

SYNTHESIS AND DYEING PERFORMANCE OF SOME NOVEL DISPERSE DYES BASED ON 1, 3, 4 – THIADIAZOLE MOIETY

¹Harshit R. Desai,²Parth Naik
¹Ph.D, Scholar,²Assistant professor
¹Department of Chemistry,
¹Uka Tarsadiya University, Bardoli, India.

Abstract: The synthesis and application of azo dyes derived from 2-amino 5-mercapto 1, 3, 4 – thiadiazole on polyester fiber are described. These dyes were characterized by IR spectra, ¹H – NMR spectra and elemental analysis. The dyed fiber showed good to excellent fastness properties. The dye bath exhaustion and fixation on polyester fiber was found to be very good.

Key words: Amino thiadiazole, disperse azo dyes, tertiary aromatic amines, fastness properties.

1. INTRODUCTION

Azo compounds are class of chemical compounds that are continuously receiving attention in scientific research. They are usually strongly coloured compounds which can be intensify yellow, red, orange, blue, green depending on the exact structure of the molecule. As a result of their colour, azo compounds are tremendous importance as dyes and also as pigment for a long time. Infact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts.

Disperse dyes are aromatic compounds and soluble in organic solvents but sparingly soluble in water. They can dye hydrophobic fibers such as nylon, polyester and acetate at high pressure and temperature. Interest in the design of azo dyes containing heterocyclic moieties stems from their high degree of brightness shade compared to analogous dyes derived from carbocyclic aromatic systems.

The present paper reports on the synthesis of some novel heterocyclic azo compounds based on 2-amino 5-mercapto 1,3,4 – thiadiazole and coupled with various tertiary amine to form disperse dyes which were applied on polyester fiber and their fastness properties were evaluated.

2. Materials & Methods

All the employed chemicals were of analytical reagent grade. The tertiary aromatic amines shown in Table – II which were used for coupling were gifted by colourtax ltd, Sachin, Gujarat. Melting points were determined by open capillary method and are uncorrected. The IR spectra were recorded in KBr pellets on a Perkin Elmer spectro-400 (SAIF, Chandigarh). An Infra colour dyeing machine was used for dyeing of polyester fabrics.

2.1 Experimental:

Step-I Preparation of N,N'-bis(thiocarbamoyl) hydrazine

The mixture of mono hydrazine sulphate (5 gms, 0.06 mole) and ammonium thiocyanate (3.4 gms,0.03 mole) and water (10 ml) was refluxed 4 hrs. on a water bath, after a few minutes the solution becomes clear yellow and a vigorous reaction took place with evolution of H₂S and NH₃, after 40-50 minutes, a white crystals formed. After 4 hrs. Heating, the mixture was boiled 15-20 minutes, then the reaction mixture cooled, the white crystals of N.N'-bis(thiocarbamoyl) hydrazine is formed, filtered and washed with water. Recrystallised from hot water.

Step-II Preparation of 2-amino 5-mercapto 1,3,4- thiadiazole

2-amino 5-mercapto 1,3,4-thiadiazole was synthesized from N.N'-bis(thiocarbamoyl)hydrazine with HCl in presence of H₃PO₂. The mixture of 2.5 ml 1% H₃PO₂ diluted to 40 ml with water and 10 ml concentrated HCl heated for half an hour, then add N.N'- bis (thiocarbamoyl)hydrazine (1.53 gms, 0.01 mole), refluxed the mixture till the reaction is complete, cooled to room temperature, the crystals formed, filtered off, washed with water and dried at 90°C.

Step-III Diazotisation of 2-amino 5-mercapto 1,3,4- thiazole

Dry Sodium nitrite (0.69g, 0.01 mole) was added portion wise to concentrated sulphuric acid (2.0mL) under stirring below 5°C. Then it is cooled to 0°C and 2-amino 5-mercapto 1,3,4-thiadiazole(1.33g, 0.01mole) was added portion wise and stirring is continued at 0° C for 2 hours. The excess of nitrous acid (gave a positive test on SI paper) was decomposed by adding required amount of urea. Thus resulting diazonium salt solution was used for the subsequent coupling reaction.

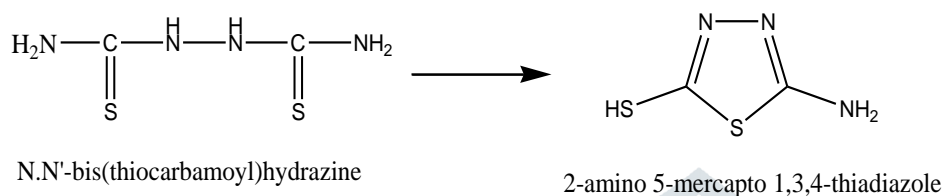
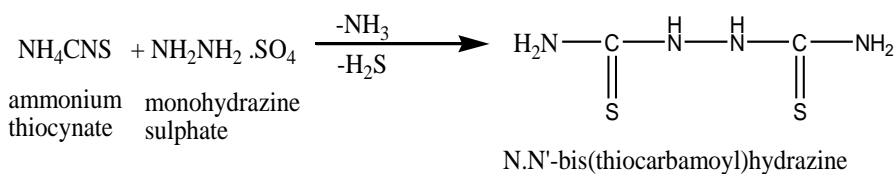
Step-IV

Preparation of various disperse dyes

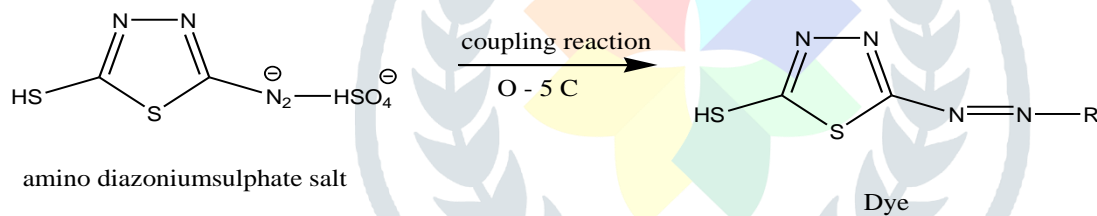
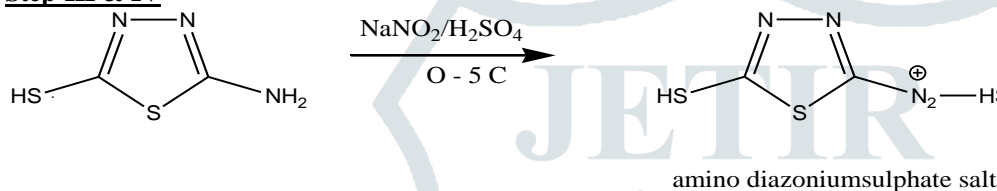
In this step, the diazonium salt prepared in step-III was coupled with various substituted tertiary amines at pH 4-5 at temperature 0-5°C for 1 hours to yield disperse dyes with yield 70 to 85%. In the similar way different coupling compounds were used to form a series of various acid dyes as shown in Table-1.

2.2 Reaction scheme

Step- I & II



Step-III & IV



R= Various coupling compounds

2.3 Process of Dyeing

0.04 gm weighed sample of dye is taken in a 100 ml beaker and dissolving it in 2 ml of DMF solution. The solution is furthering diluted with dispersing solution. Dispersing agent used is dispergator FNA. Water is used as a solvent. The cloth is folded and put in hot pots sequentially. The temperature is set at 130° C. Initially the temperature is 31.5 °C and it is increase at the rate of 30° C for every 1 min. After 1 hour, the dyed cloth is removed and washed with sodium hydrogen sulphite and NaOH solution.

Table- I Dye batch material used

Dye Bath Materials	
Materials	Polyester
Fibre(g)	2 g
Amount of dye (g)	0.04 g
Glauber's salt (20%)	2.5-3.0 ml
Acetic acid solution	1.5-2.0 ml
pH	5.0
MLR	1:50
Dyeing time (min)	60 min
Dyeing temp. (° C)	130°C
Total volume	100 ml

3. Result and Discussion:

3.1 Physical properties of the dyes

A series of azo dyes were prepared by diazotization and coupling reaction. The synthesized dyes were then dried in oven at temperature of 50° C. These dyes were then recrystallised from acetone and DMF solvents and obtained as crystalline powders. These dyes gave wide range of colours ranging from reddish orange to violet.

3.2 Analytical and spectral data of dyes

The IR & ¹H NMR data of synthesized dyes are given in table III & IV.

3.3 Dyeing properties of dyes

The disperse mono azo dyes were applied at a 2% depth on polyester fiber. Their dyeing properties are given in table –VI , VII. These dyes gave wide range of colours varying from reddish orange to violet shades with excellent brightness and depth on fiber. The variation in the shades of the dyed fabric results from both the nature and position of the substitute present on the coupling compound. The dyed fiber showed good to excellent fastness to washing and perspiration (acidic and alkaline). Washing fastness of the selected dyes were carried out according to ISO 105 CO3 method. Perspiration (acidic and alkaline) fastnesses of the selected dyes were carried out according to the ISO 105 E04 method.

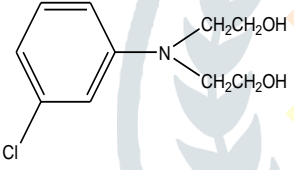
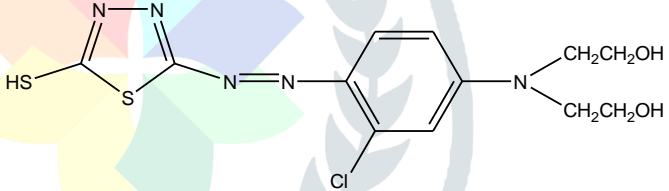
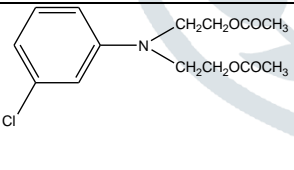
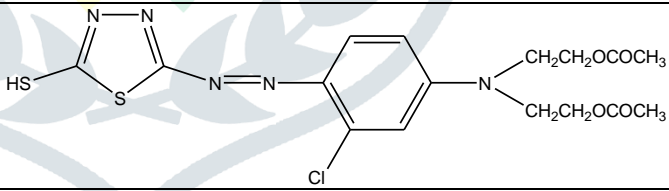
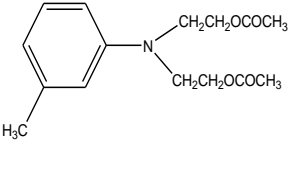
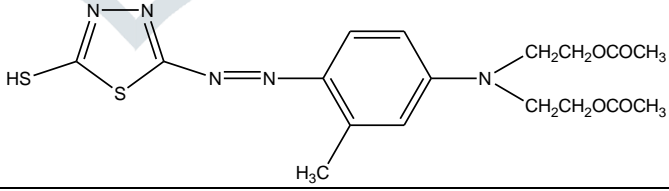
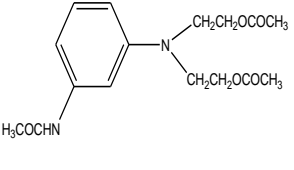
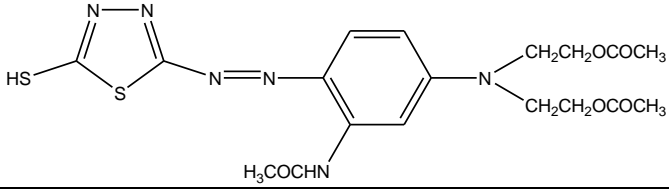
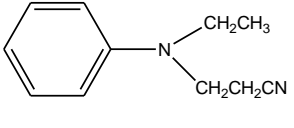
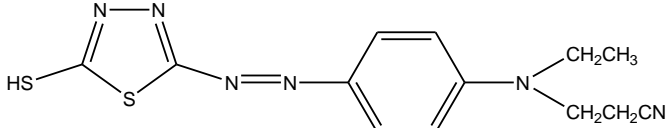
3.4 Determination of percentage exhaustion and fixation

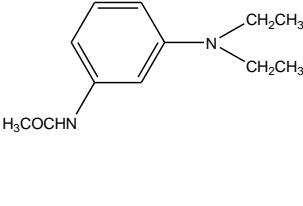
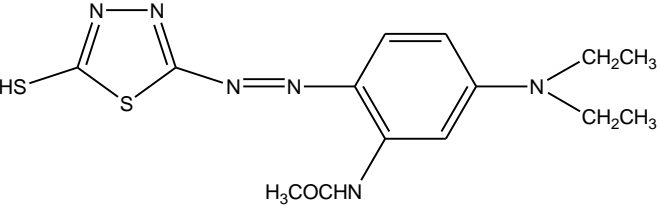
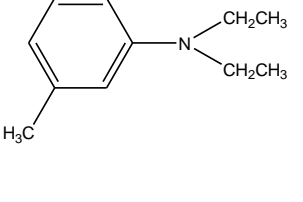
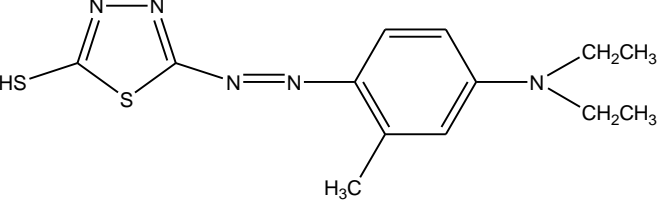
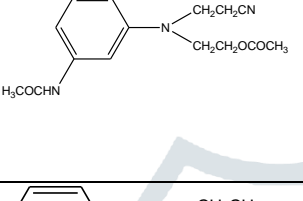
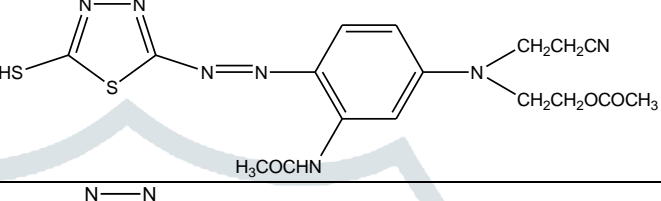
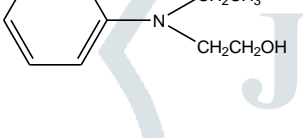
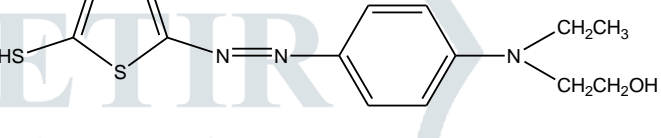
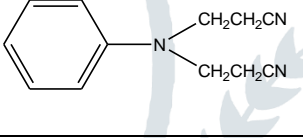
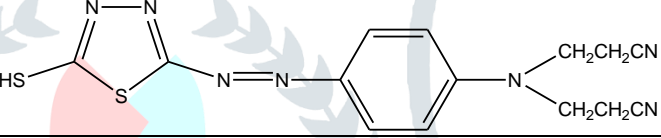
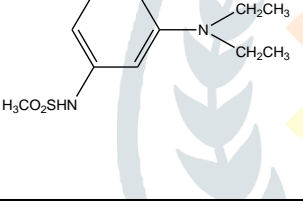
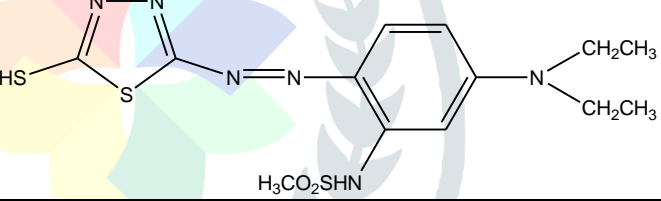
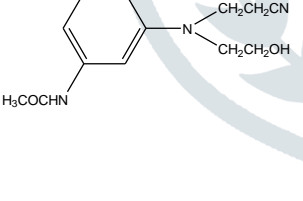
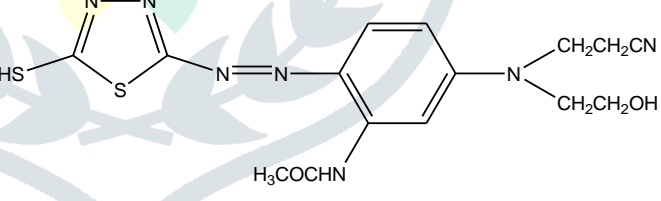
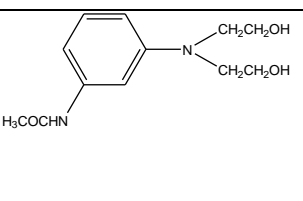
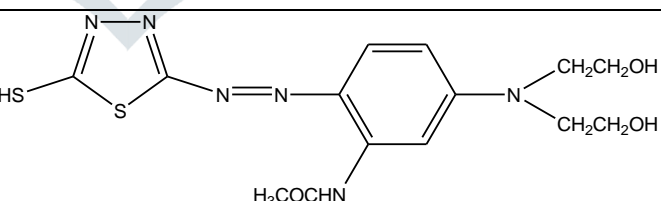
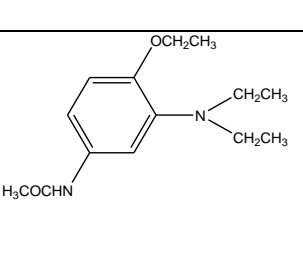
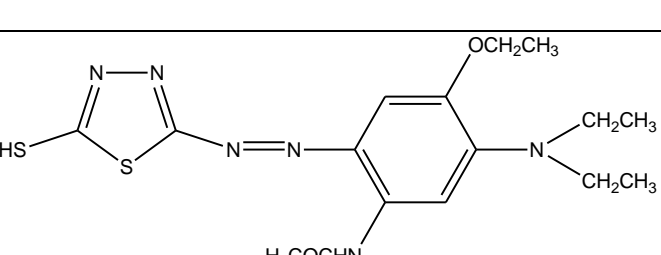
The percentage exhaustion and fixation of the dyed fiber were determined according to the reported method. The percentage exhaustion was observed for each dye between 76-90% and the percentage fixation was observed for each dye between 76-85 %.

4. Conclusion:

All the reported newly synthesized mono azo dyes showed good to magnificent fastness properties. Furthermore these dyes show level dyeing, excellent dispersability and dye ability. Exhaustion and fixation of these dyes are very good which indicates that the dyes have good compatibility with fiber. These properties of dyes which have aided the rise to importance of such diazo components as replacement for the benzenoid colorants usually used on nylon fabric.

Table-II Structure of the coupling components and corresponding disperse azo dyes

Dye No.	Coupling component	Disperse Azo Dye Structure
D1		
D2		
D3		
D4		
D5		

D6		
D7		
D8		
D9		
D10		
D11		
D12		
D13		
D14		

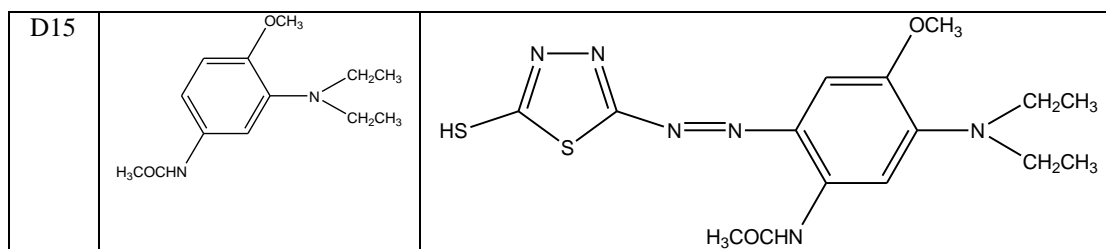


Table – III IR spectra data of selected dyes

Sr.No.	Dye	IR (KBr, cm ⁻¹)
1	D10	3194 cm ⁻¹ (C-H stretching)
		2245 cm ⁻¹ (C-N stretching for cyanide)
		1500 cm ⁻¹ (N=N stretching)
		817 cm ⁻¹ (C-S stretching)

Table – IV ¹H-NMR spectral data of selected dyes

Dye	Chemical Shifts (in ppm)	Multiplicities	Relative number of protons	Assignment
D10	2.50	S	1	-SH group
	7.22-7.02	D	2	Aromatic ring
	6.90-6.69	D	2	Aromatic ring
	3.75-3.69	T	4	-CH ₂ - group
	2.78-2.74	T	4	-CH ₂ CN group

Table – V Different coupling components to form various disperse dyes at pH 4.0.

Dye No.	Coupling Component(R)	Molecular Formula	Molecular Weight	% Yield	Melting Point (°C)	%Analysis Calc. (Found)		
						C	H	N
D ₁	2-[(3-chloro phenyl)-(2-hydroxy ethyl)-amino] ethanol	C ₁₂ H ₁₄ ClN ₅ O ₂ S ₂	359	84%	286	40.05 (40.01)	3.92 (3.90)	9.85 (9.82)
D ₂	Acetic acid 2-[(2-acetoxy ethyl)-(3-chloro phenyl)-amino] ethyl ester	C ₁₆ H ₁₈ ClN ₅ O ₄ S ₂	443	79%	292	43.29 (43.26)	4.09 (4.05)	7.99 (7.96)
D ₃	Acetic acid 2-[(2-acetoxy ethyl) m-tolyl-amino] ethyl ester	C ₁₇ H ₂₁ N ₅ O ₄ S ₂	423	82%	230	48.21 (48.18)	5.00 (4.98)	16.54 (16.51)
D ₄	N,N- diacetoxy ethyl m-amino acetanilide	C ₁₈ H ₂₂ N ₆ O ₅ S ₂	466	83%	310	46.34 (46.30)	4.75 (4.72)	18.01 (17.99)
D ₅	3-(ethyl phenyl amino) propionitrile	C ₁₃ H ₁₄ N ₆ S ₂	318	82%	312	49.04 (49.02)	4.43 (4.40)	26.39 (26.36)
D ₆	N-(3-dimethylamino) acetamide	C ₁₄ H ₁₈ N ₆ OS ₂	350	81%	288	47.98 (47.94)	5.18 (5.15)	23.98 (23.93)
D ₇	Diethyl m-tolyl amine	C ₁₃ H ₁₇ N ₅ S ₂	307	83%	316	50.79 (50.76)	5.57 (5.54)	22.78 (22.75)
D ₈	Acetic acid 2-[(3-acetyl amino phenyl)-(2-cyano ethyl)-amino]ethyl ester	C ₁₇ H ₁₉ N ₇ O ₃ S ₂	433	80%	296	47.10 (47.08)	4.42 (4.39)	22.62 (22.58)

D ₉	2-(ethyl phenyl amino) ethanol	C ₁₂ H ₁₅ N ₅ O ₅ S ₂	309	84%	290	46.58 (46.55)	4.89 (4.86)	22.63 (22.59)
D ₁₀	3-[(2-cyano ethyl) phenyl amino] propionitrile	C ₁₄ H ₁₃ N ₇ S ₂	343	77%	310	48.96 (48.93)	3.82 (3.79)	28.55 (28.51)
D ₁₁	N-(3-diethylamino phenyl) methanesulfonamide	C ₁₃ H ₁₈ N ₆ O ₂ S ₃	386	74%	292	40.40 (40.36)	4.69 (4.66)	21.74 (21.71)
D ₁₂	N-[3-{(2-cyano ethyl)-(2-hydroxy ethyl) amino}-phenyl]-acetamide	C ₁₅ H ₁₇ N ₇ O ₂ S ₂	391	76%	318	46.02 (45.98)	4.38 (4.37)	25.05 (25.03)
D ₁₃	N-[3-{bis-(2-hydroxy ethyl)-amino}-phenyl]-acetamide	C ₁₄ H ₁₈ N ₆ O ₃ S ₂	382	80%	316	43.97 (43.94)	4.74 (4.71)	21.97 (21.96)
D ₁₄	N-(3-diethylamino 4-ethoxy phenyl) acetamide	C ₁₆ H ₂₂ N ₆ O ₂ S ₂	394	84%	310	48.71 (48.67)	5.62 (5.59)	21.30 (21.27)
D ₁₅	N-(3-ethylamino phenyl) propionamide	C ₁₅ H ₂₀ N ₆ O ₂ S ₂	380	82%	294	47.35 (47.31)	5.30 (5.27)	22.09 (22.07)

Table – VI Results of washing fastness properties on polyester fiber and staining on multifiber

Sr. No.	Dye	Colour shade on fibre	Change in shade	Multifibre staining					
				Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
1	D3	Pink	4-5	4-5	4-5	4-5	4	4-5	4-5
2	D6	Magenta	4	4	4-5	4-5	3	4	4
3	D7	Brownish crimson	4-5	4	4-5	4-5	2-3	4	4-5
4	D8	Rose pink	4	4	4-5	4	2-3	3-4	3-4
5	D9	Hot pink	4-5	4	4-5	4-5	2-3	4	4-5
6	D10	Orange	4	4-5	4	4	4	4	4-5

[Grading: 5-excellent, 4- very good, 3- good, 2- Fair, 1- Poor]

Table – VII Results of perspiration (acidic and alkaline) fastness properties on polyester fiber and staining on multifiber

Sr. No.	Dye	Colour shade on fibre	Medium	Change in shade	Multifibre staining					
					Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
1	D3	Pink	Acidic	4	4-5	4-5	4-5	4-5	4-5	4-5
			Alkaline	4-5	4	4-5	4-5	4-5	4-5	4-5
2	D6	Magenta	Acidic	4-5	4-5	4-5	4-5	4-5	4-5	4-5
			Alkaline	4	4-5	4-5	4-5	4	4	4-5
3	D7	Brownish crimson	Acidic	4	4-5	4-5	4-5	4	4	4-5
			Alkaline	4-5	4	4-5	4-5	4	4	4
4	D8	Rose pink	Acidic	4-5	4	4-5	4-5	4	4	4-5
			Alkaline	4-5	4-5	4	4	3-4	3-4	4
5	D9	Hot pink	Acidic	4-5	4	4	4	4	4	4-5
			Alkaline	4-5	4	4-5	4-5	4	4	4-5
6	D10	Orange	Acidic	4	4	4-5	4	4	4-5	4-5
			Alkaline	4-5	4	4	4	4	4-5	4

[Grading: 5-excellent, 4- very good, 3- good, 2- Fair, 1- Poor]

5. Acknowledgements:

The author express their gratitude to the Head, Department of Chemistry and principal of Naran Lala college, Navsari for providing necessary research facilities, sophisticated Analytical Instrumentation facility, Chandigarh for spectral studies and Atul Ltd., Atul for providing dyeing and analytical facilities.

6. References

- [1] Song John, Fitchett Gilmer Trower .Production of N,N-bis(thiocarbamoyl)hydrazine and 2-amino 5-mercapto 1,3,4- thoadazole [internet], American cynamid Co. [internet]
[Updated 1955] <https://patents.google.com/patent/US2966495>
- [2] John Song and Gilmer T. Fitchett,1956, (to American cynamid Co.),U.S. 2,759,947
- [3]Mitsubishi Chemical Industries Co Ltd, 1980,Jpn Kokai Tokkyo Koho 80.133.458
- [4] Parton, B. British,1981, UK Patent 2.028.856
- [5] Sumitomo Chemical Co Ltd,1992, Jpn Kokai Tokkyo Koho JP 57.161.653
- [6] Nakamura, Y.; Murata, 1993,J. Jpn Kokai Tokkyo Koho 5.155.870
- [7] Hahn, E.; Wiesenfeldt,M.; Reichelt, H.; Gruettner, 1993,S. German Offen 4.120.362
- [8] Sens, R.; Etbach, 1995,H. German Offen, 4.426.023
- [9] Tsein,H.; Chu,K. -P.; Chang,H., 1998, US Patent 5.652.344
- [10] Bello, K. A.; Martins, C.M. O.A.; Adamu, I. K. Colourage 1995,4229.
- [11] Desai, K. R.; Modi, B.R.; Mistry, B.D., 1995, J. Indian Chem. Soc,72, 141.
- [12] Griffiths,J.; Riepl, C. 1998,J.Chem. Commun. ,13,1349.
- [13] Hallas,G.; Choi, J. -H .,1999 Dyes Pigm. ,42,249
- [14] Chikhalia,K. H.; Desai,K. R.,1998, J. Inst. Chem. (India) , 70, 142.
- [15] Rangnekar,D. W.; Kanetkar, V.R.; Shankarling,G.S.; Malanker,J.V.J. 1998,Indian council chem. ,15,28.
- [16] Towns, A. D. Dyes Pigm. 1999,42,3.
- [17] Kochergin, P.M. Zhur. Obsheci. Khim. 1956,26,2897.
- [18] Maradiya, H.R.; Patel, V.S. 2000.High Perform. Polym.,12,335
- [19] Maradiya, H.R.; Patel, V.S. 2001. Bull.Chem. Technol. Macedonia
- [20] AATCC Technical Manual, AATCC, USA
- [21] MARKS & SPENCER Test Methods, M & S, UK.
- [22] Venkataraman, K. 1952. The chemistry of synthetic dyes, vol. II. New York and London: Academic Press.
- [23] Venkataraman, K. 1970. The chemistry of synthetic dyes,vol. III. New York and London: Academic Press, 30

