



Synthesis and Application of Monoazo Reactive Dyes on Silk, Wool and Cotton Fibers

Alkesh B. Patel¹, Parikshit I. Vashi¹, Vijay D. Patel¹, Dharmishtha H. Patel²,
Keshav C. Patel¹ and Paresh S. Patel^{1*}

1. Department of Chemistry, Veer Narmad South Gujarat University, Surat-395007, **INDIA**

2. Narmada College of Science and Commerce, Zadeshwar, Bharuch-392011, **INDIA**

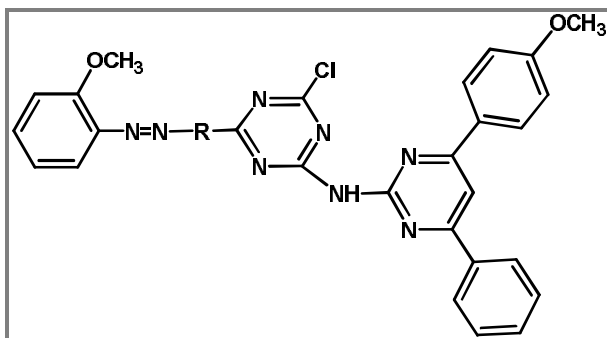
Email: ncscpsp@gmail.com

Accepted on 11th April, 2019

ABSTRACT

Various monoazo reactive dyes have been synthesized by coupling of diazotized *o*-anisidine with various 4-(4'-methoxyphenyl)-6-phenylpyrimidin-2-yl-amino cyanurated coupling components such as *H*-acid, *Gamma* acid, *J*-acid, *S*-acid, *Koch* acid, *Bronner* acid, *Tobias* acid, *Cleve* acid, *Peri* acid and *Laurant* acid. They were characterized by nitrogen elemental analysis, IR and ¹HNMR spectra. The dyeing performance of all these dyes on silk, wool and cotton has also been assessed.

Graphical Abstract



Synthesis of monoazo reactive dyes.

Keywords: 2-Amino-4-(4'-methoxyphenyl)-6-phenylpyrimidine, Characterization, Monoazo reactive dyes, Application.

INTRODUCTION

Reactive dyes constitute a very important class for dyeing cellulosic fiber and a high rate of growth is predicted in future. These dyes are coloured compounds which contain one or two groups capable of forming covalent bonds between a carbon 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

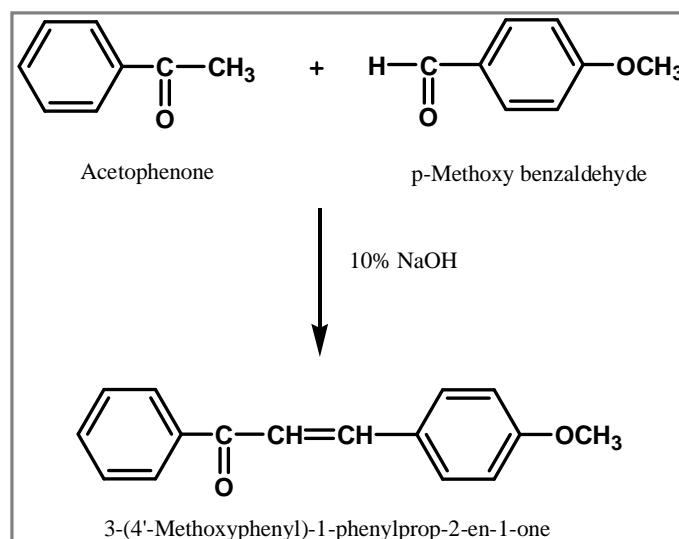
substrate. Such covalent bonds are formed with the amino, hydroxyl groups of cellulosic fibers, with the amino, hydroxyl and mercapto groups of protein fibers and with the amino groups of polyamides [1]. In general, reactive dyes are the only textile colour designed to bond covalently with the substrate on application. They are used for the dyeing and printing of cellulose and to a lesser extent polyamide fibers. They are valued for their brilliance and variety of hue, versatility and high wet fastness profiles.

The first commercial reactive dyes for cellulose were synthesized by Rattee and Stephen and marketed by ICI in 1956 under the trade name Procion M [2-7]. Several new reactive systems have been introduced from time to time, which covers the subject of innumerable patents and publications [8-10]. Over the last decade a number of major changes have been taken place, primary aimed at minimizing the major weakness of reactive dyes for facilitating new application condition. In this period, monoazo reactive dyes [11-13] and bisazo reactive dyes [14-16] have been established as a major group for fixation to cellulose.

MATERIALS AND METHODS

The melting points of the compounds were determined using open capillary and are uncorrected. The purity of dyes was determined by thin-layer chromatography using silica gel-G coated Al plates. IR spectra were recorded on SHIMADZU, Model: FTIR 8400S using KBr pellets. ¹H NMR spectra were obtained on Bruker Avance-II 400 NMR spectrometer using D₂O solvent and TMS as internal reference (chemical shifts in δ, ppm).

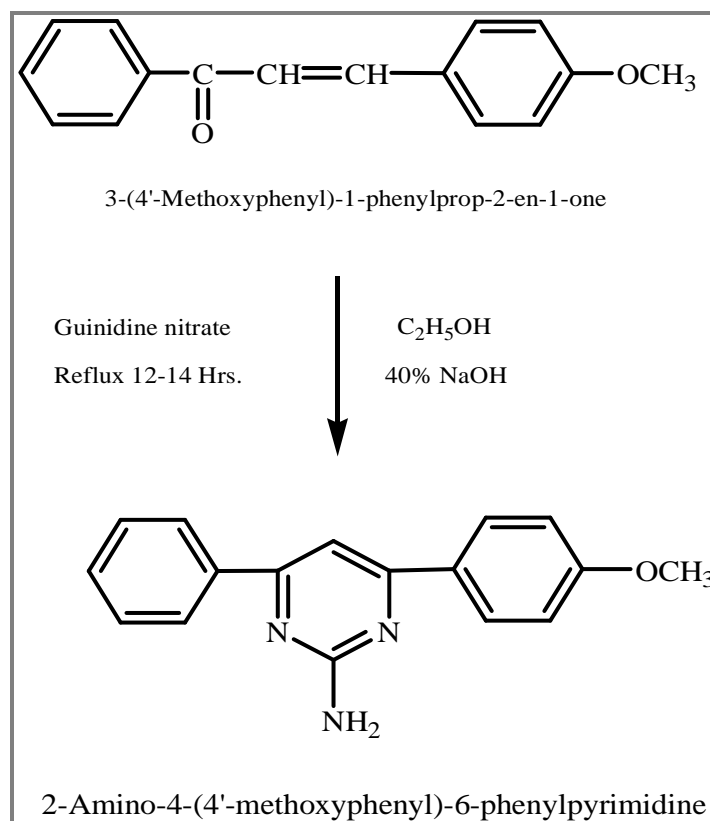
Step-1: Synthesis of 3-(4'-methoxyphenyl)-1-phenylprop-2-en-1-one [17]: To a stirred mixture of acetophenone (1.2015 g, 0.01 mol) and 4-methoxy benzaldehyde (1.3615 g, 0.01 mol) in absolute ethanol (10.0 mL), sodium hydroxide (10% w/v, 10.0 mL) was added dropwise and continues stirring for two hours at room temperature and allowed to stand reaction mixture for 12 h. The content was then poured over crushed ice and acidified with dilute hydrochloric acid. Filtered the precipitate, and washed with cold ethanol, dried and recrystallized from ethanol, Yield 87%, m.p 79°C.



Step 1. Synthesis of 3-(4'-methoxyphenyl)-1-phenylprop-2-en-1-one.

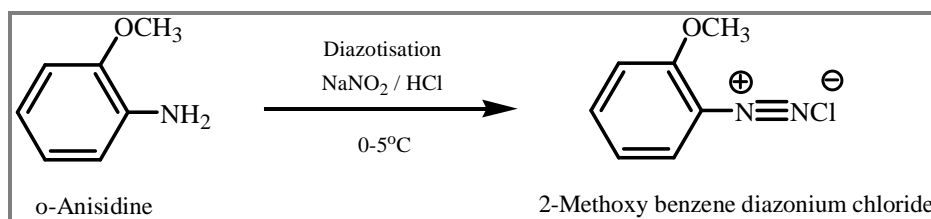
Step-2: Synthesis of 2-amino-4-(4'-methoxyphenyl)-6-phenylpyrimidine [18]: A mixture of substituted chalcone (2.38 g, 0.01 mol) and guanidine nitrate (1.22 g, 0.01 mol) was dissolved in ethanol (30 mL). Aqueous solution of sodium hydroxide (40%, 1.0 ml) was added and the reaction mixture was refluxed. Further installments of sodium hydroxide (4x1 mL) were added during two

hours to the refluxing solution. Refluxing was continued (10-12 h) and the completion of the reaction was monitored by TLC. The resultant mixture was cooled at room temperature, diluted with water (3 x 100 mL) and neutralized with cold dilute HCl (10%). The product thus separated was filtered out, washed with water dried and crystallized from ethanol, Yield : 85%, m.p: 92°C. Found: N, 15.13%, required: 15.16%.



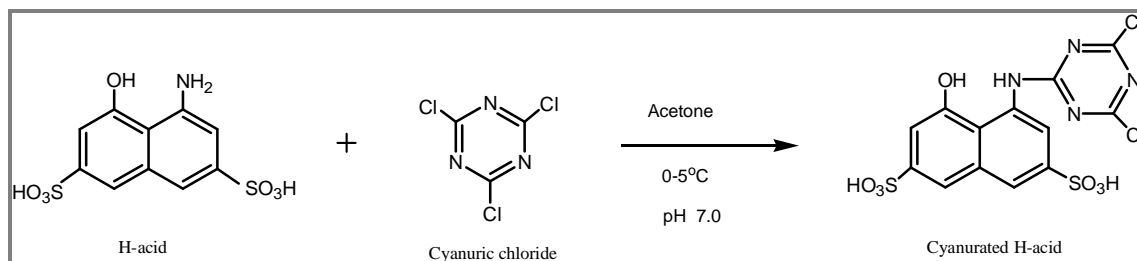
Step 2. Synthesis of 2-amino-4-(4'-methoxyphenyl)-6-phenylpyrimidine.

Step-3:Diazotization of o-anisidine [19]: o-Anisidine (1.23 g, 0.01 mol) was suspended in water (120 mL). Hydrochloric acid (1.09 g) was added dropwise to this well stirred suspension. The mixture was gradually heated up to 70°C, till clear solution obtained. The solution was cooled at 0-5°C in an ice bath. A solution of NaNO₂ (1.38 g) in water (8 ml) previously cooled to 0°C, was then added over a period of five minutes with stirring. The stirring was continuous for an hour, maintaining the same temperature, with positive test for nitrous acid on starch iodide paper. After just destroying excess of nitrous acid with require amount of a solution of sulphamic acid. The clear diazo solution at 0-5°C was used for subsequent coupling reaction.



Step 3. Diazotization of o-anisidine.

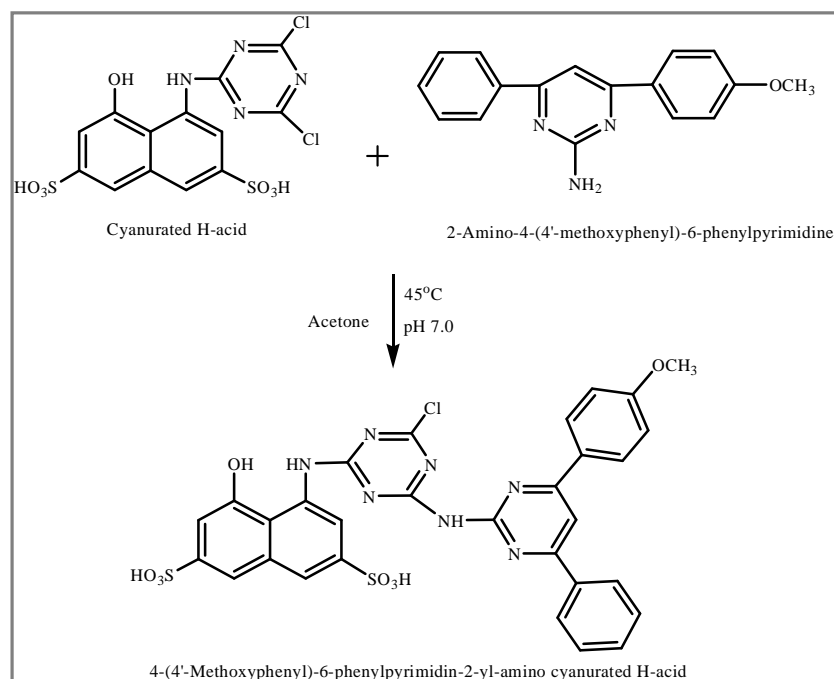
Step-4: Synthesis of 4-(4'-methoxyphenyl)-6-phenylpyrimidin-2-yl-amino cyanurated H-acid: It consists two steps: 1. Cyanuration of H-acid, 2. Condensation with 2-amino-4-(4'-methoxyphenyl)-6-phenylpyrimidine.



Step 4. Synthesis of 4-(4'-methoxyphenyl)-6-phenylpyrimidin-2-amino cyanurated H-acid
1. Synthesis of cyanurated H-acid

Cyanuration of H-acid: Cyanuric chloride (1.85 g, 0.01 mol) 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 mol) in aqueous Na₂CO₃ 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 stirred at 0-5°C for further 4 h then clear solution was obtained. The cyanurated H-acid solution was used for subsequent coupling reaction.

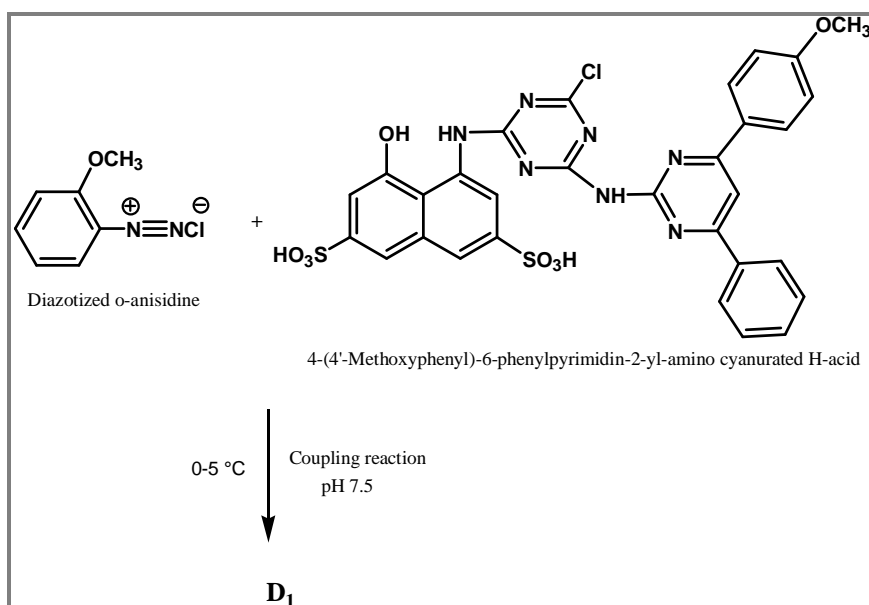
Condensation with 2-amino-4-(4'-methoxyphenyl)-6-phenyl pyrimidine: The temperature of ice-cooled well stirred solution of cyanurated H-acid was gradually raised to 45°C for half an hour. To this cyanurated H-acid, the 2-amino-4-(4'-methoxyphenyl)-6-phenylpyrimidine (2.77g, 0.01 mol) dissolve in acetone was added dropwise at same temperature, during a period of 30 min, 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 4-(4'-methoxyphenyl)-6-phenylpyrimidin-2-yl-amino cyanurated H-acid solution thus obtained was subsequently used for further coupling reaction.



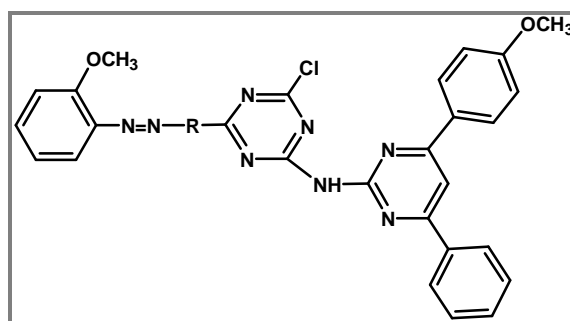
2. Synthesis of 4-(4'-methoxyphenyl)-6-phenylpyrimidin-2-amino cyanurated H-acid

Step-5: Synthesis of monoazo reactive dyes

Coupling of diazo solution with 4-(4'-methoxyphenyl)-6-phenylpyrimidin-2-yl-amino cyanurated H-acid: To an ice cold and stirred solution of 4-(4'-methoxyphenyl)-6-phenylpyrimidin-2-yl-amino cyanurated H-acid, a freshly prepared solution of diazo solution as previously prepared 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 an hour. The solid purple dye separated out was filtered, washed with minimum amount of acetone and dried at room temperature, Yield 84%. Found: N, 14.20 %, required: 14.22 %.



Synthesis of D₁



Where, R = Various coupling components such as Gamma acid, J-acid, S-acid, Koch acid, Bronner acid, Tobias acid, Cleve acid, Peri acid and Laurant acid.

Step 5. Coupling reaction of diazotized o-anisidine with 4-(4'-methoxyphenyl)-6-phenylpyrimidin-2-yl-amino cyanurated H-acid :
Synthesis of D₁ to D₁₀:

RESULTS AND DISCUSSION

Visible absorption spectra: The visible absorption spectra of all synthesized dyes have been recorded on in water and observed in the range of 547-425 nm. The colour observed for each dye is due to the oscillation of electrons and presence of substituents.

IR spectra: IR Spectra of D₂ showed O-H stretching vibration of -OH group at 3451 cm⁻¹, N-H stretching vibration of -NH-group at 3310 cm⁻¹, C-H stretching vibration of -OCH₃ group at 2820 cm⁻¹, C=C stretching vibration of aromatic ring at 1490 cm⁻¹ and 1660 cm⁻¹, C-N stretching vibration of tertiary amine at 822 cm⁻¹, 880 cm⁻¹ and 1420 cm⁻¹, N=N stretching vibration of azo group at 1445 cm⁻¹, S=O stretching vibration of -SO₃Na group at 1035 cm⁻¹, 1176 cm⁻¹ and 1260 cm⁻¹, S=O stretching vibration of SO₂ group at 1130 cm⁻¹ and C-Cl stretching vibration at 780 cm⁻¹.

IR Spectra of D₄ showed O-H stretching vibration of -OH group at 3464 cm⁻¹, N-H stretching vibration of -NH- group at 3220 cm⁻¹, C-H stretching vibration of -OCH₃ group at 2840 cm⁻¹, C=C stretching vibration of aromatic ring at 1490 cm⁻¹ and 1662 cm⁻¹, C-N stretching vibration of tertiary amine at 847 cm⁻¹, 880 cm⁻¹ and 1420 cm⁻¹, N=N stretching vibration of azo group at 1456 cm⁻¹, S=O stretching vibration of -SO₃Na group at 1040 cm⁻¹, 1180 cm⁻¹ and 1262 cm⁻¹, S=O stretching vibration of SO₂ group at 1117 cm⁻¹ and C-Cl stretching vibration at 780 cm⁻¹.

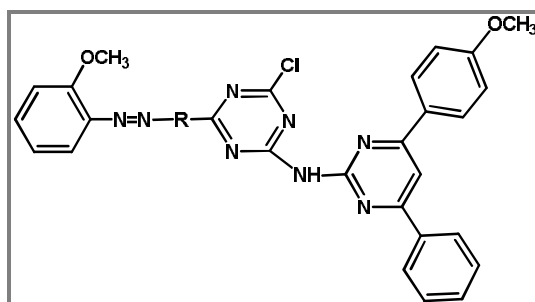
IR Spectra of D₈ showed O-H stretching vibration of -OH group at 3460 cm⁻¹, N-H stretching vibration of -NH- group at 3240 cm⁻¹, C-H stretching vibration of -OCH₃ group at 2820 cm⁻¹, C=C stretching vibration of aromatic ring at 1490 cm⁻¹ and 1660 cm⁻¹, C-N stretching vibration of tertiary amine at 847 cm⁻¹, 882 cm⁻¹ and 1410 cm⁻¹, N=N stretching vibration of azo group at 1445 cm⁻¹, S=O stretching vibration of -SO₃Na group at 1030 cm⁻¹, 1176 cm⁻¹ and 1260 cm⁻¹, S=O stretching vibration of SO₂ group at 1117 cm⁻¹ and C-Cl stretching vibration at 780 cm⁻¹.

¹HNMR spectra: ¹HNMR Spectra of dye D₈ showed signals at 2.77(s, 6H, -OCH₃ protons, 4.72(s, 2H, -NH- protons) and 6.8-8.30 (m, 19H, aromatic protons).

APPLICATION

Dyeing of fibers: All the dyes were applied on silk, wool and cotton fibers by using the standard procedures [20] (Table 1).

Table 1. Characterization of monoazoreactive dyes



Where, R = various coupling components

Dye No.	Coupling component (R)	Molecular Formula	Mol. Weight g mol ⁻¹	Yield (%)	%Nitrogen		R _f Value
					Found	Required	
D ₁	H-acid	C ₃₇ H ₂₆ O ₉ N ₉ ClS ₂ Na ₂	886	85%	14.20	14.22	0.39
D ₂	Gamma acid	C ₃₇ H ₂₇ O ₆ N ₉ ClSNa	784	83%	16.04	16.07	0.42
D ₃	J-acid	C ₃₇ H ₂₇ O ₆ N ₉ ClSNa	784	83%	16.03	16.07	0.45
D ₄	S-acid	C ₃₇ H ₂₇ O ₆ N ₉ ClSNa	784	79%	16.05	16.07	0.39
D ₅	Koch acid	C ₃₇ H ₂₆ O ₉ N ₉ ClS ₂ Na ₂	886	82%	14.19	14.22	0.38
D ₆	Bronner acid	C ₃₇ H ₂₇ O ₅ N ₉ ClSNa	768	84%	16.37	16.40	0.41
D ₇	Tobias acid	C ₃₇ H ₂₈ O ₂ N ₉ Cl	666	85%	18.89	18.92	0.44
D ₈	Cleves acid	C ₃₇ H ₂₇ O ₅ N ₉ ClSNa	768	83%	16.37	16.40	0.38
D ₉	Peri acid	C ₃₇ H ₂₇ O ₅ N ₉ ClSNa	768	80%	16.36	16.40	0.36
D ₁₀	Laurent acid	C ₃₇ H ₂₇ O ₅ N ₉ ClSNa	768	78%	16.38	16.40	0.41

Exhaustion and Fixation study: The percentage exhaustion of 2% dyeing on silk fiber ranges from 67.70-75.92 %, for wool ranges from 67.22-74.62 % and for cotton ranges from 68.57-75.40 %. The percentage fixation of 2% dyeing on silk fiber ranges from 87.36-91.94 %, for wool ranges from 87.02-91.60 % and for cotton ranges from 87.85-91.48% (Table 2).

Table 2. Dyeing performance of Dyes D₁ to D₁₀

Dye No.	Shade on silk fiber	Shade on wool fiber	Shade on cotton fiber	% Exhaustion			% Fixation		
				S	W	C	S	W	C
D ₁	Maroon	Wine red	Light pink	75.92	68.77	70.02	90.87	91.60	90.68
D ₂	Reddish brown	Dark brown	Brown	67.97	71.72	75.40	91.94	89.22	89.52
D ₃	Light maroon	Maroon	Dark brown	72.75	69.47	69.17	91.40	89.24	89.62
D ₄	Brown	Brown	Light brown	70.70	67.22	70.47	90.52	87.02	90.10
D ₅	Yellow	Yellow	Light yellow	68.65	73.05	68.57	91.76	88.98	91.14
D ₆	orange	Orange	Light yellow	75.05	67.00	72.95	91.27	88.05	90.47
D ₇	Yellowish brown	Yellow	Light yellow	67.70	74.62	70.50	91.58	87.77	91.48
D ₈	Brown	Yellowish brown	Light brown	74.40	67.82	73.17	87.36	91.41	88.82
D ₉	Light orange	Light orange	Light pink	70.67	70.97	72.27	90.55	89.46	87.85
D ₁₀	Orange	Orange	Light yellow	74.22	68.22	73.97	88.24	90.87	88.54

Fastness properties: Fastness to light was assessed in accordance with BS:1006-1978 [21]. The rubbing fastness test was carried out by using Crock meter (Atlas) in accordance with the AATCC-1961 [22] and the wash fastness was carried out in accordance with IS:765-1979 [23].

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

Table 3. Fastness properties of dyes D₁ to D₁₀

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

CONCLUSION

o-Anisidine was diazotized and coupled with various 4-(4'-methoxyphenyl)-6-phenylpyrimidin-2-yl-amino cyanurated coupling components gave corresponding monoazo reactive dyes (D₁ to D₁₀). These dyes gave violet to yellow 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. The presence of triazine group of dye molecule improves the exhaustion, fixation and fastness properties.

ACKNOWLEDGEMENTS

Authors are thankful to Atul Products Ltd., Atul, Valsad, India for providing dyeing facility and SAIF, Chandigarh for spectral data.

REFERENCES

- [1]. H. Zollinger, Color Chemistry, 2nd Ed., Weinheim: VCH, **1991**.
- [2]. D. M. Lewis, *Wool Science Review*, **1974**, 49, 13.
- [3]. C. V. Stead, *Colourage Annual*, **1969**, 17, 69.
- [4]. H. K. Rouette, J. F. K. Wilshire, I. Yamase, H. Zollinger, Dye Fiber Bond stabilities of Some Reactive Dyes with Wool, *Textile Research Journal*, **1971**, 41(6), 518-525.
- [5]. D. M. Lewis, A. H. M. Renfrew, A. A. Siddique, The synthesis and application of a new reactive dye based on disulfide-bis-ethylsulfone, *Dyes and Pigments*, **2000**, 47(1-2), 151-167.
- [6]. I. D. Rattee, W. E. Stephen, *Journal of the Society of Dyers and Colourists*, **1960**, 76(1), 6.
- [7]. P. J. Dolby, *American Dyestuff Reporter*, **1976**, 65(3), 28.
- [8]. Sumitomo Chemical Co. Ltd., Jap. Kokai Tokkyo Koho JP 81, 103, 249, **1981**.
- [9]. E. Seigel, The Chemistry of Synthetic Dyes, Ed. K. Venkataraman, 6, 130, Academic Press, New York, **1972**.
- [10]. ICI, BP 727, 892, **1967**, EGP 68, 58, **1968**.
- [11]. Pratixa K. Patel, Sandip K. Patel, Paresh S. Patel and Keshav C. Patel, Synthesis of Monoazo Reactive Dyes based on 4,4'-Methylene bis-(2-nitro aniline) and their Dyeing Performance on Various Fibres *International Journal of Science and Research*, **2014**, 3(12), 2269-2274.
- [12]. Pratixa K. Patel, Sandip K. Patel, Paresh S. Patel, Keshav C. Patel, Synthesis of monoazo reactive dyes and their dyeing performance on various fibres *International Journal of Recent Scientific Research*, **2015**, 6(2), 2646-2649.
- [13]. Prakash M. Bhate, Rajkumari Vijilata Devi, Rajaram Dugane, Pratik R. Hande, Lisan Shaikh, Samiksha Vaidya, Shruti Masand, A novel reactive dye system based on diazonium salts, *Dyes and Pigments*, **2017**, DOI 10.1016/j.dyepig. 2017. 06.007.
- [14]. Dharmishtha H. Patel, Paresh S. Patel, Keshav C. Patel, Synthesis of bisazo reactive dyes and their dyeing performance on various fibres *International Journal of Recent Scientific Research*, **2015**, 6(12), 7655-7600.
- [15]. M.S. Patel, S.K. Patel, K.C. Patel, Proceeding of National Academic of Science India, Sec.A, **2001**, 71(1), 5
- [16]. Hongjuan Zhang, Han Yang, Kongliang Xie, Aiqin Hou, Aiqin Gao, Novel reactive dyes with intramolecular color matching combination containing different chromophores, *Dyes and pigments*, **2018**, DOI:10.1016/j.dyepig.2018.07.031.
- [17]. Alka Choudhary, Vijay Juval, Synthesis of chalcone and their derivatives as antimicrobial agents, *International Journal of Pharmacy and Pharmaceutical Science*, **2011**, 3(3), 125-128.
- [18]. Clark, English, Winnek, Marson, *Cole and Clapp, J.Am.Chem.Soc.*, **1946**, 68,96.
- [19]. S. M. Burkinshaw, G. M. Collins, *Dyes and Pigm.*, **1994**, 25, 31.
- [20]. V. A. Shenai, Chemistry of Dyes and Principle of Dyeing, Sevak Publication, Mumbai, **1973**.
- [21]. Standard Test Method BS 1006(UK); ISO 105, India, **1994**.
- [22]. AATCC Test Method, **1961**, 8.
- [23]. Indian Standard, ISO, **1979**, 765.