



SYNTHESIS AND CHARACTERIZATION OF REACTIVE DYES BASED ON 4-AMINO-N-(5-METHYLISOXAZOL-3-YL)-BENZENESULFONAMIDE AND THEIR DYEING APPLICATION ON VARIOUS FIBRES.

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ABSTRACT A new series of cold brand reactive dyes (D1 to D12) were synthesized by the coupling of diazotized 4-Amino-N-(5-methylisoxazol-3-yl)-benzenesulfonamide with various cyanurated coupling components in good yield. These reactive dyes were confirmed by ¹H NMR analysis and FTIR. The synthesized dyes have been applied to cotton, silk, and wool fibres. They exhibited a variety of color shades with good depth and informality on the fibres. % Exhaustion and % fixation of dyes were determined by using Glauber salt as a fixing agent at various temperature conditions.

KEYWORDS : 4-Amino-N-(5-methylisoxazol-3-yl)-benzenesulfonamide, Dyeing, % exhaustion, % fixation, Glauber salt

INTRODUCTION

Reactive dyes are a highly successful class of modern synthetic dyes owing to their wide shade gamut, their flexibility in application, and the excellent fastness properties they offer when dyed on wool, silk, cotton, and regenerated cellulosic fibres^{1,2}. Fibre reactive dyes are colored organic compounds that are capable of forming a covalent bond between reactive groups of the dye molecule and nucleophilic groups on the polymer chains within the fibre³⁻⁶. Such covalent bonds are formed with the amino, hydroxyl groups of cellulosic fibres with the amino, hydroxyl, and mercapto groups of protein fibres and the amino groups of polyamides⁷. Reactive dyes can be classified into different groups as follows:

(1) Reactive dyes containing cyanuric chloride nucleus which is subdivided into (a) Mono-Chloro Triazine reactive systems (Hot brand reactive dyes) (b) Di-Chloro Triazine reactive systems (Cold brand reactive dyes) classes. (2) Reactive dyes containing Chloro Pyrimidine nucleus (3) Reactive dyes containing Chloro Pyridazine nucleus (4) Reactive dyes containing Di-Chloro-Quinoxaline nucleus (5) Reactive dyes containing Vinyl Sulphone group (6) Reactive dyes containing Acryl amide group (7) Reactive dyes containing an Epoxy group. Various above reactive systems are known but cyanuric chloride (Trichloro-Triazine), and Vinyl Sulphone derivatives are widely used because the presence of 1,3,5 triazine structure in the dye molecules improves their dyeing ability and possibility for application⁸ and S-Triazine based chemicals have been widely used in the manufacture of polymers, dyes, explosives, pesticides, and commodity chemicals⁹.

In the present research, we wish to report a new series of reactive dyes from 4-Amino-N-(5-methylisoxazol-3-yl)-benzenesulfonamide and various cyanurated coupling components, then the coupling components tested as reactive dyes against various fabrics. In addition to the dyes, an evaluation of their technical properties and a color assessment were performed.

EXPERIMENTAL:

MATERIALS AND METHODS:

Commercially available silk, wool, and cotton fibres were used for dyeing. The chemicals and reagents were obtained from Sigma-Aldrich and all the coupling components were received from Atul Ltd., Valsad, Gujarat, India, and used without further purification. All melting points taken by the open capillary method are uncorrected and are expressed at °C. TLC analysis was carried out on silica gel G F254-precoated aluminum sheets¹⁰. IR spectra were recorded on a Shimadzu Model 8400S system using the potassium bromide wafer technique. ¹H-NMR (400 MHz) and in D₂O solvent, TMS is as internal standard, UV-vis absorption spectra were recorded on a Thermo Scientific Evolution 300 Spectrophotometer at the wavelength of maximum absorption (λ_{max}) using water as solvent. The rota dyer instrument was used for dyeing in laboratory.

SYNTHESIS:

STEP-1: Synthesis of 4-Amino-N-(5-methylisoxazol-3-yl)-benzenesulfonamide¹¹(A)

3-amino-5-methyl-Isloxazole (4.90gm, 0.05 mol) and p-acetamidobenzene sulfonyl chloride (11.64gm, 0.05 mol) were taken at room temperature. The reaction mixture was then stirred until a solid product was formed. A white-separated solid was filtered, washed with water, and recrystallized from ethanol.

Yield: 79%. m.p. 168°C

STEP-2 : Diazotization of 4-Amino-N-(5-methylisoxazol-3-yl)-benzenesulfonamide (B)

4-Amino-N-(5-methylisoxazol-3-yl)- benzenesulfonamide (1.27g, 0.005mol) was suspended in water (60 ml) and conc. H₂SO₄ (1.5 ml) was added dropwise to this well-stirred suspension. The mixture was gradually heated up to 80°C, till a clear solution was obtained. The solution was cooled at 0-5 °C in an ice bath. A solution of NaNO₂ (0.6 gm) in water (5 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 a positive test for nitrous acid on starch iodide paper. After just destroying the excess of nitrous acid with the required amount of a solution of sulphamic acid, the clear yellow diazo solution-B at 0-5°C thus obtained was used for the subsequent coupling reaction.

STEP-3: Cyanuration of H-acid (C)

Cyanuric chloride (1.85 g, 0.01 mole) was stirred in acetone (25ml) 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 an aqueous sodium carbonate solution (10% w/v) was then added in small lots for about an hour. The pH was maintained neutral by the simultaneous addition of sodium carbonate solution (1% w/v). The reaction mass was then stirred at 0-5 °C for further 4 hours then a clear solution was obtained. The cyanurated H-acid solution was used for subsequent coupling reactions.

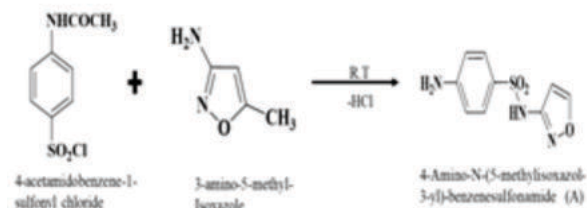
STEP-4: General method for the Synthesis of dye D₁, Coupling of the diazo solution – B with cyanurated H-acid ©:

To an ice-cold and well-stirred solution of cyanurated H-acid (4.67g, 0.01 mole) a freshly prepared solution of diazo solution-B as previously prepared was added dropwise over a period of 10-15 minutes. The pH was maintained at 7.5 to 8.5. During addition stirring was continued for 4 hours, maintaining the temperature below 5°C. Solution chloride (12 g) was then added and the mixture was stirred for an hour. The solid dye separated out was filtered, washed with a minimum amount of acetone, and dried at room temperature. Yield: 85 %

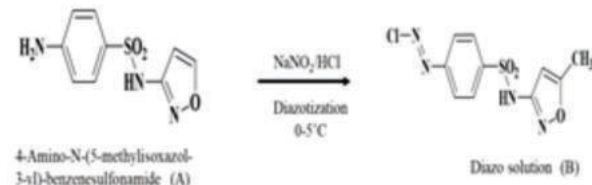
Following the above procedure other reactive dyes, D₂ to D₁₂ were synthesized using various cyanurated coupling components.

Reaction scheme:

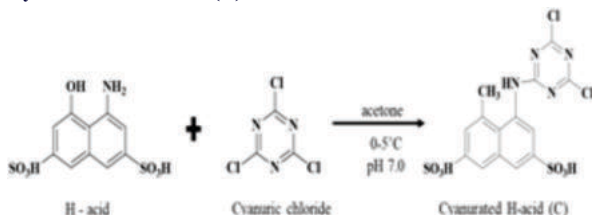
Synthesis of 4-amino-N-(5-methylisoxazol-3-yl)-benzenesulfonamide (A):



Diazotization of 4-amino-N-(5-methylisoxazol-3-yl)-benzenesulfonamide (B):



Cyanuration of H-acid (C):



Synthesis of Dye D₁:

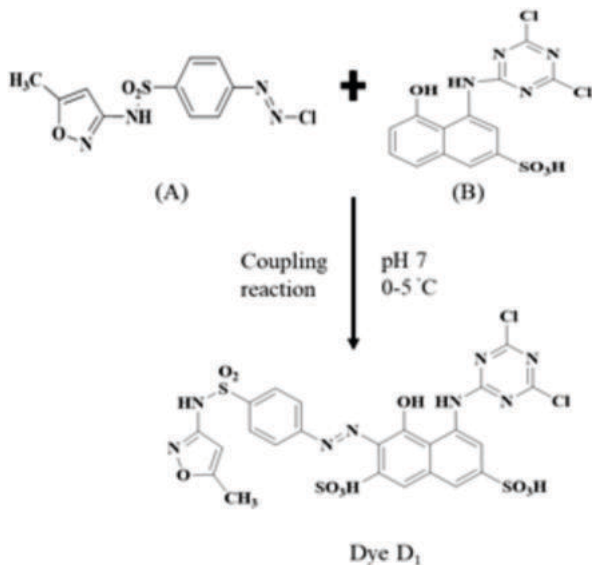


Table 1: Characterization Of Dyes (D₁ To D₁₂):

No.	Coupling Components (R)	Molecular Formula	Mole Wt(g)	Yield (%)	% Nitrogen		R _f value
					Found	Require	
D ₁	H-acid	C ₂₂ H ₁₆ Cl ₂ N ₆ O ₁₂ S ₂	733.52	85	15.30	15.32	0.42
D ₂	I-acid	C ₂₂ H ₁₆ Cl ₂ N ₆ O ₁₂ S ₂	651.46	56	17.18	17.20	0.43
D ₃	K-acid	C ₂₂ H ₁₆ Cl ₂ N ₆ O ₁₂ S ₂	733.52	72	15.28	15.32	0.38
D ₄	Per-acid	C ₂₂ H ₁₆ Cl ₂ N ₆ O ₁₂ S ₂	635.46	54	17.61	17.63	0.36
D ₅	Lauric acid	C ₂₂ H ₁₆ Cl ₂ N ₆ O ₁₂ S ₂	585.42	82	17.59	17.63	0.40
D ₆	lithos acid	C ₂₂ H ₁₆ Cl ₂ N ₆ O ₁₂ S ₂	635.46	80	17.61	17.63	0.35
D ₇	thiolo lithos acid	C ₂₂ H ₁₆ Cl ₂ N ₆ O ₁₂ S ₂	733.52	83	15.82	15.86	0.40
D ₈	Gamma acid	C ₂₂ H ₁₆ Cl ₂ N ₆ O ₁₂ S ₂	651.46	66	17.16	17.20	0.45
D ₉	Deiner's acid	C ₂₂ H ₁₆ Cl ₂ N ₆ O ₁₂ S ₂	635.46	83	17.62	17.63	0.44
D ₁₀	N-Methyl-I-acid	C ₂₂ H ₁₆ Cl ₂ N ₆ O ₁₂ S ₂	665.49	79	16.79	16.84	0.42
D ₁₁	N-Phenyl-I-acid	C ₂₂ H ₁₆ Cl ₂ N ₆ O ₁₂ S ₂	725.58	80	15.41	15.44	0.46
D ₁₂	N-Methyl-Gamma acid	C ₂₂ H ₁₆ Cl ₂ N ₆ O ₁₂ S ₂	665.49	81	16.80	16.84	0.43

Dyeing Process:

All the dyes were applied on silk, wool, and cotton fibres using the reported procedure¹². The variation in the hues of the dyed fabric results from both the nature and position of the substituent present on the coupler ring. The percentage dye bath exhaustion (%E) and percentage dye bath fixation (%F) of the dyed fibres were determined by using the reported method¹³. The light fastness was assessed in accordance with BS: 1006-1978 and the wash fastness was carried out in accordance with IS: 765-1979. The rubbing fastness test was carried out by using a Crock meter (Atlas) in accordance with the AATCC-1961. Table-2

Dyeing Of Cotton:

The dye stuff under study was dissolved by pasting it up in cold water and then the addition of hot water. Anhydrous Glauber's salt solution (1.0 ml, 20% w/v) and NaCl (0.5 g) were added to it. The pH of the dye bath was adjusted to 8.0 by adding the required soda ash solution (1.0 ml, 4% w/v) and the total volume was adjusted to 80 ml by adding the required amount of distilled water. The dye bath solution was transferred to a 250 ml conical flask fitted with an air condenser. The temperature of the dye bath was raised to 40° C and the cotton pattern was introduced into the dye liquor with stirring. The temperature of the dye bath was gradually increased to 100° C over a period of 30 min. The dyed fibre was then washed several times with cold water, soaped and dried.

Dyeing of Wool:

The dyestuff under study was dissolved by pasting it up in cold water and then the addition of hot water. Anhydrous Glauber's salt solution (1.5 ml, 20% w/v) was added to it. The pH of the dye bath was adjusted to 3.0 by adding the required formic acid solution (1.5 ml, 4% w/v) and the total volume was adjusted to 80 ml by adding the required amount of distilled water. The dye bath solution was transferred to a 250 ml conical flask fitted with an air condenser. The temperature of the dye bath was raised to 50° C and the wool pattern was introduced into the dye liquor with stirring. The temperature of the dye bath was gradually increased to 100° C over a period of 30 min. The dyed fibre was then washed several times with cold water, soaped, and dried.

Dyeing of Silk:

The dyestuff under study was dissolved by pasting it up in cold water and then the addition of hot water. Anhydrous Glauber's salt solution (1.0 ml, 20% w/v) was added to it. The pH of the dye bath was adjusted to 3.0 by adding the required acetic acid solution (1.0 ml, 4% w/v) and the total volume was adjusted to 80 ml by adding the required amount of distilled water. The dye bath solution was transferred to 250 ml conical flask fitted with an air condenser. The temperature of the dye bath was raised to 50° C and the silk pattern was introduced into the dye liquor with stirring. The temperature of the dye bath was gradually increased to 85° C over a period of 30 min. The dyed fibre was then washed several times with cold water, soaped, and dried.

Table 2: Materials And Conditions For 2% Shade:

Materials	Cotton	Wool	Silk
Weight of fabric	2.0 gm	2.0 gm	2.0 gm
Amount of the dye under study	40 mg	40 mg	40 mg
Glauber's salt solution (20% w/v)	1.0 ml	1.5 ml	1.0 ml
Soda ash solution (10% w/v)	1.0ml	-	-
Formic acid solution (10% w/v)	-	1.5 ml	-
Acetic acid	-	-	1.5 ml
Sodium chloride	0.5 g	-	-
MLR	1:40	1:40	1:40
Total volume of the solution in dye bath	80 ml	80 ml	80 ml
pH of the dye bath	8.0	3.0	3.0
Dyeing temperature	100° C	100° C	85° C
Time for dyeing	90 min	60 min	40 min

RESULT AND DISCUSSION:

IR Spectral data of selected dyes D₁ and D₁₀

Dye-D₁: IR spectra of Dye-D1 showed O-H stretching vibration of-

OH group at 3458 cm⁻¹, N-H stretching vibration of secondary amine is 3210 cm⁻¹, C-H stretching vibration of -CH₃ group at 1720 cm⁻¹, C-N stretching vibration of tertiary amine group at 1620 cm⁻¹, N=N stretching vibration of the azo group at 1497 cm⁻¹, S=O stretching vibration of SO₂ group at 1384 cm⁻¹, S=O stretching vibration of SO₂H group at 1165 and 1048 cm⁻¹, C-Cl stretching vibration of Chloro group at 548 cm⁻¹.

Dye-D₁₀: IR spectra of Dye-D₁ showed O-H stretching vibration of -OH group at 3435 cm⁻¹, N-H stretching vibration of secondary amine is 3244 cm⁻¹, C-N stretching vibration of tertiary amine group at 1615 cm⁻¹, N-H stretching vibration of secondary amine at 1570 cm⁻¹, N=N stretching vibration of azo group at 1500 cm⁻¹, S=O stretching vibration of SO₂ group at 1376 cm⁻¹, S=O stretching vibration of SO₂H group at 1155 and 1092 cm⁻¹, C-Cl stretching vibration of Chloro group at 589 cm⁻¹.

¹H-NMR Spectral Data Of Dyes:

D1:

2.18 – SO₃H (2H), Singlet, 2.35-CH₃ (3H), Singlet
4.78-NH (2H), Singlet, 6.10-OH (1H), Singlet
7.01 -8.15 (8H), multiplet

D2:

2.24 – SO₃H (1H), Singlet, 2.306-CH₃ (3H), Singlet
4.78-NH (2H), Singlet, 6.06-OH (1H), Singlet, 6.99-8.25 (9H), multiplet

Exhaustion And Fixation Study:

The results of the exhaustion and fixation study of each dye are presented in Table 3.

The percentage exhaustion of 2% dyeing on cotton fibre ranges from 66 to 77 %, wool fibre ranges from 66 to 76% and silk fibre ranges from 66 to 76%. The results of the exhaustion study reveal that exhaustion on cotton and silk is comparatively better than wool. The results of the fixation study reveal that fixation on silk and wool is comparatively better than on cotton. The percentage fixation of 2% dyeing on cotton fibre ranges from 83 to 92 %, wool fibre ranges from 88 to 92 %, and silk fibre ranges from 87 to 93%. (Table 5).

Table 3: Exhaustion And Fixation Data:

Dye No.	Shade on Dyed fibre	λ_{max}	Exhaustion (%)			Fixation (%)		
			Cotton	Wool	Silk	Cotton	Wool	Silk
D ₁	Violet	518	72.98	72.00	71.83	91.81	90.28	91.89
D ₂	Orange	482	72.55	72.83	72.00	91.66	90.63	90.88
D ₃	Light yellow	470	67.38	71.90	72.18	83.86	89.01	87.29
D ₄	Brown	480	76.08	74.88	72.30	90.04	90.82	92.67
D ₅	Dark Orange	498	69.98	70.10	73.40	89.32	92.01	91.97
D ₆	Light yellow	470	67.15	66.30	66.83	87.86	90.50	90.05
D ₇	Light yellow	470	67.33	67.00	66.40	87.63	88.81	88.10
D ₈	Dark pink	501	67.80	68.73	71.00	89.97	90.21	90.14
D ₉	Light yellow	470	68.83	69.35	68.43	86.45	90.84	87.69
D ₁₀	Black	496	74.15	75.23	74.98	91.06	91.72	90.70
D ₁₁	Orange	511	73.28	75.92	75.80	92.12	90.22	91.02
D ₁₂	Orange	490	66.73	72.58	74.95	89.92	91.63	91.39

Fastness Properties:

Fastness to light was assessed in accordance with BS: 1006-1978 (Standard Test Method, 1994)15. The rubbing fastness test was carried out by using a Crock meter (Atlas) in accordance with the AATCC-1961(AATCC Test, 1961) and the wash fastness was carried out in accordance with IS:765-1979 (Indian Standard,1979)16. All the dyes show generally fair to good light fastness properties. The washing and rubbing fastness properties range from very good to excellent fastness on silk, wool, and cotton (Table 4).

All the dyes show generally moderate to very good light fastness properties. The washing fastness properties range from good to excellent fastness on cotton, wool, and silk. (Light fastness: 1- poor, 2-

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

Table 4: Fastness Properties Of Reactive Dyes (D₁ to D₁₂):

Dye No.	Light fastness			Wash fastness			Rubbing fastness					
	Cotton	Wool	Silk	Cotton	Wool	Silk	Dry			Wet		
							Cotton	Wool	Silk	Cotton	Wool	Silk
D ₁	5-6	5	6	5	4-5	5	4-5	5	4-5	4	4-5	4
D ₂	5	5	5-6	4-5	4	5	4	4	4-5	4	3-4	4
D ₃	4	4-5	4	3-4	4	3-4	4	3-4	4	3-4	4	3-4
D ₄	4	5	5	3-4	4-5	4	3-4	4-5	4-5	4	4	4
D ₅	3-4	4-5	5	3	4	4-5	4	4	4-5	3-4	3-4	4
D ₆	4-5	4	4	4-5	4	4	4	3-4	4	3-4	4	3-4
D ₇	4-5	4	4	4	3-4	4	4	3-4	3-4	3-4	3	3
D ₈	4	4	4	4	3-4	4	4	4	4	3-4	4	4
D ₉	4	4	5	4	3-4	4-5	4	3-4	4	3-4	4	3-4
D ₁₀	4-5	5	5-6	4	4-5	5	4	5	5	3-4	4	4-5
D ₁₁	5	5	5	5	4-5	4-5	4-5	5	5	4	4-5	4-5
D ₁₂	4-5	4	5	4	4	4-5	4	4	4-5	3-4	3-4	4

CONCLUSIONS:

A new series of cold brand reactive dyes D₁ to D₁₂ were synthesized by the process of direct diazotization and coupling in good yields. These dyes were applied on hydrophilic fibres like cotton, wool and silk which give violet to yellow shade. The dyeing performance of all these dyes on various fibres gave moderate to good light fastness, good to excellent wash fastness and rubbing fastness. Percentage exhaustion and fixation of these dyes have good compatibility with the fibres.

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