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# Synthesis And Dyeing Performance Of A Series Of Mono AZO Reactive Dyes Derived From 1,3,4-Thiadiazole Moiety On Cotton Fibre

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***Abstract***

*The cyclization of N, N'- bis (thiocarbamoyl) hydrazine yielded 2-amino 5-mercapto 1,3,4-thiadiazole(A). The chemical (A) is used to prepare various mono azo reactive dyes that are symmetrical. To prepare mono azo reactive dyes, the molecule (A) is diazotized and coupled with different coupling reagents. IR spectra, 1H-NMR spectra, and elemental analysis were used to investigate these dyes. The fastness characteristics of these dyes were tested after they were applied to cotton fibre. All of the dyes have excellent fastness characteristics. The dye-bath exhaustion and fixation percentages were determined to be satisfactory.*

***Keywords:*** *Amino thiadiazole, mono azo reactive dyes, fastness properties, cyannurated naphthoic acids*

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## I. INTRODUCTION

In the history of synthetic dyes, the development of reactive dyes was a breakthrough (Shenai, 1994). In the dyeing of cellulose, such as cotton or flax, reactive dyes are most often employed (Patel et al, 2004). These dyes create a covalent connection with cellulose's hydroxyl group (-OH group) or protein's amino group (-NH2 group) (Bird and Boston, 1975). Because the functional group also binds to water, causing hydrolysis, reactive dyes have a lower utilisation rate than other types of dyestuff. [1] In the late 1800s, reactive dyes were investigated by first adding functionalized dyes to the substrate and then fixing the dyes. Trichloro triazine is still a common reactive dye platform.

The focus of this research was to develop symmetrical mono azo reactive dyes with a greater level of activity. The symmetrical mono azo reactive dyes based on 2-amino 5-mercapto 1,3,4-thiadiazole were synthesised and dyeing properties were studied.

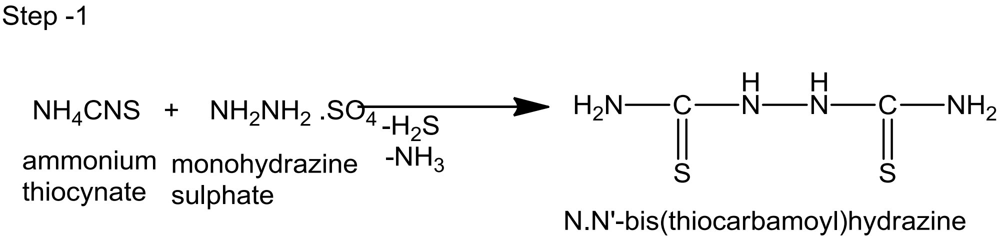
## II. MATERIALS AND METHODS

The chemicals used were all analytical reagent grade. Atul Ltd., Atul, Guajarat, provided the naphthoic acid that was utilised as a coupling component. The open capillary technique was used to determine melting points, and the results are uncorrected. Makevale acrylics Pvt. Ltd., Vadodara, used a Perkin – Elmer Spectro 400 IR spectrophotometer to record the IR spectrum of a selected dye in KBr. At SAIF, Punjab University, Chandigarh, the PMR spectrum of a selected dye was generated using a BRUKER ADVANCE II 400 NMR spectrometer using TMS as an internal standard in DMSO solvent. The rubbing fastness test was performed using ISO 105 X12, the wash fastness test was performed using ISO 105 CO2, and the perspiration fastness test was performed using ISO 105 EO4 (Indian Standard, ISO, 1979).

### 3.1 Experimental

The reactive dyes based on 2- amino 5- mercapto 1,3,4- thiadiazole moiety can be made in five steps.

**Reaction scheme**



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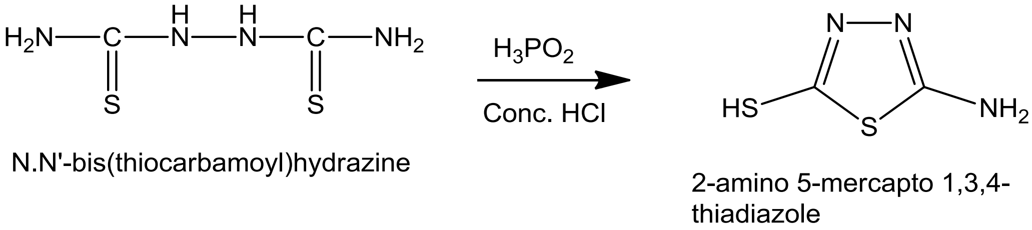

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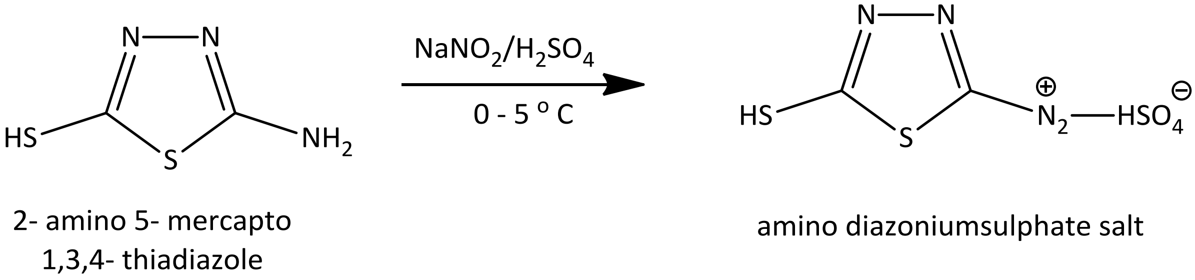

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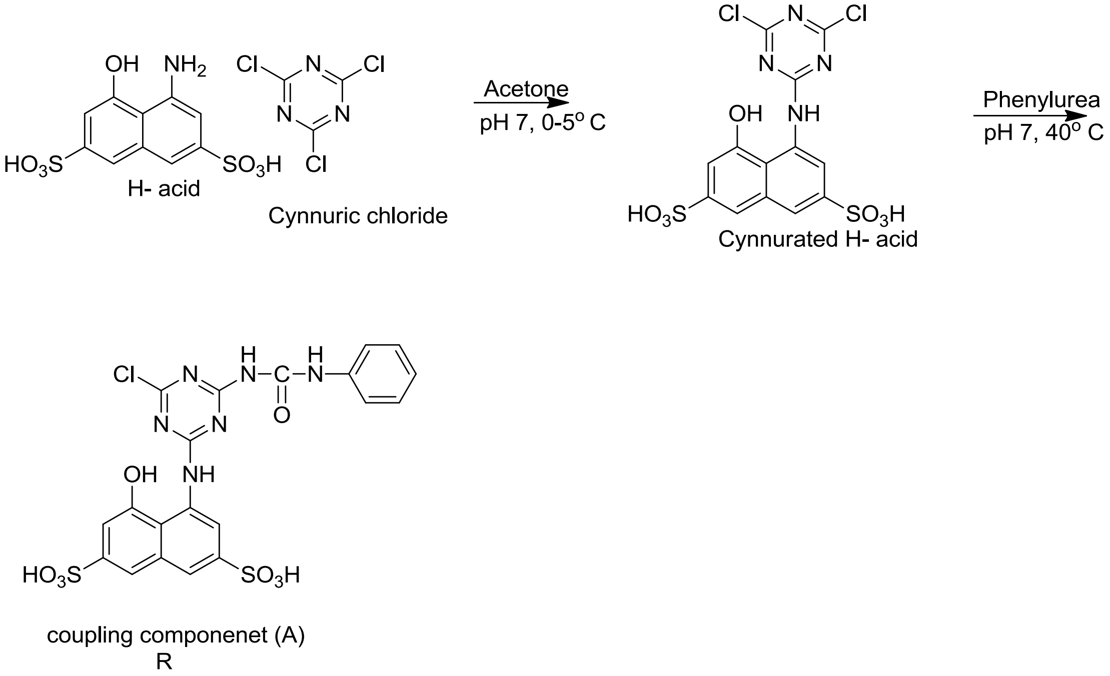
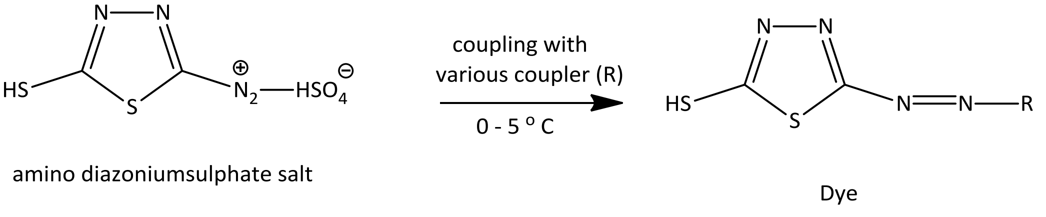


Step - 5



*Where R= various coupling compounds*

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

The mixture of mono hydrazine sulfate (50 gm, 0.6 moles) and ammonium thiocyanate (34 gm,0.3 moles) and water (100 ml) was refluxed for 4 hours on a water bath. The solution becomes clear yellow and a vigorous reaction took place with the evolution of $H_2S$ and $NH_3$ gases. After 4 hours of heating, the reaction mixture was cooled, the crystals of N.N'-bis(thiocarbamoyl)hydrazine is formed, the product was filtered and washed with water and recrystallized from hot water. M.P., 198˚C,77% yield

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

The mixture of 50 ml 1% $H_3PO_2$ was diluted to 400 ml with water and 200 ml concentrated HCl heated for half an hour, then add N,N'- bis (thiocarbamoyl) hydrazine (30.6 gm, 0.2 moles), refluxed the mixture till the reaction was completed. After completion of the reaction, the reaction mixture was cooled to room temperature, the shiny white crystals are formed, which was filtered off, washed with water, and dried at 90˚ C. M.P. 234˚C,79% yield

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

Dry sodium nitrite (0.69g, 0.01 mole) was slowly added to concentrated sulphuric acid (2.0 ml) in an ice bath by stirring, and then the solution was cooled to 0-5˚ C. Then 2-amino 5-mercapto 1,3,4-thiadiazole(1.33g, 0.01mole) was added portion wise and stirring continued for 2 hours at 0-5 ˚ C. The excess of nitrous acid (positive test on SI paper) was degraded by the addition of the necessary amount of urea. In the ensuing coupling reaction, the pure diazonium salt solution thus obtained was used immediately.

**Step IV: Preparation of cynnurated coupling compound**

Cyanuric chloride (1.85gm, 0.01 mole) was added in acetone (25 ml) at 0-5˚ C and stirred for one hour. Then, a neutral solution of H-acid (3.19 gm, 0.01mole) in aqueous sodium carbonate solution (10% w/v) was added portion wise. By simultaneous addition of sodium carbonate solution (10 % w/v), the pH was kept neutral. The reaction mass was then stirred at 0-5˚C for a further 4 hours. Cyanurated H-acid is formed in a clear solution.

The temperature of cyanurated H acid (4.67 gm, 0.01 mole) ice-cooled well-stirred solution was steadily increased to 45˚ C. Phenyl urea (1.36 gm, 0.01 mole) was introduced slowly to this cyanurated H acid over a 30-minute interval, the pH was retained neutral by adding sodium carbonate (10 % w/v) solution simultaneously. Stirring proceeded for an additional 2 hours after the addition was finished. For further coupling reaction, the coupling compound thus obtained was subsequently used.

**Step V: Preparation of Reactive dye**

A freshly prepared diazonium solution, as previously prepared, was introduced dropwise for 10-15 minutes to an ice-cold and well-stirred solution of coupling component. Via simultaneous addition of sodium carbonate solution (10 % w/v), the pH was kept neutral.The stirring continued for three hours, keeping the temperature below 5 ° C. Then sodium chloride was added and stirred the mixture for an hour. The dye was filtered and dried. M.P. > 300˚C, 84% yield.

## 1.1 Process of Dyeing

The following method was done by dyeing with all reactive dyes on cotton fibre.

**Materials and conditions for 2% shade:**

| | | |
|---|---|---|
| Weight of the cotton fibre | - | 2.0 gm |
| Amount of dye taken | - | 40 mgm |
| Glauber's salt solution (20% w/v) | - | 1.0 ml |
| Soda ash solution (10% w/v) | - | 1.0 ml |
| Sodium chloride | - | 0.5 gm |
| Material: Liquor Ratio | - | 1:40 |
| Total volume of the solution in dye-bath | - | 80 ml |
| pH of the dye-bath | - | 8.0 |
| Dyeing Temperature | - | 100˚C |
| Time for dyeing | - | 90 minutes |

This involves two steps: (a) pretreatment of the fibre (b) dyeing

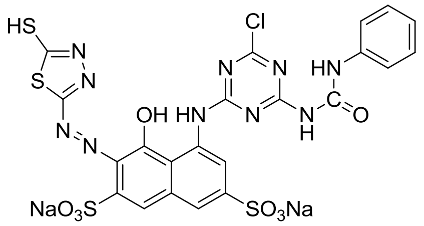
### (a) Pretreatment of the fibre

In solution of soap (0.2 gm) & ammonia (0.05 ml) in water, cotton fiber (2.0 gm) was scoured at 50 °C for 10 minutes (100 ml). The fiber was removed from the bath & rinsed with water several times, squeezed, dried & conditioned in an atmospheric state for two days & then used for dyeing.

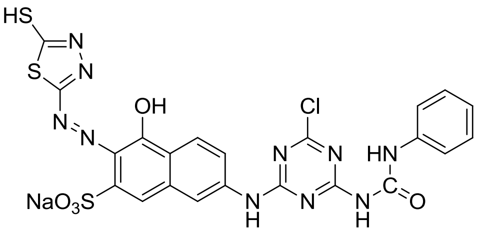
### (b) Dyeing procedure

By pasting up cold water & then applying hot water, dyestuff under analysis was dissolved. Salt solution (1.0 ml, 20 percent w/v) & sodium chloride (0.5 gm) from Anhydrous Glauber salt were added to it. By adding soda ash solution (1.0 ml, 4.0 percent w/v), the pH of the dye-bath was increased to 8.0 & overall volume was changed to 80 ml by adding the necessary amount of purified water. 250 ml conical flask fitted with air condenser was supplemented with dye bath solution. Dye bath temperature was increased to 40˚C, & cotton fiber was added to dye liquor with stirring. For 30 minutes, dye bath temperature was steadily elevated to 100˚C

& this temperature was held for further 60 minutes. Flask was shaken constantly during the dyeing process. Afterward, dyed fiber was cleaned & dried with cold water several times. Mixed dye liquor & wash solution is then further diluted with water to 250 ml. Furthermore, 5 ml of this solution was diluted with water to 250 ml & absorption of this solution was measured.



**D61**



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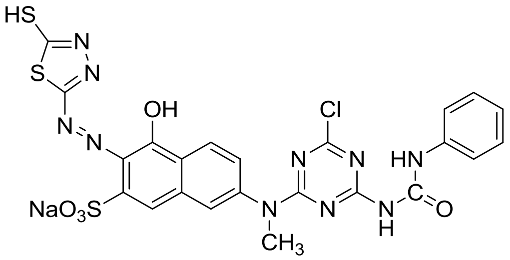

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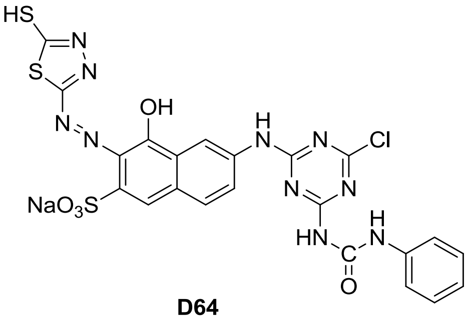

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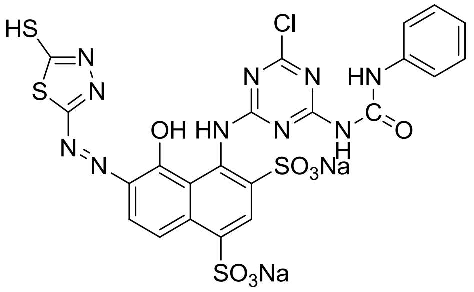
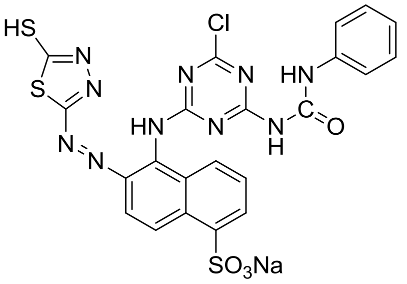
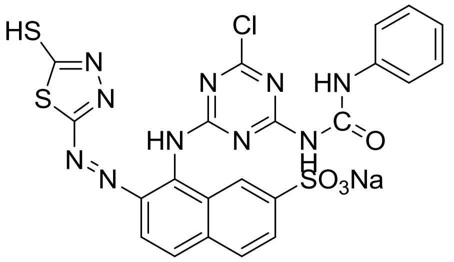


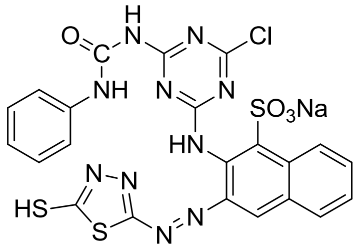
**D65**



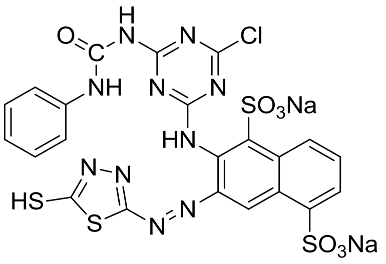
**D66**



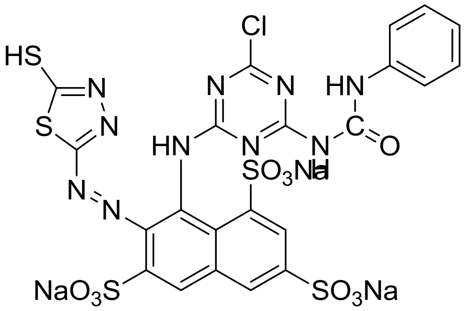
**D67**



**D68**



**D69**



**D70**

### Table 1: Characterization of Reactive Dyes Derived From Thiadiazole ($D_{61}$ to $D_{70}$)

| Dye No. | Cyannurated Coupling Component(R) | Molecular Formula | Molecular Weight | % Yield | Melting Point (°C) | %Analysis Calc. (Found) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N |
| $D_{61}$ | H acid | $C_{22}H_{13}ClN_{10}Na_2O_8S_4$ | 755 | 84 | >300 | 34.94<br>(34.99) | 1.71<br>(1.74) | 18.52<br>(18.55) |
| $D_{62}$ | J acid | $C_{22}H_{14}ClN_{10}NaO_5S_3$ | 653 | 75 | >300 | 40.50<br>(40.46) | 2.12<br>(2.16) | 21.41<br>(21.45) |
| $D_{63}$ | Methyl J acid | $C_{23}H_{16}ClN_{10}NaO_5S_3$ | 667 | 78 | >300 | 41.35<br>(41.41) | 2.45<br>(2.42) | 21.03<br>(21.00) |
| $D_{64}$ | Gamma acid | $C_{22}H_{14}ClN_{10}NaO_5S_3$ | 653 | 82 | >300 | 40.41<br>(40.46) | 2.12<br>(2.16) | 21.40<br>(21.45) |
| $D_{65}$ | S acid | $C_{22}H_{13}ClN_{10}Na_2O_8S_4$ | 755 | 80 | >300 | 34.35<br>(34.99) | 1.72<br>(1.74) | 18.52<br>(18.55) |
| $D_{66}$ | Laurent acid | $C_{22}H_{14}ClN_{10}NaO_4S_3$ | 637 | 78 | >300 | 41.45<br>(41.48) | 2.19<br>(2.22) | 21.96<br>(21.99) |
| $D_{67}$ | Mix Cleve's acid | $C_{22}H_{14}ClN_{10}NaO_4S_3$ | 637 | 82 | >300 | 41.44<br>(41.48) | 2.18<br>(2.22) | 21.94<br>(21.99) |
| $D_{68}$ | Tobias acid | $C_{22}H_{14}ClN_{10}NaO_4S_3$ | 637 | 80 | >300 | 41.49<br>(41.48) | 2.24<br>(2.22) | 21.96<br>(21.99) |
| $D_{69}$ | Peri acid | $C_{22}H_{14}ClN_{10}NaO_4S_3$ | 637 | 86 | >300 | 41.46<br>(41.48) | 2.21<br>(2.22) | 21.97<br>(21.99) |
| $D_{70}$ | Koch's acid | $C_{22}H_{12}ClN_{10}Na_3O_{10}S_5$ | 814 | 79 | >300 | 31.44<br>(31.41) | 1.41<br>(1.44) | 16.62<br>(16.65) |

### Table :2 IR Spectral data of Selected dye

| Dye | υ ($cm^{-1}$) | Assignments |
|---|---|---|
| $D_{62}$ | 3300 – 3400 | -OH stretching (broad, strong) |
| | 3200 – 3300 | $-NH_2$ stretching ( 2° - amine, strong) |
| | 2349 | -SH stretching |
| | 1614 | -C=N stretching ( thiadiazole ring) |
| | 1103 & 1048 | $-SO_3H$ stretching (two bonds, strong) |
| | 876 | -C-Cl stretching ( strong) |

### Table :3 PMR Spectral data of Selected dye

| Dye | Chemical shifts (δ in ppm) | Multiplicities | Relative no. of protons | Assignments |
|---|---|---|---|---|
| $D_{62}$ | 3.46 | s | 1 | 2° - amine (-NH-) |
| | 5.50 | s | 1 | Phenolic -OH |
| | 5.95 | s | 1 | -OH of – $SO_3H$ |
| | 8.82 | s | 1 | -NH- of phenyl area |

### Table- 4: %exhaustion , % fixation and colour yield of selected Reactive dyes

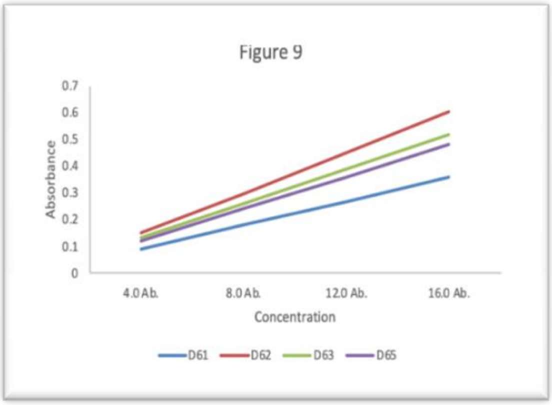
| Dye No. | Shade on fibre | $\lambda_{max}$ in nm | Amount of dye remained in dye-bath (X mgm) | Amount of dye exhausted from dye-bath (40-X)= Y mgm | % exhaustion = ( Y mgm / 40mgm) x 100 | Amount of dye in 0.1 gm of dyeing a mgm | Amount of dye in 2.0 gm of dyeing ( total weight 20a = Z mgm ) | % fixation = ( Z mgm/ Y mgm) x 100 | Colour yield = (Z mgm/40mgm) x 100 |
|---|---|---|---|---|---|---|---|---|---|
| D61 | Denim blue | 540 | 9.57 | 30.43 | 76.08 | 1.26 | 25.2 | 82.81 | 63.00 |
| D62 | Cherry red | 542 | 7.69 | 32.31 | 80.78 | 1.31 | 26.2 | 81.09 | 65.50 |
| D63 | Strawberry pink | 548 | 5.72 | 34.28 | 85.70 | 1.35 | 27.0 | 78.76 | 67.50 |
| D65 | Navy blue | 545 | 8.85 | 31.15 | 77.88 | 1.32 | 26.4 | 84.75 | 66.00 |

### Table- 5: Calibration data for exhaustion study of selected Reactive dyes

| **Dye No.** | **Wavelength** | **Absorption of the dye solution at specified wavelength Conc. X $10^{-3}$ mgm.ml$^{-1}$** | | | | **Slope of linear plot $K^*$** |
|---|---|---|---|---|---|---|
| | | **4.0 Ab.** | **8.0 Ab.** | **12.0 Ab.** | **16.0 Ab.** | |
| D61 | 540 | 0.150 | 0.310 | 0.460 | 0.610 | 38.15 |
| D62 | 542 | 0.060 | 0.120 | 0.180 | 0.250 | 15.65 |
| D63 | 548 | 0.080 | 0.170 | 0.260 | 0.310 | 19.35 |
| D65 | 545 | 0.160 | 0.310 | 0.480 | 0.620 | 38.75 |

**Table-6 Calibration data for fixation study of selected Reactive dyes**

| **Dye No.** | **Wavelength** | **Absorption of the dye solution at specified wavelength Conc. X $10^{-3}$ mgm.ml$^{-1}$** | | | | **Slope of linear plot $K^*$** |
|---|---|---|---|---|---|---|
| | | **4.0 Ab.** | **8.0 Ab.** | **12.0 Ab.** | **16.0 Ab.** | |
| D61 | 540 | 0.060 | 0.130 | 0.180 | 0.250 | 15.65 |
| D62 | 542 | 0.130 | 0.260 | 0.390 | 0.520 | 32.50 |
| D63 | 548 | 0.160 | 0.320 | 0.490 | 0.650 | 40.65 |
| D65 | 545 | 0.110 | 0.220 | 0.330 | 0.440 | 27.50 |



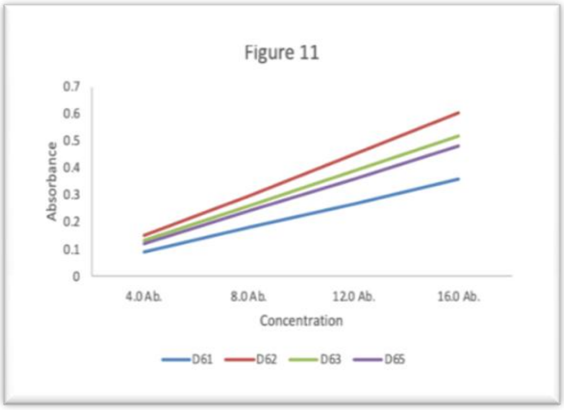


**Table-7: Fastness to Washing of selected Reactive dyes**

[ 1- poor, 2-fair, 3-good, 4- very good, 5- excellent]

| **Sample** | **Change In Shade** | **Stain on multifiber** | | | | | |
|---|---|---|---|---|---|---|---|
| | | **Acetate** | **Cotton** | **Nylon** | **Polyester** | **Acrylic** | **Wool** |
| D61 | 3 | 4 | 4-5 | 4-5 | 4-5 | 4 | 4-5 |
| D62 | 3 | 4 | 4-5 | 4-5 | 4-5 | 4 | 4-5 |
| D63 | 3 | 4-5 | 4-5 | 4-5 | 4-5 | 4-5 | 4-5 |
| D65 | 3 | 4-5 | 4-5 | 4-5 | 4-5 | 4-5 | 4-5 |

**Table-8: Fastness to Rubbing (Dry and Wet) of selected Reactive dyes**

[ 1- poor, 2-fair, 3-good, 4- very good, 5- excellent]

| **Sample** | **Staining on Cotton** | |
|---|---|---|
| | **Dry** | **Wet** |
| D61 | 4 | 4 |
| D62 | 4 | 4 |
| D63 | 4 | 4 |
| D65 | 3-4 | 4 |
| | | |

## III. RESULTS AND DISCUSSION

### 2.1 Physical properties of the dyes

Diazotization was used to make a set of mono azo reactive dyes, which were then coupled simultaneously. After that, the dyes were dried in an oven at 60 °C. On TLC, it was shown to be effective for confirming for the presence of an unreacted diazo compound. These dyes gave wide range of colours ranging from reddish orange to violet.

### 2.2 IR and PMR spectral data

The IR and PMR spectral data are given in table 2 and 3.

### 2.3 Dyeing Properties of dyes

Mono azo reactive dyes were produced and applied to cotton fibre at a depth of 2%. These dyes produced a wide range of colours on fibre, ranging from reddish orange to violet, with great brightness and depth. Synthesized dyes on cotton fibre showed good to very good fastness to wash and rubiing (dry and wet) as per data in Tables 7 and 8.

### 2.4 Determination of percentage exhaustion and Fixation

According to the described procedure, the percentage exhaustion and fixation of the fibre were determined. Table-4 shows the results of dye-bath exhaustion and fixation studies on chosen reactive dyes. The percentages of exhaustion and fixation were found to be in the range of 76-87 % and 77-85 %, respectively. These dyes have excellent percentage exhaustion and fixing. This shows that dyes and fibre have a strong affinity and solubility. Tables 5 and 6 additionally include calibration data for exhaustion and fixation studies of selected reactive dyes.

## IV. CONCLUSION

2-amino 5-mercapto 1,3,4-thiadiazole is used to prepare a variety of mono azo reactive dyes. These dyes produced a wide variety of colours, ranging from reddish orange to violet, with good to excellent colour fastness. The nature and position of the substitute present on the coupling compound cause variations in the colours of dyed fibre. These dyes have a high % of exhaustion and fixation, indicating that they are compatible with fibre. The high level of levelness after washing and rubbing (dry and wet) demonstrates that these dyes have strong penetration and affinity for the fibre.

## ACKNOWLEDGEMENT

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