-Elmer spectrophotometer (model 377) using KBr pellets. Dyes D_1 to D_{13} showed characteristic band at 2890–2880 ($-\text{CH}_2-$)⁹, 800–790 (s-triazine), 1010–1000 (C–F), 1560–1530 ($-\text{NH}$), 1390–1380 ($-\text{N}=\text{N}-$), 1080–1070 ($\text{S}=\text{O}$) and 3420–3220 cm^{-1} due to (O–H).

The PMR spectra (300 MHz, CDCl_3) of a representative dye showed signals at 3.65 (2H, $-\text{CH}_2$), 7.17–8.12 (aromatic ring), 8.74 (2H, $-\text{NH}$).

TABLE-1
CHARACTERISATION OF DYES

Dye No.	Cyanurated coupling component (R)	m.f.	m.w.	Yield (%)	N (%) Found (required)	R _f value
D ₁	H-acid	$\text{C}_{39}\text{H}_{18}\text{N}_{12}\text{O}_{14}\text{Cl}_4\text{F}_2\text{S}_4\text{Na}_4$	1278	79	13.02 (13.03)	0.42
D ₂	Chicago acid	$\text{C}_{39}\text{H}_{18}\text{N}_{12}\text{O}_{14}\text{Cl}_4\text{F}_2\text{S}_4\text{Na}_4$	1278	74	13.01 (13.03)	0.39
D ₃	K-acid	$\text{C}_{39}\text{H}_{18}\text{N}_{12}\text{O}_{14}\text{Cl}_4\text{F}_2\text{S}_4\text{Na}_4$	1278	84	13.01 (13.03)	0.43
D ₄	Koch acid	$\text{C}_{39}\text{H}_{16}\text{N}_{12}\text{O}_{18}\text{Cl}_4\text{F}_2\text{S}_6\text{Na}_6$	1450	86	11.40 (11.41)	0.4
D ₅	Sulpho tobias acid	$\text{C}_{39}\text{H}_{20}\text{N}_{12}\text{O}_6\text{Cl}_4\text{F}_2\text{S}_2\text{Na}_2$	1042	78	15.94 (15.96)	0.40
D ₆	Gamma acid	$\text{C}_{39}\text{H}_{20}\text{N}_{12}\text{O}_8\text{Cl}_4\text{F}_2\text{S}_2\text{Na}_2$	1074	77	15.47 (15.48)	0.38
D ₇	J-acid	$\text{C}_{39}\text{H}_{20}\text{N}_{12}\text{O}_8\text{Cl}_4\text{F}_2\text{S}_2\text{Na}_2$	1074	88	15.51 (15.48)	0.39
D ₈	N-phenyl-J-acid	$\text{C}_{51}\text{H}_{28}\text{N}_{12}\text{O}_8\text{Cl}_4\text{F}_2\text{S}_2\text{Na}_2$	1228	80	13.55 (13.57)	0.41
D ₉	N-methyl-J-acid	$\text{C}_{41}\text{H}_{24}\text{N}_{12}\text{O}_8\text{Cl}_4\text{F}_2\text{S}_2\text{Na}_2$	1102	83	15.02 (15.03)	0.46
D ₁₀	Tobias acid	$\text{C}_{39}\text{H}_{22}\text{N}_{12}\text{Cl}_4\text{F}_2$	838	79	20.03 (20.01)	0.44
D ₁₁	Laurent's acid	$\text{C}_{39}\text{H}_{20}\text{N}_{12}\text{O}_6\text{Cl}_4\text{F}_2\text{S}_2\text{Na}_2$	1042	80	15.93 (15.99)	0.41
D ₁₂	Peri acid	$\text{C}_{39}\text{H}_{20}\text{N}_{12}\text{O}_6\text{Cl}_4\text{F}_2\text{S}_2\text{Na}_2$	1042	83	15.98 (15.99)	0.39
D ₁₃	Bronner's acid	$\text{C}_{39}\text{H}_{20}\text{N}_{12}\text{O}_6\text{Cl}_4\text{F}_2\text{S}_2\text{Na}_2$	1042	86	15.93 (15.99)	0.38

Fastness Properties

The percentage exhaustion, fixation and fastness properties of dyes **D₁** to **D₁₃** are given in Tables 2 and 3. All the dyes **D₁** to **D₁₃** showed good affinity for silk, wool and viscose rayon and gave fair to very good light, washing and rubbing fastness and good to very good exhaustion and fixation.

TABLE-2
SHADE, PERCENTAGE EXHAUSTION AND FIXATION OF REACTIVE DYES ON
WOOL, SILK AND VISCOSE RAYON

Dye No.	Shade on dyed fabric	λ_{\max} (nm)	% Exhaustion			% Fixation		
			W	V	S	W	V	S
D ₁	Pink	440	75.15	71.95	58.25	91.15	90.34	72.10
D ₂	Reddish brown	540	77.70	70.20	58.05	93.95	89.74	72.35
D ₃	Reddish yellow	490	71.10	67.80	53.95	87.20	86.28	67.66
D ₄	Light pink	470	70.15	68.70	53.65	86.24	87.34	68.03
D ₅	Yellowish brown	540	71.50	69.45	54.80	87.41	88.55	68.43
D ₆	Light pink	480	73.15	70.05	56.70	88.86	89.94	71.42
D ₇	Light brown	510	71.65	68.65	52.90	87.93	87.40	66.16
D ₈	Brown	450	69.40	66.55	52.30	85.74	83.40	66.09
D ₉	Brownish red	440	69.35	65.55	53.30	85.80	82.38	67.54
D ₁₀	Light orange	440	67.45	63.90	50.70	82.28	82.16	65.09
D ₁₁	Pale yellow	495	70.95	68.45	55.85	86.68	86.92	70.72
D ₁₂	Dark brown	430	72.70	67.00	56.20	88.72	83.58	71.17
D ₁₃	Light orange	480	75.90	70.80	57.75	92.93	90.40	71.86

where W = wool, V = viscose rayon and S = silk.

TABLE-3
FASTNESS PROPERTIES OF REACTIVE DYES ON WOOL, SILK
AND VISCOSE RAYON

Dye No.	Light fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	W	V	S	W	V	S	W	V	S	W	V	S
D ₁	5-6	4	5-6	4-5	4	4-5	3-4	3	5	4	2-3	4-5
D ₂	5-6	3-4	4-5	5	3-4	3-4	4	2-3	4-5	3	2	4-5
D ₃	4-5	2-3	4	4-5	2-3	3-4	4	2-3	4	3-4	2-3	4
D ₄	4	3	3	3-4	3	4-5	3-4	2-3	3	3	2-3	3-4
D ₅	3	4	5	3	4	4	4	3	3	3-4	2-3	3
D ₆	4	4	4	4	3-4	4	4	2-3	3	4	2-3	3-4
D ₇	4-5	3-4	3	3	3	3	3-4	2-3	3-4	4	2	3-4
D ₈	5	3	5	4	3-4	4	4	3	4-5	4-5	3	3
D ₉	4	4	5	4-5	4	3	3-4	3-4	4	3-4	3	4-5
D ₁₀	4	3-4	4-5	3-4	3	3-4	4	3	3-4	4	2-3	3-4
D ₁₁	3-4	3	4	4	3	3	4	2	3-4	3	1-2	3
D ₁₂	5	4	6	4-5	3-4	4-5	4	2-3	5	4-5	2-3	3
D ₁₃	6	4	4	5	4	4	4-5	3	3	4-5	2-3	3

REFERENCES

1. A.H.M. Renfrew and J.A. Taylor, *Rev. Prog. Col.*, **20**, 1 (1990).
2. M. H. Hahnke, *Textilveredlung*, **21**, 285 (1986).
3. S. Abeta, T. Yoshida and K. Imada, *Am. Dyestuff Rep.*, **73**, 26 (1984).
4. M.S. Patel, S.K. Patel and K.C. Patel, *Acta Cienc. Indica*, **24C**, 27 (1998); *Chem. Abstr.*, **132**, 209138q (2000).
5. N.B. Patel, S.K. Patel and K.C. Patel, *Orient. J. Chem.*, **15**, 445 (1999); *Chem. Abstr.*, **132**, 238354k (2000).
6. R.B. Patel, Nilesh Patel, S.K. Patel and K.C. Patel, *Asian J. Chem.*, **12**, 1193 (2000).
7. V.A. Shenai, *Chemistry of Dyes and Principles of Dyeing*, Sevak Publications, Bombay (1973).
8. Bernard Fried and Joseph Sherma, *Thin-layer Chromatography Techniques and Applications*, Marcel-Dekker, Inc., New York-Basel (1982).
9. N.B. Colthup, L.H. Daly and E. Wiberley, *Introduction of Infrared and Raman Spectroscopy*, Academic Press, New York-San Francisco-London (1975).

(Received: 13 August 2001; Accepted: 9 October 2001)

AJC-2488