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Synthesis, Characterization and Application of Hot Brand Reactive Dyes on Various Fibres

A.L. PATEL, N.B. PATEL, B.M. PATEL and K.C. PATEL*
Department of Chemistry
Veer Narmad South Gujarat University, Surat-395 007, India

Various hot brand reactive dyes have been synthesized by coupling tetrazotized 4,4′-methylene bis-2,5-dichloroaniline with various *m*-toluidino cyanurated coupling components and their dyeing performance has been assessed on silk, wool and cotton fibres. The purity of the dyes was checked by thin layer chromatography. The IR spectra showed all characteristic bands and the representative dye PMR spectra showed all the signals.

Key Words: 4,4′-Methylene bis-2,5-dichloro aniline, Hot brand reactive dyes, Dyeing, Silk, Wool and Cotton.

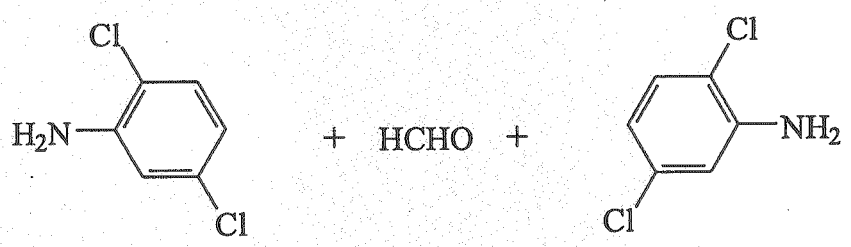
INTRODUCTION

The monochloro triazinyl reactive system is of major commercial importance in reactive dyeing[1, 2]. Reactive dyes are now a major group of dyes. Though a late entry into the family of synthetic dyes, they have very soon attained a commercial status. In the last decade, a variety of reactive dyes[3, 4] and diazo reactive dyes[5, 6] have been established as a major group for fixation to cellulose.

EXPERIMENTAL

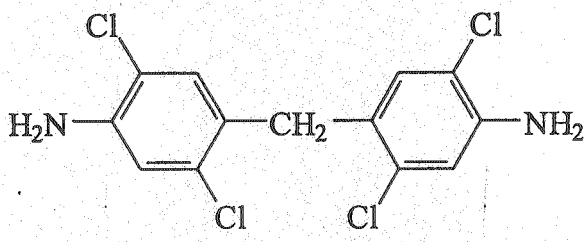
Synthesis of 4,4′-methylene bis-2,5-dichloro aniline (A): 2,5-Dichloro aniline (16.2 g, 0.1 mol) was dissolved in water (125 mL) and 36.5% hydrochloric acid (25 mL) at 50°C. The reaction mixture was then reacted with 3% aqueous formaldehyde (35 mL) solution at 60°C with stirring for 1 h and neutralized with 10% sodium hydroxide; the yellowish precipitates obtained were filtered, washed with hot water, dried and recrystallized from acetic acid. Yield 8 %, m.p. 125°C. Analysis (%) $C_{13}H_{10}Cl_4N_2$; Found: N, 8.31; Required: N, 8.33.

Tetrazotisation of 4,4′-methylene bis-2,5-dichloro aniline (B): 4,4′-methylene bis-2,5-dichloro aniline (1.68 g, 0.005 mole) was suspended in H_2O (60 mL). Hydrochloric acid (0.86 g) 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 at 0–5°C in an ice bath. A solution of $NaNO_2$ (0.7 g) in water (4 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 destroying the excess of nitrous acid with required amount of a solution of sulphamic acid the clear tetrazo solution-B at 0–5°C was used for subsequent coupling reaction.



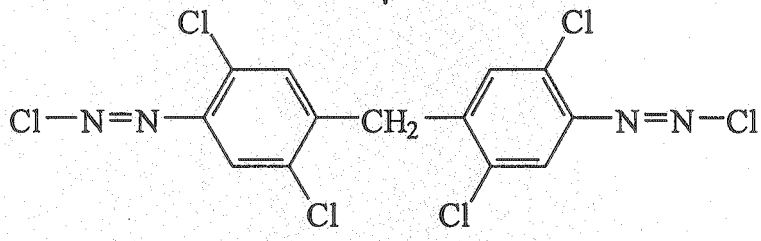
2,5-Dichloro aniline Formaldehyde 2,5-Dichloro aniline

1) HCl
2) 10% NaOH



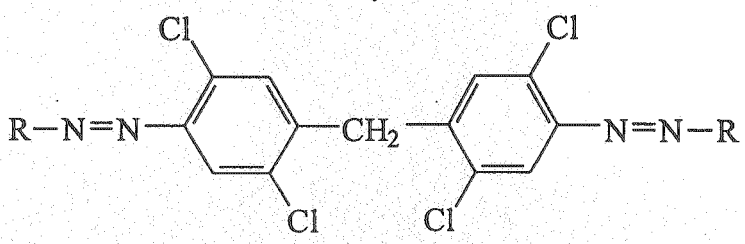
4,4'-methylene bis-2,5-dichloro aniline

Tetrazotisation
$NaNO_2$ / HCl



[B]

Coupling reaction with various coupling components [R]
pH 7.5-8.0, 0-5 °C



(D_1 to D_{13})

Reaction scheme

Preparation of *m*-toluidino cyanurated coupling components (R)

(1) Cyanuration of coupling component (R′): Cyanuric chloride (1.85 g, 0.01 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 (0.01 mol) in aqueous sodium carbonate solution (10%) (w/v) was then added in small lots in about 1 h. pH was maintained neutral by simultaneous addition of sodium carbonate solution (1%) (w/v). The reaction mass was stirred at 0–5°C for a further 4 h; then a clear solution was obtained. The cyanurated coupling solution (R′) was used for subsequent coupling reaction.

(2) Condensation with *m*-toluidine (Formation of *m*-toluidino cyanurated coupling component) [R]: The temperature of ice-cooled well stirred solution of cyanurated coupling components (R′) was gradually raised to 45°C for 30 min. To this cyanurated coupling component *m*-toluidine (1.07 g, 0.01 mol) was added dropwise at the same temperature, during a period of 30 min, maintaining the pH neutral by simultaneous addition of sodium bicarbonate solution (1%) (w/v). After the addition was completed, stirring was continued for a further 3 h. The *m*-toluidino cyanurated coupling component (R) solution thus obtained was subsequently used for further coupling reaction.

Formation of dyes (D_1 to D_{13}): To an ice-cold and stirred solution of cyanurated coupling component (R), a freshly prepared solution of tetrazo solution (B) as previously prepared was added dropwise over a period of 10–15 min. The pH was maintained at 7.5–8.5 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 *m*-toluidino cyanurated coupling components.

The purity of all the dyes was checked by TLC[7]. The IR spectra were recorded on a Perkin-Elmer model 377 spectrophotometer and PMR spectra on a Varian 60 MHz instrument using TMS as internal standard and $CDCl_3$ as solvent. UV-Vis spectra were recorded on a Beckman DB-GT grafting spectrophotometer.

Dyeing of fibres: All the dyes D_1 to D_{13} were applied on silk, wool and cotton by using different procedures[8].

RESULTS AND DISCUSSION

IR spectra of all the dyes, in general, showed O—H and N—H stretching vibrations at 3490–3400 cm^{-1}, —NH— bending vibrations at 1520–1509 cm^{-1}, —C—H stretching vibrations for methylene group at 2866–2840 cm^{-1}, —N=N— stretching vibrations at 1630–1624 cm^{-1}, C—N stretching vibrations at 1550–1400 cm^{-1}, S=O stretching vibrations at 1207–1443 cm^{-1}, C—Cl stretching vibrations at 780–770 cm^{-1}.

The PMR spectra (60 MHz, DMSO) of D_4 showed signals at 3.89 (4H, NH), 0.86 (6H, —CH_3), 2.16 (2H, —CH_2—), 6.85–8.12 (20 aromatic protons).

Exhaustion and fixation study: The percentage exhaustion of 2% dyeing on silk fibric ranges from 64–75%, of wool ranges from 66–75% and of cotton ranges from 65–73%. The percentage fixation of 2% dyeing on silk ranges from

76–93%, of wool ranges from 83–91% and of cotton fabric ranges from 82–91% (Table-2).

Fastness properties: The light fastness 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.

All the dyes show generally fair to very good fastness properties. The washing and rubbing fastness properties range from very good to excellent fastness on silk, wool and cotton (Table-3).

Preparation of *m*-toluidino cyanurated H-acid [R]:

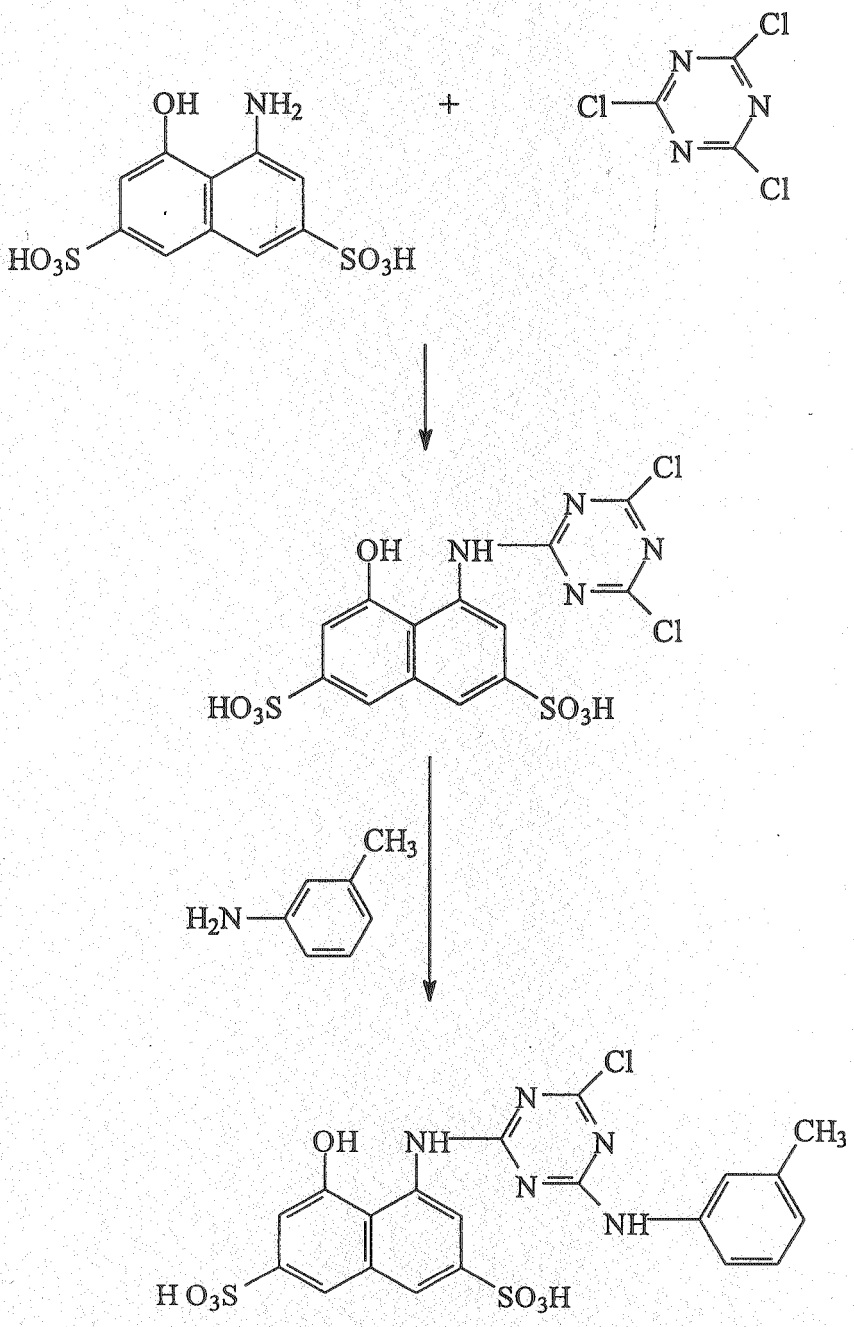


TABLE-1
CHARACTERIZATION OF REACTIVE DYES

Dye No.	*m*-Toluidino cyanurated coupling components	m.f.	m.w.	Yield (%)	Nitrogen (%)		R_f value
					Found	Reqd.	
D_1	H-acid	$C_{53}H_{32}O_{14}N_{14}Cl_6S_4Na_4$	1521	84	12.86	12.88	0.44
D_2	J-acid	$C_{53}H_{34}O_8N_{14}Cl_6S_2Na_2$	1317	80	14.85	14.88	0.42
D_3	N-phenyl J-acid	$C_{65}H_{42}O_8N_{14}Cl_6S_2Na_2$	1469	77	13.32	13.34	0.44
D_4	Bronner acid	$C_{53}H_{34}O_6N_{14}Cl_6S_2Na_2$	1285	86	15.23	15.25	0.36
D_5	Gamma acid	$C_{53}H_{34}O_8N_{14}Cl_6S_2Na_2$	1317	85	14.86	14.88	0.45
D_6	Chicago acid	$C_{53}H_{32}O_{14}N_{14}Cl_6S_4Na_4$	1521	76	12.86	12.88	0.43
D_7	Tobias acid	$C_{53}H_{36}N_{14}Cl_6$	1081	77	18.11	18.13	0.39
D_8	T-acid	$C_{53}H_{30}O_{18}N_{14}Cl_6S_6Na_6$	1693	83	11.55	11.57	0.37
D_9	N-methyl J-acid	$C_{55}H_{38}O_8N_{14}Cl_6S_2Na_2$	1355	80	14.43	14.46	0.44
D_{10}	Laurent acid	$C_{53}H_{34}O_6N_{14}Cl_6S_2Na_2$	1285	85	15.23	15.25	0.40
D_{11}	K-acid	$C_{53}H_{32}O_{14}N_{14}Cl_6S_4Na_4$	1521	75	12.87	12.88	0.42
D_{12}	Peri acid	$C_{53}H_{34}O_6N_{14}Cl_6S_2Na_2$	1285	82	15.22	15.25	0.38
D_{13}	Sulpho tobias acid	$C_{53}H_{34}O_6N_{14}Cl_6S_2Na_2$	1285	81	15.23	15.25	0.41

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

Dye No.	Shade on dyed fibre	λ_{max}	Exhaustion (%)			Fixation (%)		
			Silk	Wool	Cotton	Silk	Wool	Cotton
D_1	Violet	480	68.50	66.16	65.75	89.31	83.33	82.12
D_2	Orange	445	68.80	71.50	68.75	87.21	83.21	84.38
D_3	Maroon	455	75.25	72.75	72.95	85.71	88.65	89.10
D_4	Light orange	461	75.95	67.15	71.40	80.97	86.37	87.53
D_5	Maroon	486	73.95	69.35	69.10	89.92	85.80	85.38
D_6	Brown	450	66.05	75.95	67.35	85.74	83.28	91.31
D_7	Light orange	500	68.00	73.50	73.05	91.91	88.43	87.61
D_8	Pink	440	69.20	69.00	72.90	93.93	89.85	89.16
D_9	Orange	466	74.60	70.68	69.45	91.15	87.01	88.55
D_{10}	Brown	490	64.45	69.95	69.00	76.11	84.34	88.41
D_{11}	Brown	447	71.45	74.10	71.88	83.97	83.67	82.78
D_{12}	Light orange	443	69.85	71.13	70.15	83.07	83.66	86.24
D_{13}	Pink	483	70.10	75.35	65.85	87.73	91.63	88.83

TABLE-3
FASTNESS PROPERTIES OF REACTIVE DYES

Dye No.	Light fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	Silk	Wool	Cotton	Silk	Wool	Cotton	Silk	Wool	Cotton	Silk	Wool	Cotton
D_1	6	6	4	5	5	4	4-5	4	4	4	4	3
D_2	5	5	5	4	4	4	4	3-4	3-4	3	4	3
D_3	5-6	5-6	4	4	4-5	3	4	4	4	3-4	4	3
D_4	4	4	3	3	3	3-4	4	3	3	3	3	2
D_5	6	5	6	4-5	4	5	5	4	5	4	4	4-5
D_6	5	4	4	4	3-4	3	3-4	4	3	3	3	2
D_7	4	3	3	3	4	2-3	3	3	3	3	3	2
D_8	4-5	3	2	4	3	2	4	4	2-3	3-4	3-4	2
D_9	6	4-5	4-5	4-5	4	4	5	3-4	4	4	4	3
D_{10}	4	5	4	4	4	3-4	4	4	4	3	3	3
D_{11}	4	3	2-3	3	3-4	2	3	3	3	3	3-4	2
D_{12}	3	4	3	4	3	2	4	4	2-3	3	3	3
D_{13}	3	3	2	3	4	2-3	3-4	3	3	4	3	2

Light fastness: 1; poor, 2: slight, 3: moderate, 4: fair, 5: good, 6: very good.
Wash and rubbing fastness: 1: poor, 2: fair, 3: good, 4: very good, 5: excellent.

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