



“Synthesis Of Hot Brand Reactive Dyes Based On 4,4’-Methylene Bis(2-Fluoro Aniline) And Their Application On Various Fibres”

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ABSTRACT

Hot brand reactive dyes have been prepared by coupling diazotized 4,4'-methylene bis(2-fluoro aniline) with various 4- β -sulphatoethylsulphonylphenyl-1-amino cyanurated coupling components such as H-acid, J-acid, N-Methyl J-acid, N-Phenyl J-acid, N-Benzoyl J-acid, Gamma acid, Peri acid, Bronner acid, Laurent acid, K-acid, S-acid, Tobias acid, Cleve acid, Koch acid. They were characterized by nitrogen elemental analysis, IR and ^1H NMR spectra. The dyeing performance of all these dyes on silk, wool and cotton has also been assessed.

Keyword : Hot brand reactive dyes, 4,4'-methylene bis(2-fluoro aniline), diazotization, Dying, IR, NMR and PMR spectra.

INTERODUCTION

Reactive dyes are an important dyes and extensively used in textile industry because of their high fastness to wet treatment [1-3]. They can react with cellulose and form covalent bonding [4-6]. They are valued for their brilliance and variety of hue, versatility and high wet fastness profiles. The possibility of forming covalent bond between dyes and fibres had long been attractive to dye chemists, since attachment by physical adsorption and by mechanical obstruction had the disadvantage of either low wash fastness or high cost [7,8]. It was anticipated that the covalent attachment of the dye molecules to the fibre would produce very high fastness because covalent bonds were the strongest known binding forces between molecules [9,10]. They are used for the dyeing and printing of cellulose and to a lesser extent polyamide fibres. In addition, investigations into the development of reactive dyes

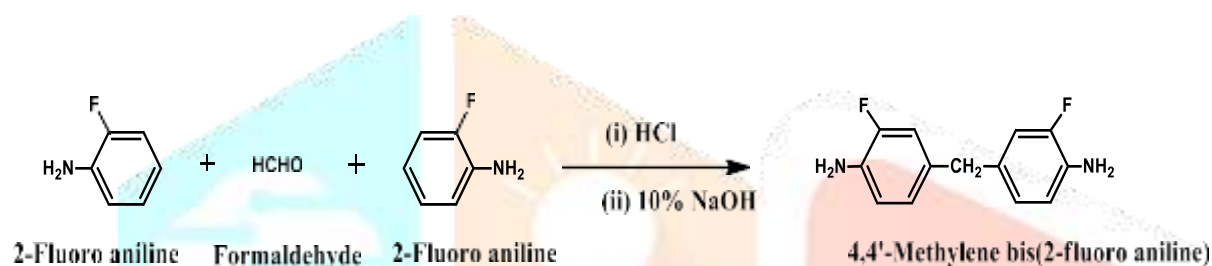
for polyester and polypropylene fibres have been demonstrated to the level of technical possibility but such dyes are not yet of commercial interest [11,12].

METHODS AND MATERIALS

Step-1: Synthesis of 4,4'-methylene bis(2-fluoro aniline) [13]

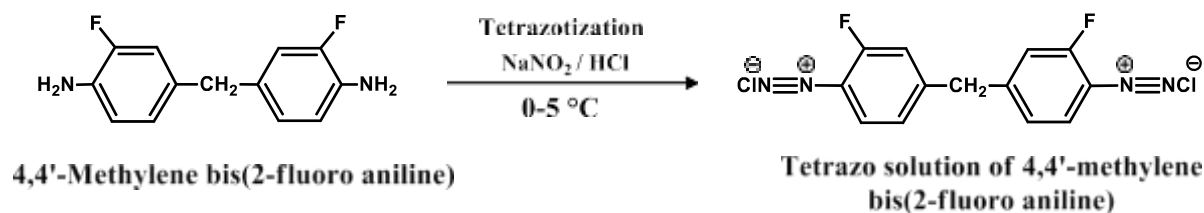
2-Fluoro aniline (11.11 g, 0.1 mol) was dissolved in water (125 ml) and 36.5% hydrochloric acid (25 ml) at 50°C. The reaction mixture was then treated with 3% aqueous formaldehyde solution (35 ml) at 60°C with stirring for an hour and neutralized with 10% sodium hydroxide to give yellow precipitates of 4,4'-methylene bis(2-fluoro aniline). It was filtered, washed with hot water, dried and recrystallized from ethanol.

Yield: 86 %, m.p. 247°C.



Step-2: Tetrazotization of 4,4'-methylene bis(2-fluoro aniline) [14]

4,4'-Methylene bis(2-fluoro aniline) (2.34 g, 0.01 mol) was suspended in H₂O (60 ml). Conc. 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 (1.38 g, 0.02 mol) in water (8 ml) was added to the above solution at 0°C temperature over a period of five minutes with continuous stirring. The stirring was continued for an hour, maintaining the same temperature, with positive test for nitrous acid on starch iodide paper. The excess of nitrous acid was destroyed with required amount of sulphamic acid solution in water. The clear tetrazotized solution at 0-5°C was obtained and used for subsequent coupling reaction.

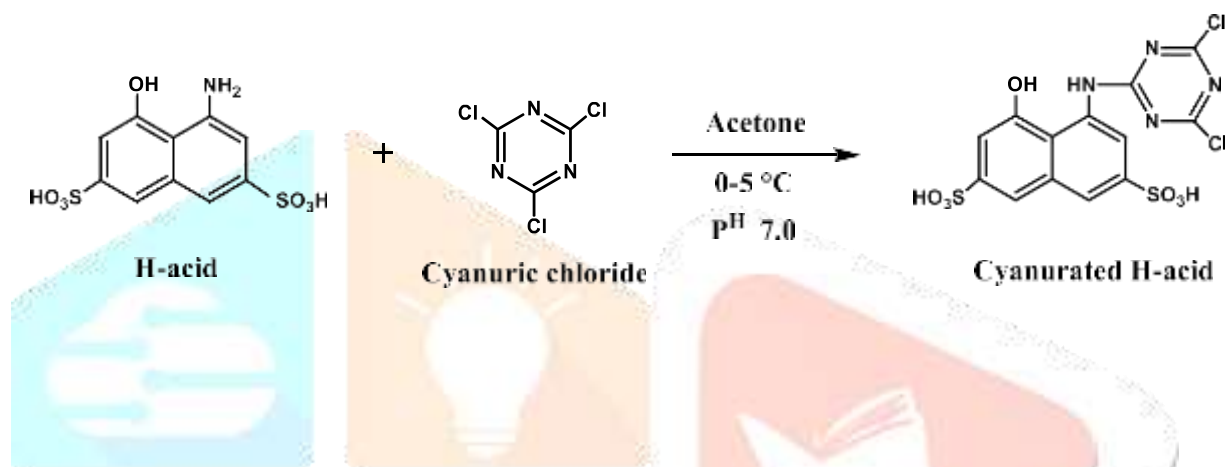


Step-3: Synthesis of 4- β -sulphatoethylsulphonylphenyl-1-amino cyanurated

H- acid [15]

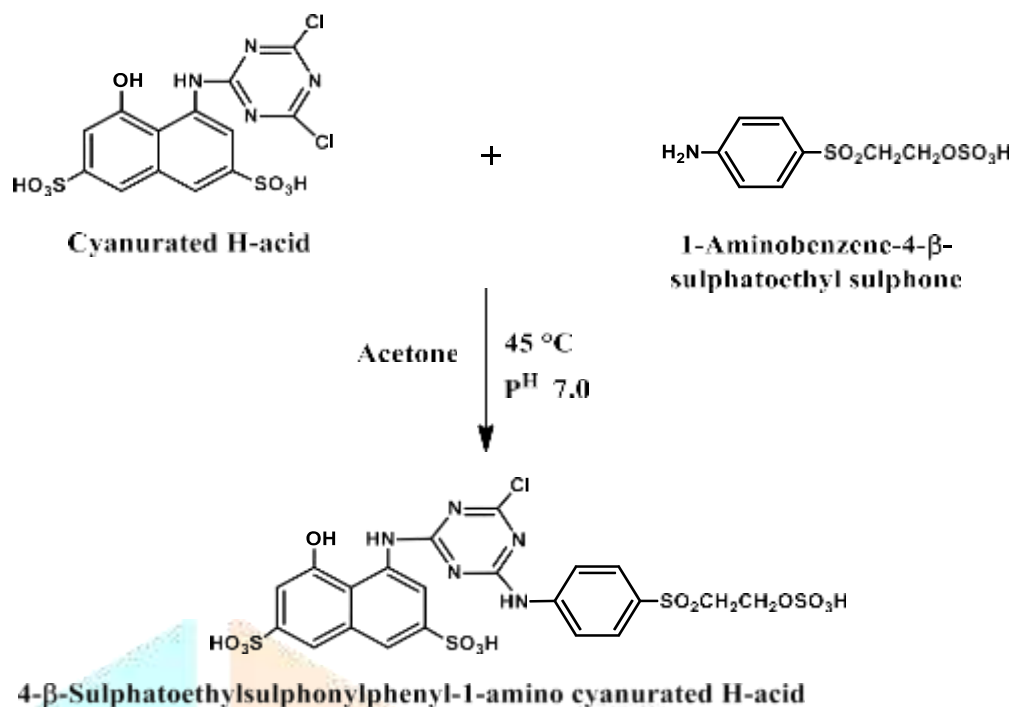
(i) Cyanuration of H-acid

Cyanuric chloride (3.69 g, 0.02 mol) was stirred in acetone (50 ml) at a temperature below 5°C for a period of an hour. A neutral solution of H-acid (6.38 g, 0.02 mol) in aqueous sodium carbonate solution (10% w/v) was then added in small lots in about an 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 4 hours. The cyanurated H-acid solution was used for subsequent coupling reaction.



(ii) Condensation with 1-aminobenzene-4- β -sulphatoethyl sulphone

The temperature of ice-cooled well stirred solution of cyanurated H-acid was gradually raised to 45°C. 1-Aminobenzene-4- β -sulphatoethyl sulphone (2.81 g, 0.01 mol) was added slowly to the cyanurated H-acid solution at same temperature during a period of 30 minutes, maintaining the pH neutral by simultaneous addition of sodium carbonate solution (1% w/v). After the addition was completed, stirring was continued for further 3 hours. The 4- β -sulphatoethylsulphonylphenyl-1-amino cyanurated H-acid solution thus obtained was subsequently used for further coupling reaction.

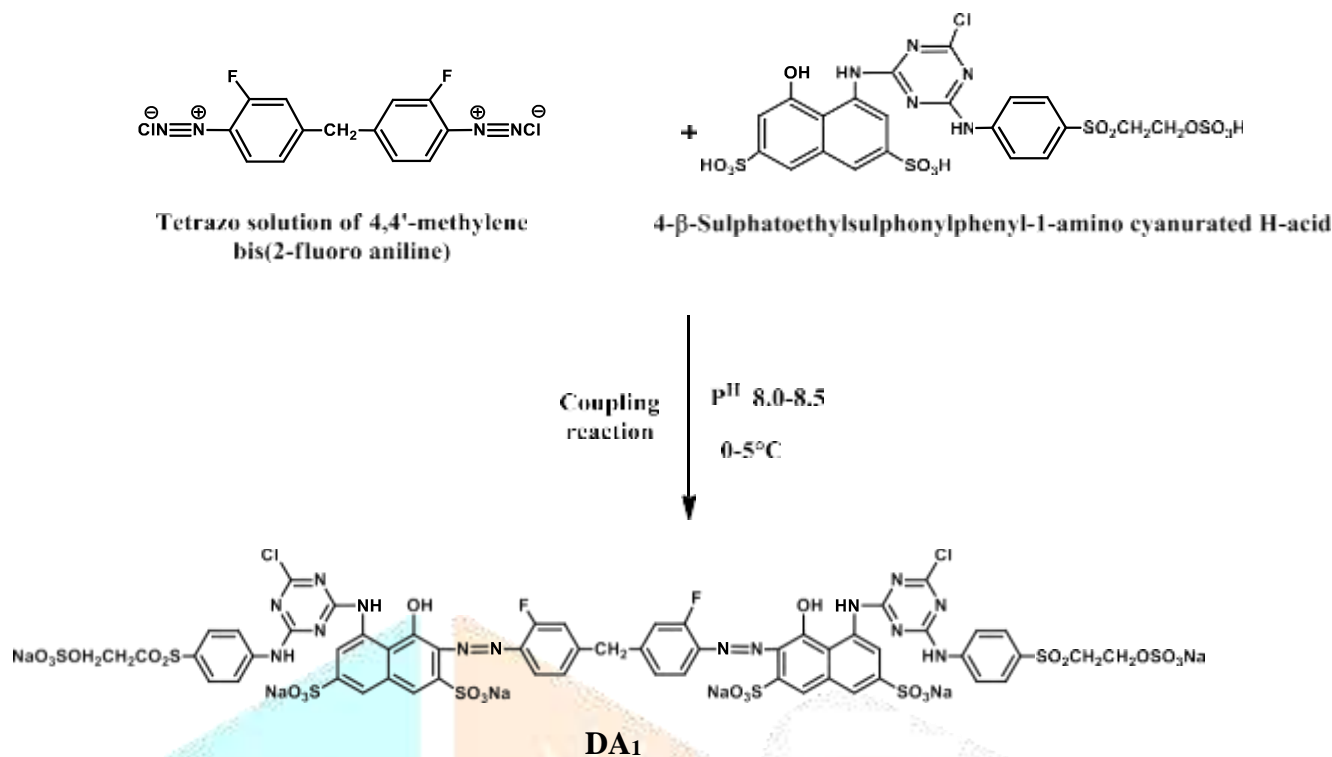


Step-4: Coupling of tetrazotized solution with 4-β-sulphatoethylsulphonylphenyl- 1-amino cyanurated H-acid coupling component:

Synthesis of dyes (DA₁ to DA₁₄)

The above mentioned freshly prepared tetrazotized solution was added to an ice cooled and well stirred solution of 4-β-sulphatoethylsulphonylphenyl-1-amino cyanurated H-acid over a period of 10-15 minutes. The pH was maintained at 8.0 to 8.5 by simultaneous addition of sodium carbonate solution (10% w/v) and stirring was continued at 0-5°C for 4 hours. Sodium chloride (15 g) was then added and the mixture was stirred for an hour. The solid dye separated out was filtered, washed with minimum amount of acetone and dried.

Following the above procedure, other reactive dyes **DA₂** to **DA₁₄** were synthesized by using 4-β-sulphatoethylsulphonylphenyl-1-amino cyanurated coupling components such as J-acid, N-Methyl J-acid, N-Phenyl J-acid, N-Benzoyl J-acid, Gamma acid, Peri acid, Bronner acid, Laurent acid, K-acid, S-acid, Tobias acid, Cleve acid and Koch acid.



RESULTS AND DISCUSSION

Dyeing of fibers: All the dyes were applied on silk, wool and cotton fibers by using the standard procedures [16]. A series of hot brand reactive dyes were synthesized in order to evaluate their stability for dyeing silk, wool and cotton fabrics. (Table- 2).

IR and ¹H NMR spectral study: The visible absorption spectra of all synthesized derivatives have been scanned in KBr pellets by using Shimadzu FTIR spectrometer. Spectrophotometer instrument region from 4000 cm⁻¹ to 667 cm⁻¹. The ¹H NMR spectra of representative dyes showed all the signals.

IR spectra: IR Spectra of DA₁ showed O-H stretching vibration of Ar-OH group at 3599 cm⁻¹, N-H stretching vibration of Secondary amine at 3466 cm⁻¹, C-H stretching vibration of -CH₂ group at 2910 cm⁻¹, and 2867 cm⁻¹, C=C stretching vibration of aromatic ring at 1626 cm⁻¹, and 1460 cm⁻¹, N-H bending of Secondary amine at 1506 cm⁻¹, C-H bending of -CH₂ group at 1475 cm⁻¹, N=N stretching vibration of azo group at 1595 cm⁻¹, O-H bending of Ar -OH group at 1396 cm⁻¹, SO₂ stretching vibration of -SO₂ group at 1338 cm⁻¹ and 1139 cm⁻¹, C-N stretching vibration of tertiary amine at 1360 cm⁻¹, S=O stretching vibration of -SO₃Na group at 1043 cm⁻¹, and 1184 cm⁻¹, C-F stretching vibration of -F group at 1139 cm⁻¹ and C-Cl stretching vibration at 761 cm⁻¹.

IR Spectra of DA₂ showed O-H stretching vibration of Ar-OH group at 3581 cm⁻¹, N-H stretching vibration of Secondary amine at 3421 cm⁻¹, C-H stretching vibration of -CH₂ group at 2910 cm⁻¹, and 2875 cm⁻¹, C=C stretching vibration of aromatic ring at 1620 cm⁻¹, and 1410 cm⁻¹, N-H bending of Secondary amine at 1519 cm⁻¹, C-H bending of -CH₂ group at 1491 cm⁻¹, N=N stretching vibration of azo group at 1450 cm⁻¹, O-H bending of Ar -OH group at 1405 cm⁻¹, SO₂ stretching vibration of -SO₂ group at 1330 cm⁻¹ and 1149 cm⁻¹, C-N

stretching vibration of tertiary amine at 1310 cm⁻¹, S=O stretching vibration of -SO₃Na group at 1066 cm⁻¹, and 1174 cm⁻¹, C-F stretching vibration of -F group at 1140 cm⁻¹ and C-Cl stretching vibration at 732 cm⁻¹.

IR Spectra of DA₆ showed O-H stretching vibration of Ar-OH group at 3599 cm⁻¹, N-H stretching vibration of Secondary amine at 3466 cm⁻¹, C-H stretching vibration of -CH₂ group at 2900 cm⁻¹, and 2850 cm⁻¹, C=C stretching vibration of aromatic ring at 1620 cm⁻¹, and 1411 cm⁻¹, N-H bending of Secondary amine at 1519 cm⁻¹, C-H bending of -CH₂ group at 1483 cm⁻¹, N=N stretching vibration of azo group at 1450 cm⁻¹, O-H bending of Ar -OH group at 1385 cm⁻¹, SO₂ stretching vibration of -SO₂ group at 1320 cm⁻¹ and 1150 cm⁻¹, C-N stretching vibration of tertiary amine at 1305 cm⁻¹, S=O stretching vibration of -SO₃Na group at 1066 cm⁻¹, and 1190 cm⁻¹, C-F stretching vibration of -F group at 1130 cm⁻¹ and C-Cl stretching vibration at 740 cm⁻¹.

¹HNMR spectra: ¹HNMR Spectra of dye DA₁ showed at 3.32-3.35(t, 4H, -CH₂- protons), 3.52(s, 2H, -CH₂- protons), 3.66 (s, 4H, -NH- protons), 3.76-3.78(t, 4H, -CH₂- protons), 4.06(s, 2H, -OH protons), 6.58-8.30 (m, 20H, aromatic protons).

Exhaustion and Fixation study: The percentage exhaustion of 2% dyeing on silk fiber ranges from 63.75 % to 75.25 %, for wool ranges from 66.25 % to 76.25 % and for cotton ranges from 68.50 % to 77.25 %. The percentage fixation of 2% dyeing on silk fiber ranges from 85.06 % to 90.45 %, for wool ranges from 84.59 % to 90.72 % and for cotton ranges from 85.40 % to 93.85% (Table-2).

Fastness properties: Fastness to light was assessed in accordance with BS:1006-1978 [17]. The rubbing fastness test was carried out by using Crock meter (Atlas) in accordance with the AATCC1961[18] and the wash fastness was carried out in accordance with IS:765-1979 [19].

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

CONCLUSION

2-fluoro aniline was diazotized and coupled with various 4-β-sulphatoethylsulphonylphenyl-1-amino cyanurated coupling components gave corresponding hot brand reactive dyes (DA₁ to DA₁₄). These dyes gave yellow to red shade on silk, wool and cotton fibers and showed fair to good light fastness, good to excellent fastness to washing and rubbing fastness. Exhaustion and fixation of these dyes are very good in order.

ACKNOWLEDGEMENTS

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Table 1: Physical properties of dyes DA₁-DA₁₄

Dye No.	Coupling component (R)	Molecular Formula	Mol. Weight g/mol	Yield (%)	M.P °C	Nitrogen %		Rf Value
						Found	Req.	
DA ₁	H-acid	C ₅₅ H ₃₆ Cl ₂ F ₂ N ₁₄ Na ₆ O ₂₆ S ₈	1812	80	>300	10.74	10.82	0.55
DA ₂	J-acid	C ₅₅ H ₃₈ Cl ₂ F ₂ N ₁₄ Na ₄ O ₂₀ S ₆	1608	79	>300	12.13	12.19	0.62
DA ₃	N-Methyl J-acid	C ₅₇ H ₄₂ Cl ₂ F ₂ N ₁₄ Na ₄ O ₂₀ S ₆	1636	82	>300	11.90	11.98	0.59
DA ₄	N-Phenyl J-acid	C ₆₇ H ₄₆ Cl ₂ F ₂ N ₁₄ Na ₄ O ₂₀ S ₆	1760	76	>300	11.21	11.14	0.58
DA ₅	N-Benzoyl J-acid	C ₆₉ H ₄₆ Cl ₂ F ₂ N ₁₄ Na ₄ O ₂₂ S ₆	1816	79	>300	10.73	10.80	0.56
DA ₆	Gamma acid	C ₅₅ H ₃₈ Cl ₂ F ₂ N ₁₄ Na ₄ O ₂₀ S ₆	1608	82	>300	12.11	12.19	0.54
DA ₇	Peri acid	C ₅₅ H ₃₈ Cl ₂ F ₂ N ₁₄ Na ₄ O ₁₈ S ₆	1576	78	>300	12.38	12.44	0.58
DA ₈	Bronner acid	C ₅₅ H ₃₈ Cl ₂ F ₂ N ₁₄ Na ₄ O ₁₈ S ₆	1576	81	>300	12.38	12.44	0.55
DA ₉	Laurent acid	C ₅₅ H ₃₈ Cl ₂ F ₂ N ₁₄ Na ₄ O ₁₈ S ₆	1576	83	>300	12.51	12.44	0.56
DA ₁₀	K-acid	C ₅₅ H ₃₆ Cl ₂ F ₂ N ₁₄ Na ₆ O ₂₆ S ₈	1812	79	>300	10.75	10.82	0.53
DA ₁₁	S-acid	C ₅₅ H ₃₈ Cl ₂ F ₂ N ₁₄ Na ₄ O ₂₀ S ₆	1608	81	>300	12.13	12.19	0.55
DA ₁₂	Tobias acid	C ₅₅ H ₄₀ Cl ₂ F ₂ N ₁₄ Na ₂ O ₁₂ S ₄	1372	83	>300	14.36	14.29	0.50
DA ₁₃	Cleve acid	C ₅₅ H ₃₈ Cl ₂ F ₂ N ₁₄ Na ₄ O ₁₈ S ₆	1576	77	>300	12.37	12.44	0.55
DA ₁₄	Koch acid	C ₅₅ H ₃₄ Cl ₂ F ₂ N ₁₄ Na ₈ O ₃₀ S ₁₀	1984	84	>300	9.82	9.88	0.60

Table 2. Dyeing performance of Dyes DA₁ - DA₁₄

Dye No.	Shade on silk fabrics	Shade on wool fabrics	Shade on cotton fabrics	Exhaustion %			Fixation %		
				S	W	C	S	W	C
DA ₁	Maroon	Dark pink	Purple	75.25	76.25	77.25	90.36	90.49	93.85
DA ₂	Brown	Dark brown	Brown	71.50	75.75	74.25	88.81	89.10	92.26
DA ₃	Orange	Orange	Light orange	70.25	73.75	74.50	88.26	88.13	90.60
DA ₄	Brown	Dark brown	Dark pink	69.75	72.75	72.50	88.17	90.72	88.28
DA ₅	Light orange	Buff	Light orange	69.50	74.25	72.00	85.61	89.56	89.58
DA ₆	Light brown	Light brown	Purple	70.75	74.75	71.50	90.45	89.63	86.71
DA ₇	Dark brown	Dark brown	Buff	71.75	76.00	74.25	88.50	88.81	89.56
DA ₈	Light orange	Orange	Light orange	69.75	75.25	71.25	88.17	88.37	90.53
DA ₉	Cream	Light orange	Cream	68.75	71.25	71.50	88.00	84.91	87.41
DA ₁₀	Light cream	Light yellow	Light cream	67.75	69.25	72.00	90.03	86.64	88.89
DA ₁₁	Light pink	Light pink	Light pink	65.25	66.25	71.00	85.06	85.28	88.73
DA ₁₂	Light orange	Orange	Orange	65.50	68.25	73.25	86.26	85.71	90.78
DA ₁₃	Light cream	Buff	Pale yellow	64.50	72.25	72.25	85.27	89.27	89.97
DA ₁₄	Light pink	Light pink	Light pink	63.75	69.75	68.50	85.49	84.59	85.40

Table 3. Fastness properties of dyes DA₁ - DA₁₄

Dye No.	Light Fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	S	W	C	S	W	C	S	W	C	S	W	C
DA ₁	5-6	5-6	5-6	4-5	5	4-5	5	4-5	4-5	5	5	4-5
DA ₂	4-5	5	4-5	5	4-5	4-5	5	5	4	4	5	4
DA ₃	5-6	4-5	3-4	5	4	4	5	5	3-4	4-5	4-5	4
DA ₄	5	5	4	4	4-5	4	4	5	3-4	5	5	4
DA ₅	3-4	4-5	4-5	3-4	5	4-5	3	4	4-5	3	3-4	4-5
DA ₆	5-6	4-5	4-5	5	5	4-5	4	4	4	4	4-5	4
DA ₇	5-6	5-6	5	5	4-5	5	5	4-5	4-5	4-5	4-5	4
DA ₈	5	5	4	4	4-5	4	4-5	5	4	4	4-5	4
DA ₉	4	4-5	3-4	3-4	4-5	3-4	4	4-5	3-4	3	4	3
DA ₁₀	4	4	3-4	5	4	3-4	5	4	4	4	4	3-4
DA ₁₁	3-4	4-5	4	3	3-4	3-4	4	4	3-4	3	3-4	4
DA ₁₂	4-5	4-5	4	4	5	3-4	4	4	4	4-5	3-4	3-4
DA ₁₃	5	5	4-5	4-5	5	4	4	4	4	4	4-5	4
DA ₁₄	4	4	3-4	3-4	4	3-4	4	4	4	4	4	4

Light fastness: 1-Poor , 2-Slight, 3-Moderate, 4-Fair, 5-Good, 6-Very good, 7-Excellent, 8- Maximum, **Wash fastness:** 1-Poor , 2-Fair, 3-Good, 4-Very good, 5-Excellent **Rubbing fastness:** 1-Poor, 2-Fair, 3-Good, 4-Very good, 5-Excellent

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