



RESEARCH ARTICLE

Synthesis and Characterization of Reactive Dyes based on 4, 4'-Diamino Diphenylsulphone and their Dying Application on Silk, Wool and Cotton fibres

Patel LA^{*1}, Patel KC², Patel SA³

¹Department of Chemistry, C. U. Shah Science College, Ahmedabad (Gujarat), India.

²Department of Chemistry, Veer Narmad South Gujarat University, Surat (Gujarat), India.

³Department of Chemistry, Navjivan Science College, Dahod (Gujarat), India.

Manuscript No: IJPRS/V4/I1/00025, Received On: 09/02/2015, Accepted On: 19/02/2015

ABSTRACT

A series of hot brand bisazo reactive dyes have been derived by tetrazotised 4, 4' diaminodiphenylsulphone with various cyanurated coupling components and their dying performance on silk, wool and cotton has been studied. The purity of all the dyes was checked by thin layer chromatography. The IR spectra showed all characteristic band and H¹ NMR spectra of representative dye showed all the signals. The percentage dye bath exhaustion on silk, wool and cotton fibers was reasonably good and acceptable. The dyed fibers showed moderate to very good fastness to light, washing and rubbing.

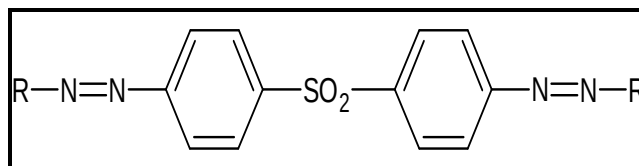
KEYWORDS

4, 4' Diaminodiphenylsulphone, Bisazo Reactive Dyes, Dyeing, Silk, Wool and Cotton

INTRODUCTION

Reactive dyes are coloured compound which contain one or two groups capable of forming covalent bond between a carbon atom or phosphorous atom of the dye ion or molecule and an oxygen, nitrogen or sulphur atom of a hydroxyl, an amino or a mercapto group respectively of the substrate^{1,2}. Mono azo reactive dyes and bisazo reactive dyes have been established as a major group for fixation to cellulose^{3,4,5}. Bisazo reactive dyes have been widely considered due to their higher fixation yield on various fibres. In the present investigation we wish to report a new series of reactive dyes from 4,4'-Diamino diphenylsulphone (C) and various cyanurated coupling components (H), then the coupling

components tested as a reactive dyes against various fabrics. In addition to the characterization of the dyes, an evaluation of their technical properties and a colour assessment were performed. The general structure of the dyes (D₁–D₁₀) is shown below.



Where, R = 2-nitro-4-chloroanilino cyanurated coupling components.

MATERIAL AND METHODS

All the melting points (m.p.) were determined in open capillaries and are uncorrected and expressed in °C. The purity of all the dyes has been checked by TLC⁶. The IR spectra were recorded in KBr on a Perkin Elmer Model-881 spectrophotometer and ¹H NMR spectra were recorded on a Bruker DRX-300 (300 MHz

***Address for Correspondence:**

Lina A. Patel

Department of Chemistry, C. U. Shah Science College,
Ahmadabad (Gujarat), India.

E-Mail Id: patlina@rediffmail.com

FTNMR) instrument using TMS as internal standard and DMSO as solvent, where the chemical shift δ are given in ppm. Absorption spectra were recorded on a Beckman DB-GT Grating spectrophotometer. The light fastness was assessed in accordance with BS: 1006–1978⁷. The rubbing fastness test was carried out with a Crockmeter (Atlas) in accordance with AATCC (1961) and the wash fastness test in accordance with ISO: 765–1979⁸.

Synthesis of *p*-acetamidobenzenesulphonyl chloride (A)

Chlorosulphonic acid (29.0 g, 0.249 mole) was added to a 250 ml three necked flask equipped with a stirrer, thermometer and a reflux condenser. The reagent was cooled to 5°C in an ice bath, and acetanilide (6.76 g, 0.05 mole) was added slowly at 5°C. The mixture was heated to 60°C and kept for 2 hours. Then 100 g of ice was added with continuous stirring, the precipitates of *p*-acetamidobenzenesulphonyl chloride were collected by filtration. It was washed with cold water, neutralized and dried. Yield 80 %.

Synthesis of 4,4'-diacetamidodiphenylsulphone (B)

Acetanilide (5.0 g, 0.33 mole) in acetone (20 ml) was stirred at room temperature. Then the solution of *p*-acetamidobenzenesulphonyl chloride (8.5g, 0.36 mole) in acetone (15 ml) was added and stirring was continued at room temperature. Pyridine (1 ml) was added after 1 hour and 2 hours respectively. Reaction progress was assessed after 5 hours. When reaction was completed, acetone was decanted and water (20 ml) was added with stirring and heating. The product mixture was filtered, washed, dried and recrystallized from benzene. Yield 82 %.

Synthesis of 4,4'-diaminodiphenylsulphone(C)

4,4'-diacetamidodiphenylsulphone was added to water (20ml). Sodium hydroxide (15ml, 20%) was slowly added with stirring. The mixture was reflux for 2 hours and cooled. The precipitates were collected by filtration to give 4,4'-diaminodiphenylsulphone and recrystallized from alcohol and water. Yield 74 %.

Tetrazotisation of 4, 4'-diaminodiphenylsulphone (D)

4,4'-diaminodiphenylsulphone (1.24 g, 0.005 mole) was suspended in H₂O (60ml). Hydrochloric acid (0.36 g) was added dropwise to this well stirred suspension. The mixture was gradually heated up to 70°C, till clear solution is obtained. The solution was cooled at 0-5°C in an ice bath. A solution of NaNO₂ (0.6 g) in water (4 ml) previously cooled to 0°C, was then added over a period of five minutes with stirring. The stirring was continued for an hour, maintaining the same temperature, with positive test for nitrous acid on starch iodide paper. After destroying excess of nitrous acid with required amount of a solution of sulphamic acid, clear tetrazo solution-H at 0-5°C was used for subsequent coupling reaction.

Cyanuration of H-Acid (E)

Cyanuric chloride (1.85 g, 0.01 mole) was stirred in acetone (25 ml) at a temperature below 5°C for a period of an hour. A neutral solution of H-acid (3.19 g, 0.01 mole) in aqueous sodium carbonate solution (10% w/v) was then added in small lots over a period of 1 hour. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1% w/v). The reaction mass was then stirred at 0-5°C for further four hours when a clear solution was obtained. The cyanurated H-acid solution thus formed was used for subsequent condensation reaction.

Condensation with 2-nitro-4-chloro aniline (F) (Formation of 2-nitro-4-chloro anilinocyanurated H-acid)

The temperature of ice-cooled well stirred solution of cyanurated H-acid (4.67 g, 0.01 mole) was gradually raised to 45°C for half an hour. To this cyanurated H-acid the *p*-chloro-*o*-nitro aniline (1.72 g, 0.01 mole) was added dropwise at same temperature, over a period of 30 minutes, maintaining the pH neutral by simultaneous addition of sodium bicarbonate (1% w/v). After the addition was completed, stirring was continued for further 3 hours. The 2-nitro-4-chloro anilinocyanurated H-acid solution thus

obtained was subsequently used for further coupling reaction.

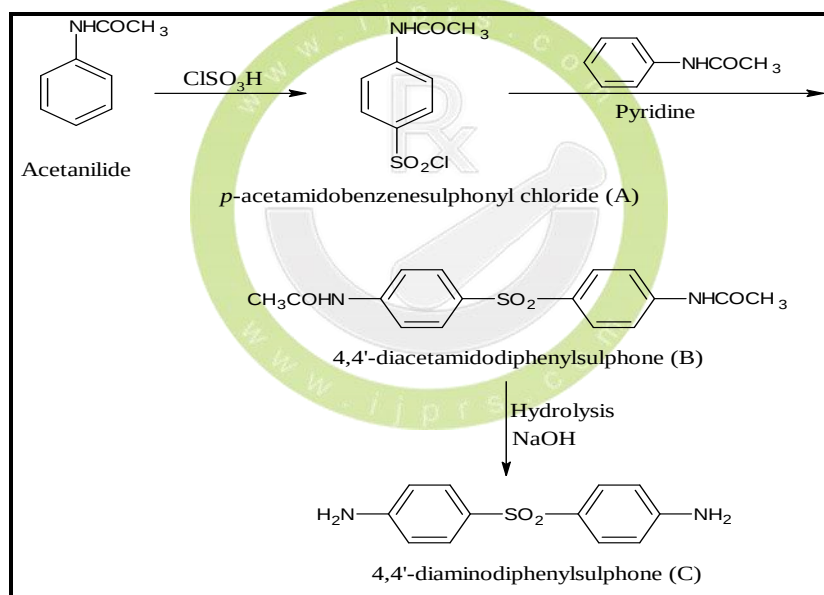
Coupling of tetrazo (D) solution with 2-nitro-4-chloro anilincyanurated H-acid (F) Formation of Dye D₁(G)

To an ice cold and stirred solution of 2-nitro-4-chloro anilincyanurated H-acid (6.03 g, 0.01 mole), a freshly prepared tetrazo solution-D (1.72 g, 0.005 mole) was added dropwise over a period of 10-15 minutes. The pH was maintained at 7.5 to 8.5 by simultaneous addition of sodium carbonate solution (10% w/v). During coupling a purple solution is formed. The stirring was continued for 3-4 hours, maintaining the temperature below 5°C. The reaction mixture was heated up to 60°C and sodium chloride

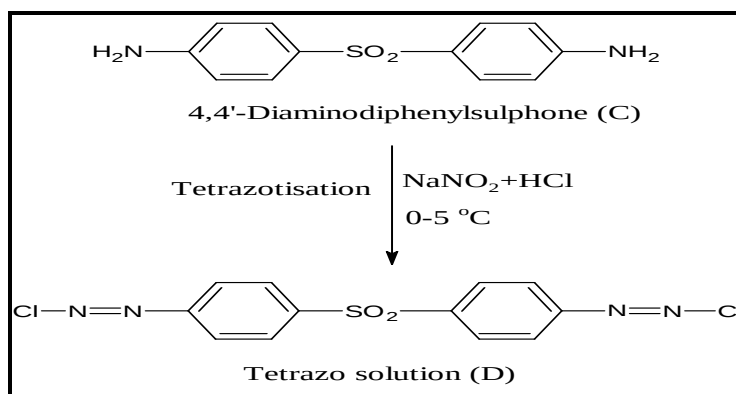
added till the colouring material was precipitated. It was stirred for an hour, filtered and washed with a small amount of sodium chloride solution (5% w/v). The solid was dried at 80-90°C and extracted with DMF. The dye was precipitated by diluting the DMF-extract with excess of chloroform. The violet dye was then filtered, washed with chloroform and dried at 60°C. Yield 85%.

Following the above procedure other reactive dyes D₂ to D₁₀ were synthesized using various 2-nitro-4-chloro anilincyanurated coupling components such as J-acid, Gamma acid, Bronner acid, Tobias acid, Koch acid, Sulpho Tobias acid, Laurant acid, N-methyl-J-acid and Chicago acid.

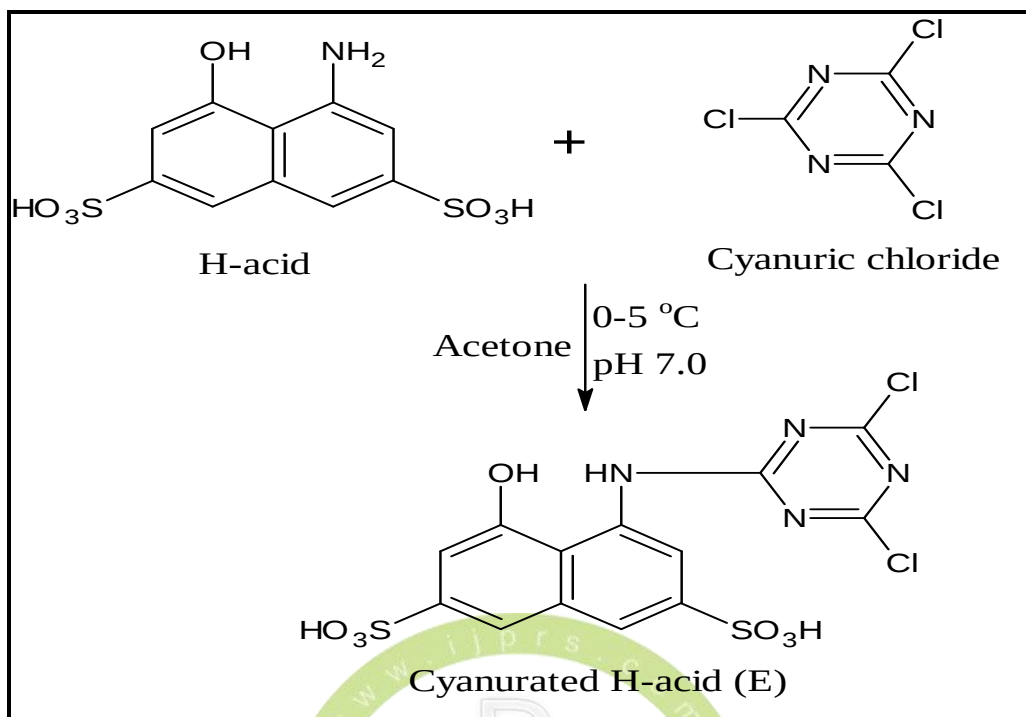
SYNTHESIS OF 4, 4'-DIAMINODIPHENYLSULPHONE (C)



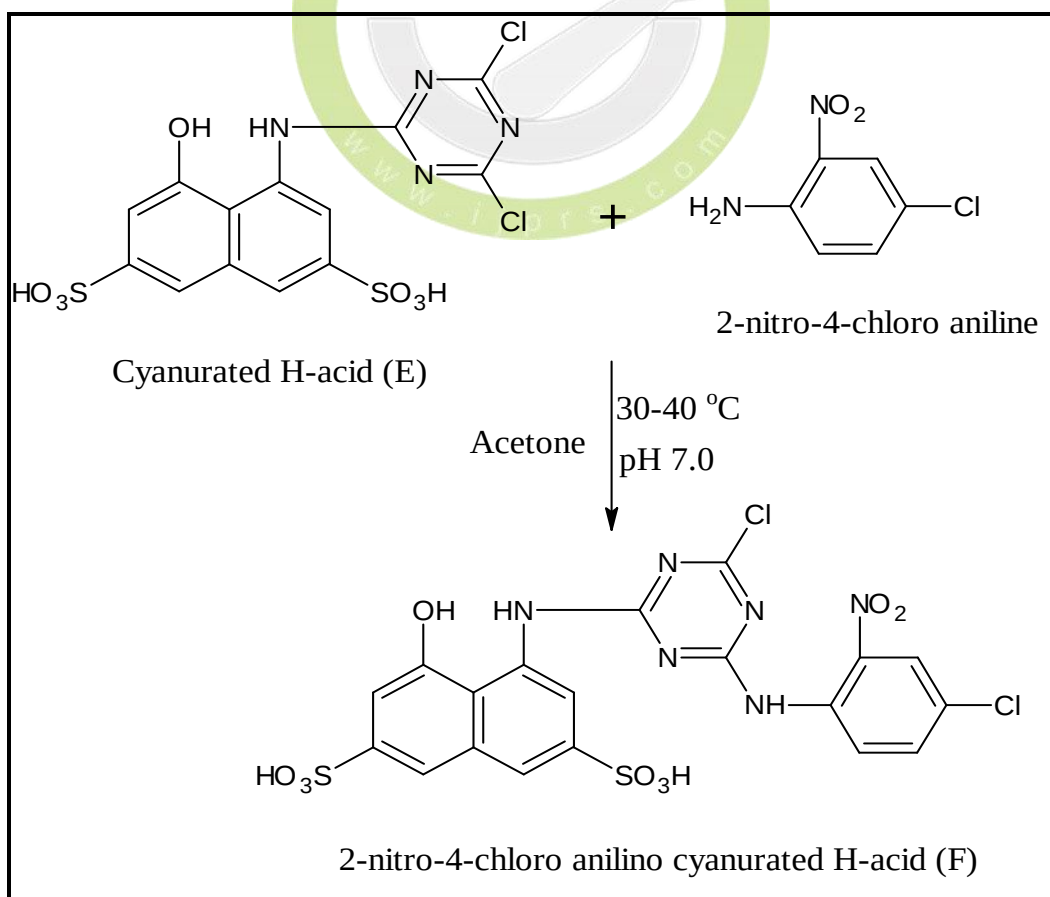
TETRAZOTISATION OF 4, 4'-DIAMINODIPHENYLSULPHONE (D)



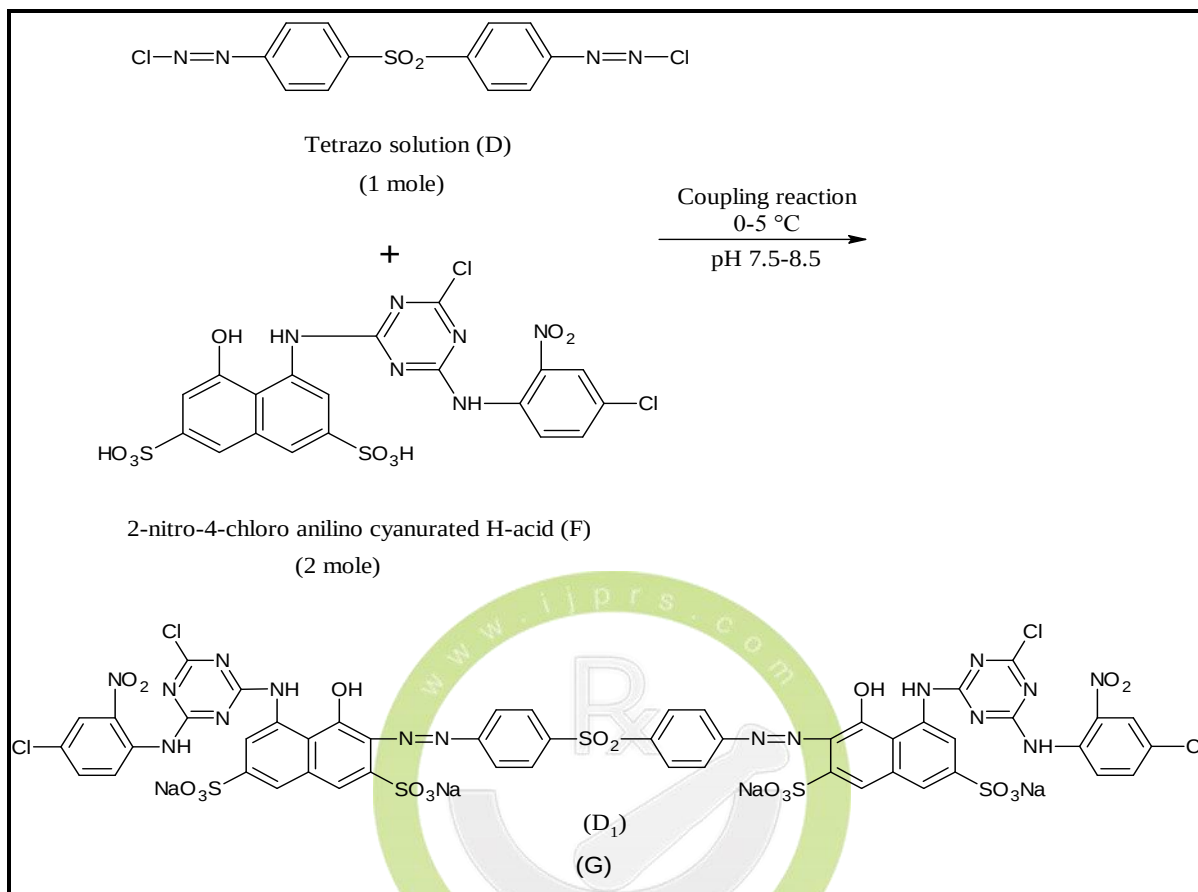
CYANURATION OF H-ACID (E)



PREPARATION OF 2-NITRO-4-CHLORO ANILINO CYANURATED H-ACID (F)



REACTION OF TETRAZO SOLUTION (D) WITH 2-NITRO-4-CHLORO ANILINO CYANURATED H-ACID – (G)



The Characterization Data of Dyes

No.	2-nitro-4-chloro anilino cyanurated coupling components (R)	Molecular Formula	Mole. Wt. (g)	Yield (%)	% Nitrogen		R _f Value
					Found	Require	
D ₁	H-acid	C ₅₀ H ₂₆ O ₂₀ N ₁₆ S ₅ Cl ₄ Na ₄	1565	85	14.25	14.32	0.42
D ₂	J-acid	C ₅₀ H ₂₈ O ₁₄ N ₁₆ S ₃ Cl ₄ Na ₂	1361	78	16.41	16.47	0.38
D ₃	Gamma acid	C ₅₀ H ₂₈ O ₁₄ N ₁₆ S ₃ Cl ₄ Na ₂	1361	76	16.38	16.47	0.36
D ₄	Bronner's acid	C ₅₀ H ₂₈ O ₁₂ N ₁₆ S ₃ Cl ₄ Na ₂	1329	78	16.82	16.86	0.40
D ₅	Tobias acid	C ₅₀ H ₃₀ O ₆ N ₁₆ SCl ₄	1125	80	19.88	19.92	0.43
D ₆	Koch acid	C ₅₀ H ₂₄ O ₂₄ N ₁₆ S ₇ Cl ₄ Na ₆	1737	76	12.82	12.90	0.35
D ₇	Sulpho Tobias acid	C ₅₀ H ₂₈ O ₁₂ N ₁₆ S ₃ Cl ₄ Na ₂	1329	78	16.80	16.86	0.36
D ₈	Laurant acid	C ₅₀ H ₂₈ O ₁₂ N ₁₆ S ₃ Cl ₄ Na ₂	1329	75	16.84	16.86	0.40
D ₉	N-methyl-J-acid	C ₅₂ H ₃₂ O ₁₄ N ₁₆ S ₃ Cl ₄ Na ₂	1389	80	16.08	16.14	0.36
D ₁₀	Chicago acid	C ₅₀ H ₂₆ O ₂₀ N ₁₆ S ₅ Cl ₄ Na ₄	1565	82	14.26	14.32	0.38

Dyeing Procedure

All the D₁ to D₁₀ were applied on silk, wool and cotton fabrics in 2% shade according to the usual procedure⁹ in the dye-bath containing the materials listed as below.

Dye-Bath

Materials	For silk	For wool	For cotton
Fabric (g)	2.0 g	2.0 g	2.0g
Amount of dye (mg)	40 mg	40 mg	40 mg
Glauber salt (20 %)	1.0 ml	1.5 ml	1.0 ml
Soda ash (10 %)	1.0 ml	----	1.0 ml
pH	3.0	3.0	8.0
MLR	1.40	1.40	1.40
Dyeing time (min)	40 min	60 min	90 min
Dyeing temp. (°C)	85°C	100°C	100°C
Total volume	80 ml	80 ml	80 ml

Colour Fastness Tests

Fastness to Washing

A dyed fabric were stitched between two pieces of undyed fabrics, all of equal length, and then washed at 50 °C for 30 min. The staining on the undyed adjacent fabrics was assessed according to the following gray scale: 1-poor, 2-fair, 3-moderate, 4-good, 5-very good and 6-excellent.

Fastness to Rubbing

The dyed fabrics were placed on the base of the Crockmeter (Atlas), so that it rested flatly on the abrasive cloth with its long dimension in the direction of rubbing. A square of white testing cloth was allowed to slide on the tested fabrics back and forth twenty times by making ten complete turns of crank. For the wet rubbing test, the testing squares were thoroughly immersed in distilled water. The rest of the procedure was the

same as in the dry test. The staining on the white testing cloth was assessed according to the gray scale: 1-poor, 2-fair, 3-moderate, 4-good, 5-very good and 6-excellent.

Fastness to Light

Light fastness was determined by exposing the dyed fabric for 40 h. The changes in color were assessed according to the following blue scale: 1-poor, 2-fair, 3-moderate, 4-good, 5-very good and 6-excellent.

Exhaustion and Fixation Study¹⁰

Table report the percentage exhaustion of 2% dyeing on cotton range from 65-76%, for silk range from 67-78% and wool range from 69-77%. The percentage fixation of 2% dyeing on cotton range from 78-92%, for silk range from 80-91% and wool range from 81-92%.

Dye uptake by the fiber was measured by sampling the dye bath before and after dyeing. The absorbance of the diluted dye solution was measured at $\lambda_{\max}$ of the dye.

$$\% \text{ Exhaustion} = \frac{\text{Initial O.D.} - \text{Final O.D.}}{\text{Initial O.D.}} \times 100$$

RESULTS

All the dyes were yellow to brown in colour and obtained in excellent yield (73 to 84 %). The purity of all the dyes has been checked by thin layer chromatography. The absorption spectra of all the dyes were recorded on Beckmann DB-GT Grafting spectrophotometer.

IR Spectra

IR spectra¹¹ of all the dyes, in general, showed –N=N stretching vibration at 1628 – 1630 cm⁻¹, -C-C- stretching vibration at 1490–1590 cm⁻¹ and 3000-3100 cm⁻¹, -OH and –NH stretching vibration at 3300–3510 cm⁻¹, -C – N stretching vibration at 1390–1400 cm⁻¹, -S=O stretching vibration at 1040–1300 cm⁻¹, -C-Cl stretching vibration at 770 – 790 cm⁻¹.

PMR Spectra

The PMR spectra¹² (300 MHz, DMSO) of D₃ showed signals at 5.5 (2H, -OH), 3.53 (4H, -NH), 7.07 – 8.10 (22 H, aromatic proton).

Fastness Properties of the Reactive Dyes on Various Fabrics

Dyes No.	Light fastness			Wash fastness			Rubbing fastness					
	S	W	C	S	W	C	Dry			Wet		
							S	W	C	S	W	C
D ₁	4-5	5	5	4	4	5	4	3	4	3	3-4	3-4
D ₂	5	4	3	6	5	3	4	3	5	4	3	4
D ₃	4	4-5	4-5	3	5	4	6	6	5	3	4	4
D ₄	5	6	5	4-5	4-5	3-4	4	3	4	6	5	4
D ₅	3	4-5	3-4	5	4	3	3	5	4	4	6	4
D ₆	4-5	4	4	4	4	3	3	5	4	3	4	5
D ₇	4	3-4	4	3	4	5	4	5	4	6	5	4
D ₈	3	5	4	5	4	5	5	6	4	4-5	5-6	3-4
D ₉	4	5	3	5	3	4	4	6	5	4	4	4
D ₁₀	4	4	3-4	3	5	3	4-5	3-4	4-5	5	4	5

Percentage Exhaustion and Fixation of Reactive Dyes

Dyes No.	Exhaustion (%)			Fixation (%)		
	S*	W*	C*	S*	W*	C*
D ₁	74.35	69.05	71.90	80.70	81.10	79.97
D ₂	69.10	76.93	70.28	89.73	82.55	91.07
D ₃	71.48	70.33	67.53	90.94	81.05	81.45
D ₄	74.50	67.53	72.28	85.23	87.38	87.17
D ₅	72.88	70.95	69.50	86.45	90.91	86.33
D ₆	69.75	69.10	75.03	88.17	81.77	87.30
D ₇	70.23	76.95	71.90	80.46	81.22	85.54
D ₈	69.15	69.55	69.10	87.49	83.39	86.11
D ₉	77.13	71.30	75.43	80.39	83.45	84.85
D ₁₀	76.60	74.38	74.75	85.51	80.67	86.96

*S=Silk, W=Wool, C=Cotton

ACKNOWLEDGEMENTS

The authors are thankful to Veer Narmad South Gujarat University, Surat for providing necessary research facility; Principal and Head of Chemistry Department, C. U. Shah Science College, Ahmadabad for providing necessary research facility; SAIF, Chandigarh for NMR spectra; Atul Ltd. (Valsad) for providing dying facility and fastness tests.

REFERENCES

1. Suwanruji, P., and Freeman, H. S.. (2006). Design, synthesis and application of easy wash-off reactive dyes, Society of Dyers and Colourists, *Coloration Technology*, 122, 27–36
2. Shah, K. M, (1994). *Hand Book of Synthetic Dyes and Pigments*, Multi- Tech. Publishing Co., (Vol. 1), 184.
3. Patel, L. A. and Patel, K. C. (2014). Synthesis, characterization and application of reactive dyes based on 4,4'diamino diphenyl sulphonamide on various fibres, *International Journal of Current Research*, 6(01), 4528-4531.
4. Mehta, J. R., Patel, K. C., Patel, S. K. and Shah, R. R. (2004). *Acta Ciencia Indica*, 30 c(1) 009.
5. Patel, R. S., Patel, K. C., Patel, S. K. and Patel, P. S., (2004). *Acta Ciencia Indica*, XXX c(2) 113.
6. Fried, B., Sharma, J., (1982). *Thin Layer Chromatography: Technique and Application*. Marcel Dekker, New York-Basel.
7. Standard Test Method, B. S. (1978). 1006, (UK): ISO (1994) 105, (India).
8. Indian standard ISO (1979). 765.
9. Patel, D. R., and Patel, K. C. (2011). *Arabian Journal of Chemistry*, 4, 279-285.
10. Sultana, Razia and Clemett, Alexandra. (2006). Choosing Appropriate Reactive Dyes for Optimal Dyeing of Cotton, 34-37.
11. Bassler, G. C., Silverstein, R. M. and Morrill, J. C., (1991). *Spectrophotometric Identification of organic compounds*. 5th Ed. Wiley New York.
12. Dean, J. A. (1968), *Chim. Chem.* 14, 324.