

## Synthesis And Dyeing Properties Of Novel Bifunctional Reactive Dyes Via 4-(4-Nitrophenyl)-1, 3-Thiazole-2-Amine, 4-(4-Methylphenyl)-1, 3-Thiazol-2-Amine And H-Acid On Nylon Fabrics.

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### -----ABSTRACT-----

Bifunctional reactive dyes are coloured compounds that possess more than one reactive moiety per molecule or groups, capable of forming covalent bonds between dye ions or molecules and the substrate. Two bifunctional reactive dyes 14e and 14f with a single monochlorotriazinyl and vinyl sulphone reactive groups were synthesised via 4-(4-Nitrophenyl)-1,3-thiazol-2-amine and 4-(4-Methylphenyl)-1,3- thiazol-2-amine. The intermediates were diazotized and coupled with H-acid and other coupling components to derive the dyes (14e) and (14f). Wavelength of maximum absorption ( $\lambda_{max}$ ) of dyes were obtained. The dyes were applied on nylon fibres at various pH and temperature conditions. The optimum % exhaustion, % fixation and fixation efficiency were determined in glubber salt as the fixing agent. Washing and light fastness properties of dye samples were determined. The result revealed a  $\lambda_{max}$  of 580nm in (14e) and 640nm in (14f) respectively, % exhaustion maximum values of 61 in (14e) and 69 in (14f) at 80 °C, 61% in (14e), and 75% in (14f) at pH 11, for 70 minutes respectively, % fixation gave maximum values of 70 and 72 in (14e) and (14f) at pH 11 respectively. The fixation efficiency gave maximum values of 70% and 60 % at pH 11 respectively. The fairly good shades observed may be due to better, substantivity as well as good covalent fixation of the dyes with nylon fabrics. The overall results suggest that nitro and methyl groups introduced on the para position of benzene ring of dye molecules induced a hypochromic shift of 60 nm on (14e) and 120nm on (14f) respectively.

**KEYWORDS**- Bifunctional Reactive dyes, %Exhaustion, Fastness properties, %Fixation, Fixation, Efficiency.

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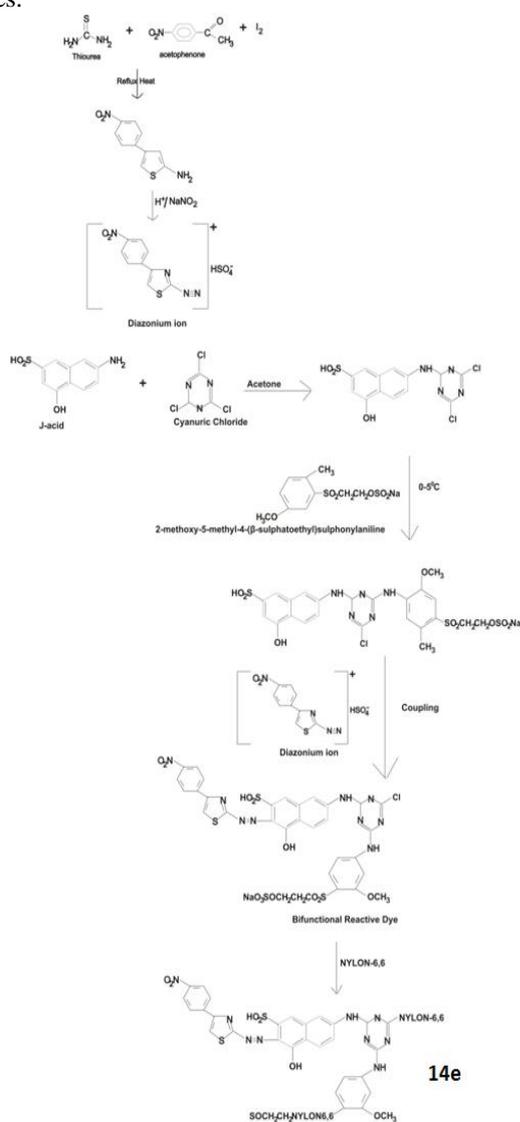


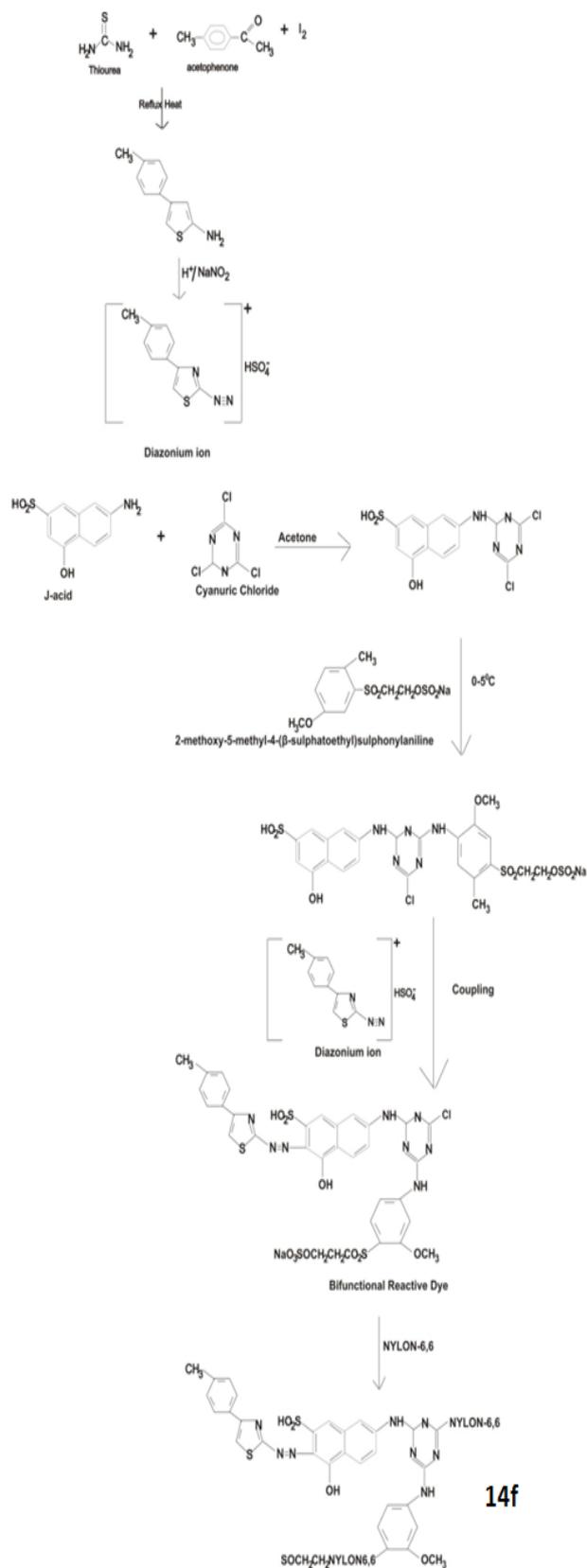
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### I. INTRODUCTION

In general, acid dyes have attracted much attention to nylon substrates due to their interaction mechanism and easy method for application (Yoon *et al*, 2001). However, to achieve satisfactory levels of wash fastness, recourse is required to an after treatment with a commercial syntan and other fixing systems. While an after treatment of the dyed nylon substrates can improve wash fastness, this treatment can impart a change in shade of ground colour but also it is temporary in nature (Burkinshaw and Son, 2001). Consequent upon this, application of reactive dyes to nylon substrates has attracted interests to solve those problems (Preston, 1986). Reactive dyes react chemically with amino groups within the nylon fibres to form a covalent bond. Theoretically, by virtue of the covalent nature of the dye-fibre bond, reactive dyeing on nylon fibres can display excellent wash fastness without any recourse to an after treatment. Especially, reactive dyes containing heterobifunctional groups can provide great opportunity for efficient dye-fibre reaction due to the sulphatoethylsulphone and monochlorotriazinyl reactive systems (Broadbent, 2001). Although this mode of attachment renders the dyeing of nylon straightforward, at least in principle, the wet fastness is usually less than ideal, and there is often a delicate balance to be struck between level dyeing performance and wet fastness (Hunger, 2008) Loss of colour and staining of adjacent fabrics arises from the facile partial dissociation of ion-ion links between dye and nylon (Soleimani-Gorgani and Taylor, 2005). In order to render reactive dyes for nylon attractive to potential customers it is necessary that any such products exhibit an attractive balance of

technical and commercial properties. Desirable technical features include high fixation, good build-up and fastness properties (Dalal and Desai, 1996). The thrust of most published work on reactive dyes for nylon has been a comparison of the relative efficacies, of nylon, of existing cellulose reactive dyes. However, much less has been reported on the effect of other dye parameters, such as molecular size and fixed sulphonation, on the application properties of reactive dyes on nylon. Molecular size and shape are important in determining final dye fixation (Soleimani-Gorgani and Taylor, 2005). In the case of dyeing nylon, at various pH, at fixed degree of sulphonation, hence low net negative charge, might be expected to lead to greater attraction with the positive charged fibre (Nylon-NH<sub>3</sub><sup>+</sup> under various conditions (Soleimani-Gorgani and Taylor, 2005). Additionally, the net charge of the nylon is negative, due to presence of anionic carboxylic acid groups and hence, at various pH values and fixed level sulphonation of dye may be expected to lead to increased attraction between dye and nylon (Yoon *et al*, 2001). Applying the dye at pH 11 generate two important advantages, it would firstly increase the elimination of the temporarily anionic sulphatoethylsulphone groups, and secondly maximize the concentration of the nucleophilic amino end groups on the fiber (Trotman, 1984). This may suggest that the nonionic bifunctional vinylsulphone derivative of the dye, generated from the elimination reaction of the two temporarily anionic sulphatoethylsulphone groups, in addition to the presence of the monochlorotriazine reactive group, can maximize the nucleophilic reaction with the amino groups on both fabrics (Giles, 1974). This paper concerns the build-up characteristics and wash fastness properties of the mixed anchor reactive dyes of heterobifunctional reactive dyes (Hunger, 2008). Exhaustion (%E), fixation (%F) and fixation efficiency (FE) were examined at various pH conditions and dyeing temperatures.





## II. MATERIALS AND METHODS

### 2.1 Synthesis of Intermediates: (4-(4-NitroPhenyl)-1,3-thiazol-2-Amine (1e) and 4-(4-MethylPhenyl)-1,3-thiazol-2-Amine (1f)

Resublimed Iodine (7.6 g, 0.03 mol) was added to the slurry of acetophenone 33cm<sup>3</sup> and thiourea (4.56 g, 0.06 mol) and the mixture was heated in an oil bath at 130 - 140 °C over night. After cooling, the reaction mixture was diluted with distilled water (50 cm<sup>3</sup>) and heated to dissolve most of the solid, cooled to ambient temperature and treated with 25 % aqueous ammonium hydroxide drop-wise to a pH of 9-10. The precipitated thiazole was collected and purified by recrystallization from hot ethanol. The melting point was then determined using Gallenkamp melting point apparatus.

### 2.2 Preparation of the Coupling Component using H - ACID.

Cyanuric Chloride (1.9504 g, 0.0106 mole) was stirred with acetone (40 cm<sup>3</sup>) and water (10 cm<sup>3</sup>) for 1 hour to form a fine suspension at the temperature (-2 °C). After 1 hour, a 83cm<sup>3</sup> solution of 5-naphthol-2-amino-7-sulphonic acid (prepared by adding 3.16 g to 10cm<sup>3</sup> water followed by adding 10% w/v sodium bicarbonate solution to a neutral pH) was added while maintaining the temperature at 5 °C. The reaction mixture was stirred while maintaining the pH of 6.9 - 7 for 3 hrs. To the above solution, a further addition of a fresh solution 10cm<sup>3</sup> of 2-methoxy-5-methyl-4-(β-Sulphatoethyl) Sulphonyl aniline (prepared by dissolving 3.18 g, 0.098 mole in 10 cm<sup>3</sup> of water) was made. The mixture was stirred for half an hour at 0-5 °C, with a gradually raising of the temperature to 35 °C while adjusting the pH to 7.5. The mixture was stirred for 3 to 4 hrs. It was then filtered, washed with cold water and the resultant product was used for subsequent coupling reactions (Dalal and Desai, 1996).

### 2.3 General Method of Diazotization

Diazotization was carried out by method described by Dalal, and Desai, (1996).

### 2.4 General Method of Coupling

The prepared coupling compound was stirred thoroughly at 0 °C, and added slowly to the diazonium chloride solution of **1e** and **1f** over 1.0 hr while maintaining the pH at 7.0. The pH was adjusted to 7 or below using sodium bicarbonate such that sulphatoethyl sulphone functional group would remain unaffected. The stirring was continued for 4 hours at 0-5 °C. A 10 % solution each of sodium hydrogen phosphate and potassium dihydrogen phosphate and then sufficient sodium chloride (15.20 g) was added to precipitate the product. Impurities were removed by washing with a small portion of diethyl ether (Dalal and Desai, 1996).

### 2.5 Purification of Fabric

Cotton fabrics were purified by scouring, bleaching and mercerization by methods prescribed by Sadov *et al*, (1967); Trotman(1984).

### 2.6 Dyeing

Dyeing was carried out as described by (Giles, 1974). Weighing were carried out using Sauter RC 8021 digital weighing balance and optical density measurements were conducted using Jenway 6305 Spectrophotometer. The dye liquors were prepared and a blank containing all the reagents except the dye. Dyeing was done at various pH values by adjusting the dye liquors pH values to 3,5,7,9,11, and 13 respectively with acetic acid and sodium hydroxide. The dye liquors and the blanks were placed in the water bath and the temperature of each maintained at an optimum of 80 °C. A 2.0 cm<sup>3</sup> portion each of the solution in the dye liquors and blanks was taken using syringes for initial optical density (OD<sub>0</sub>) measurements, and then followed with the addition of moist nylon fabric. Dyeing was allowed for 1 hour at 80 °C, after which 2.0 cm<sup>3</sup> was again drawn from the dye liquors. The samples drawn were diluted to 25 cm<sup>3</sup> and evaluated for absorbance at 580 and 640 nm respectively. The initial and final absorbance values obtained were used to calculate % exhaustion for the dyeing at each pH. The values were tabulated and the graph of % exhaustion was plotted against pH. The experiment was repeated varying temperature and Time. % exhaustion was plotted against each variable respectively (Giles, 1974).

## 2.7 Measurement and Analyses

### Determination of dye % Exhaustion

The dye % exhaustion of nylon fabrics (E%) is calculated according to the following equation (Giles, 1974).

$$\% \text{ Exhaustion} = \frac{\text{Initial OD}_0 - \text{Final OD}_1}{\text{Initial O.D}_0} \times 100$$

Where OD = Optical density

OD<sub>0</sub> = values taken before the start of dyeing

OD<sub>1</sub> = values taken at the end of dyeing.

Determination of  $\lambda_{\text{max}}$

The absorbance of dye solutions (14e and 14f) was measured on Jenway 6305 UV visible Spectrophotometer at 0.001 % of solution at  $\lambda_{\text{max}}$  (580 and 640nm) respectively for 14e and 14f.

### 2.8 Stripping process

The dye fixation ratio (%f) is the percentage of the exhausted dye chemically bound to the fabrics (nylon) was measured by refluxing the dyed fabrics samples in 25 % pyridine prepared by measuring 25cm<sup>3</sup> into a beaker, and volume was made upto 100ml with distilled water) for 10 min to extract the unfixed dye (Giles, 1974). The procedure is repeated until the extract was clear. The concentration of extract was measured spectrophotometrically at  $\lambda_{\text{max}}$  of the dyes. The % fixation ratio (%f) and fixation efficiency (FE), which is the percentage of dye chemically bound relative to the total amount of dye used, were calculated using equation (2) and (3) respectively.

$$\%F = \frac{D_0 - D_1 - D_e}{D_0 - D_1} \times 100 \quad (2)$$

$$FE = \frac{(E \times F)}{100} \quad (3)$$

Where D<sub>e</sub> is the amount of extracted dye at the end of dyeing period.

### 2.9 Fastness testing

The dyed samples were tested according to the American Association of Textile Chemists and Colourists (AATCC) standard methods(AATCC, 1999).

### 2.10 Colour fastness to washing:

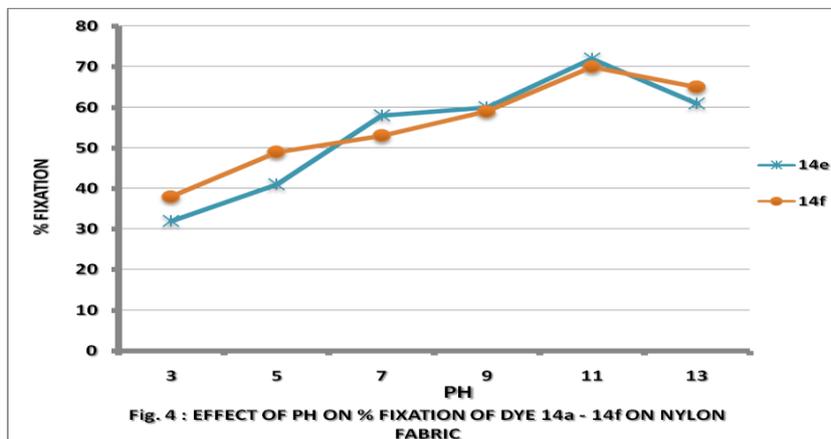
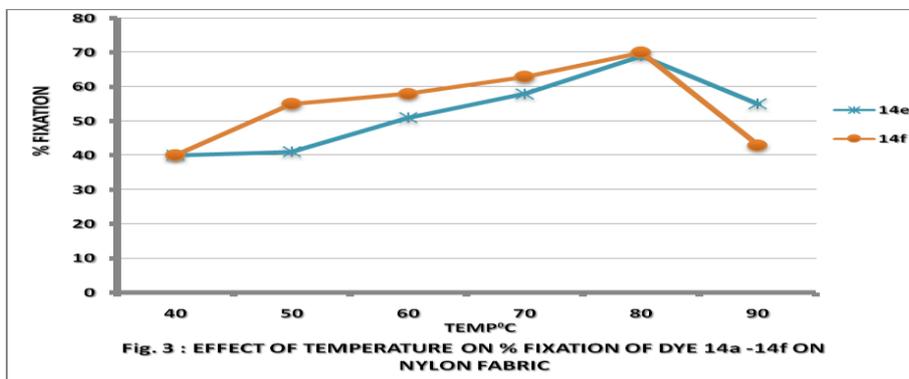
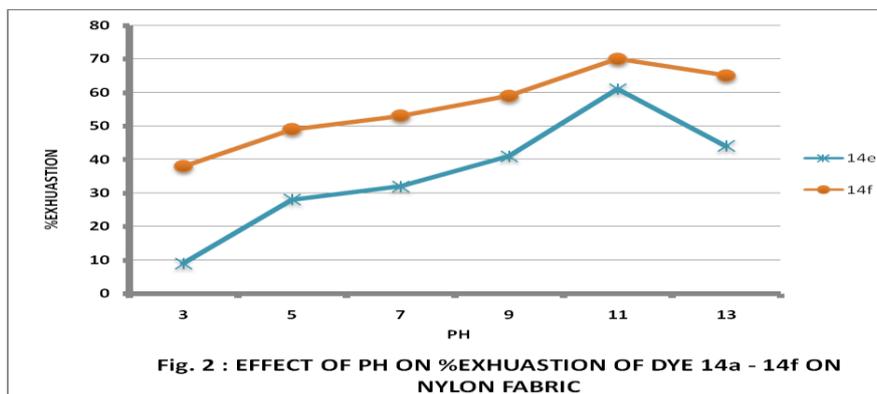
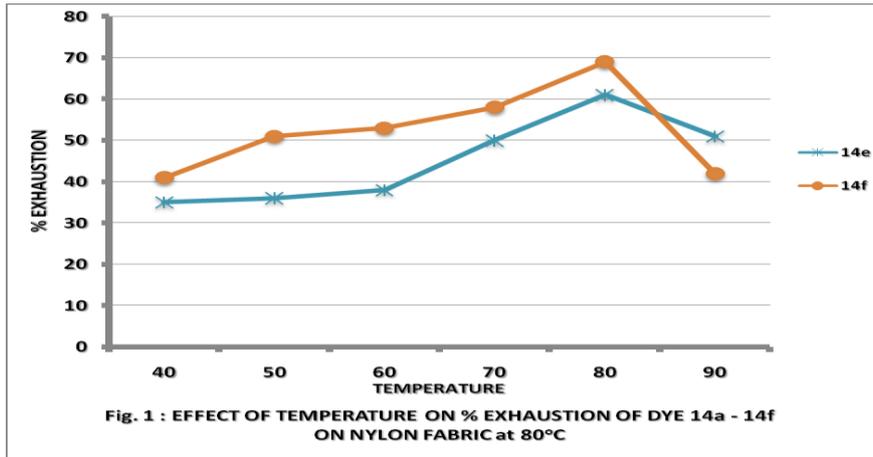
- (i) The composite specimens are sewed between two pieces of bleached cotton fabric and wool fabrics.
- (ii) The composite specimen is immersed into an aqueous solution containing 5g/l soap non-ionic detergent, at 60°C with L.R. 1:50 v/v, the samples are then removed, rinsed in hot and then cold distilled water.
- (iii) Evaluation of the wash fastness is established using the Grey-Scale for the change in colour for dyed samples and staining for nylon 6, 6 fabrics (BS, 1978).

### 2.11 Colour fastness to light:

- (i) A specimen from the dyed fabric to be tested and standards are exposed simultaneously under specified amounts of colour change.
- (ii) The specimens are exposed to the light for about 20 hours.
- (iii) Evaluation of results is carried out by using the Grey-
- (iv) Scale (BS, 1978). If the final assessment is greater, the preliminary assessment becomes significant with very high light fastness, standard fades to a contrast equal to Grade (4) in gray scale (Fan, *et al*, 2004). If the final assessment is slower the rating to a contrast equals to grade 3 indicates that the sample has change very slightly.

## III. RESULT AND DISCUSSION

The effect of temperature on the absorption of 14e and 14f dyes on nylon 6,6 is investigated in the temperature range of 40-90°C at 2 % shade and pH 11.0 in presences of 50 g/dm<sup>3</sup> sodium sulphate (SS) and 20 g/dm<sup>3</sup> sodium carbonate. Figure 1 shows the effect of temperature on percentage exhaustion of dyes 14e and 14f on nylon fabrics. Figure 2, shows the effect of pH on % exhaustion on nylon fabrics. Figure 3, shows the effect temperature on % fixation of 14e and 14f on nylon fabrics. Figure 4, shows effect pH on % fixation of 14e and 14f on nylon fabrics, while figure 5, shows the effect of pH on fixation efficiency both dye samples on nylon fabrics.



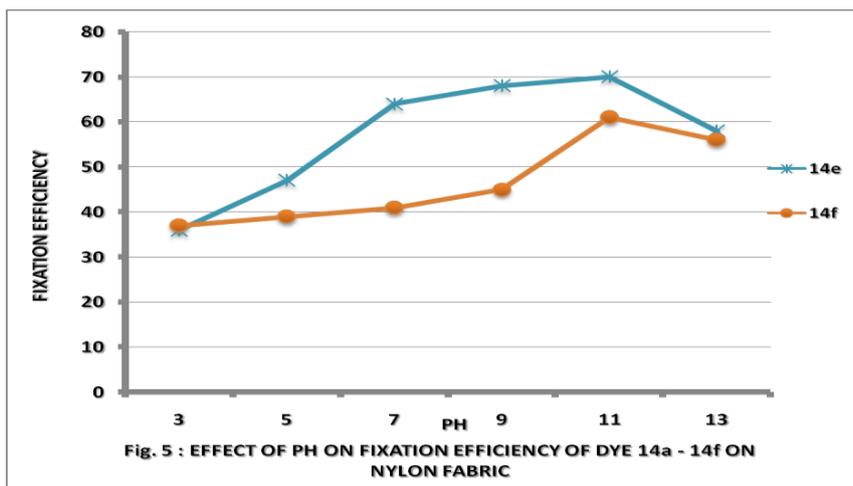


Fig. 5 : EFFECT OF PH ON FIXATION EFFICIENCY OF DYE 14a - 14f ON NYLON FABRIC

### 3.1 Effect of temperature on % exhaustion of dye 14e and 14f on nylon fabrics

In Figure 1, the % exhaustion (14e) increases with temperature from 39 % at 40 °C to 61 % at 80 °C and, the % exhaustion of dye 14f on nylon fabric increased from 39 % at 40 °C to 69 % at 80 °C and decreased as the temperature is extended above 80 °C. The decrease in % exhaustion at the temperature above 80 °C for nylon may be due to the instability of the dye molecules at high temperature. Figure 1 shows that the adsorption of 14e and 14f dyes on nylon enhanced with raise in temperature up to 80 °C for both dyes indicate that high temperature favoured the dye adsorption onto nylon fibre. However, temperature higher than 80 °C for 14e and 14f dyes, respectively resulted to decrease in adsorption, which may be attributed to dye molecule instability at higher temperatures (Ali *et al*, 2009). The increase in temperature increase the mobility of large dye ions as well as produce a swelling effect with the internal structure of the fibre, thus enabling the large dye molecules to penetrate further (Yoshida *et al*, 1993; Venkat *et al*, 2007). This may also be due an increase in the mobility of dye molecules with an increase in their kinetic energy, and the enhanced rate of intra particle diffusion of sorbate with rise in temperature. It is clear that the sorption of 14e and 14f dyes onto nylon fiber is an endothermic process.

### 3.2 Effect of pH on % exhaustion of dye 14e and 14f on nylon fabrics

In Figure 2, the % exhaustion of dye 14e on nylon fabrics increased with pH from 24 % at pH 3 and attains a maximum value of 61 % at pH 9 while 14f increased from 24 % at pH 3 and attains a maximum of 75 % at pH 11 and decreased as the pH is extended further. The low % exhaustion at the acidic medium may be due to the non ionization of the amino group of nylon fabric which facilitate the covalent bonding between the more electrophilic reactive groups of dyes base on monochlorotriazine and vinyl sulphone and the NH<sub>2</sub> groups of nylon fabric, This reflects the advantages of the combined reactive groups having different reactive levels, that complement each other for variations in dyeing conditions. Applying the dye at pH 11 generate two important advantages, firstly would increase the elimination of the temporarily anionic sulphatoethylsulphone groups, secondly maximize the concentration of the nucleophilic amino end groups on the fibre (Mohammed *et al*, 2013). This may suggest that the nonionic bifunctional vinylsulphone derivative of the dye, generated from the elimination reaction of two temporarily anionic sulphatoethylsulphone groups, in addition to the presence of the monochlorotriazine reactive group, can maximize the nucleophilic reaction with the amino groups on both fabrics.

### 3.3 Effect of temperature on % fixation of dye 14e and 14f on nylon fabrics

The results given in Figure 3 clearly show that the dye displays good build up and exhibits good rate of exhaustion on nylon fabric then but decreased in samples (14e and 14f) at further dyeing temperature, probably due to its good substantivity. It is also clear that the total fixation yield of the dye increases as the dyeing proceeds. This may be due to the hydrophobic character of the nonionic (vinylsulphone)/ MCT reactive systems in the dyes, generated from elimination reaction of the temporarily anionic (SES) groups, not only imparts high substantivity under the alkaline dyeing but also effectively exhibits high fixation efficiency. Figure 3 shows the effect of temperature on % fixation of dyes 14e, 14f on nylon fabrics. In figure 3, the % fixation of dye 14e on nylon fabrics increased with temperature from 40 % at 40 °C and attains a maximum value of 70 % at 80 °C while 14f increased from 40 % at 40 °C and attains a maximum fixation of 72 % at 80

°C and decreased as the temperature is extended further. The observation is similar to the report of Rattanaphani *et al*, (2007).

### 3.4 Fixation efficiency

The fixation efficiency shows the effectiveness and efficiency of the dye in the dyeing process. It gives a comparison between the exhaustion and fixation of the dye on fabrics (nylon) with respect to pH (Hunger,2008). Figure 5 shows the fixation efficiency of dye 14e on nylon fabrics increased with pH from 35 % at pH 3 and attains a maximum value of 70 % at pH 11 while 14f increased from 35 % at pH 3 and attains a maximum of 60 % at pH 11, decreased as pH is extended further probably due to its good substantivity, on both fabrics. This may be due to the hydrophobic character of the nonionic bis(vinylsulphone) reactive system in the dye, generated from elimination reaction of bis sulphatoethylsulphone) groups, not only imparts high substantivity under the alkaline dyeing but also effectively exhibits high fixation rate (Farouk *et al*, 2012).

**Table 1: Colour fastness according to AATCC Standard for dyes 14e and 14f at 2% shade in presence of glauber salt at pH 11.0.**

Period in weeks	14e		14f	
	Wash fastness	Light fastness	Wash fastness	Light fastness
1	4-5	4-5	4-5	4-5
2	4-5	4-5	4-5	4-5
3	4-5	4-5	4-5	4-5
4	4-5	4-5	4-5	4-5
5	4	4	4	4
6	4	4	4	4

**Table 2: The dye serial numbers, λmax,molecular weight and melting point,**

Dyes	λmax (nm)	molecular weight	Mpt (°C)
14e	580	908.31	306
14f	640	1021.96	309

### 3.5 Fastness properties

The fastness properties of the dyes on nylon fabrics at 2 % shade, liquor ratio 250:1, pH 11 and 80 °C, were investigated and are given in Table 1. The results show that the fastness to washing and light on nylon displayed a good fastness to washing and light.

## CONCLUSION

A new bifunctional reactive dye, derived from 2-amino thiazole containing two anionic SES and MCT reactive groups, has been synthesised and shown to have good dyeing performance on nylon 6,6 fabrics. Optimum exhaustion and fixation on fabrics was achieved by dyeing at pH 11 and 80 °C. The β-elimination of the two anionic SES groups under alkaline conditions results in the formation of a nonionic reactive vinylsulphone derivative in combination with monochlorotriazine as having different reactivity level, achieving a complementary behaviour to resist variations in dyeing conditions, which in turn increase the dye–fibre interaction and thus improve dye fixation on nylon 6,6 fabrics. Nitro and methyl group introduced on the para position of benzene ring of dye molecules induced a hypochromic shift of 60nm and 120nm respectively.

## REFERENCES

- [1] AATCC Technical Manual, American Association of Textile Chemists and Colorists, 75, 311, North Carolina, USA (1999).
- [2] Abofarha, S.A., Gamal, A.M., Sallam, H.B., Mahmoud, G.E.A. and Ismai L.F.M.. (2010): *Journal of American Science*. Pp117,119. <http://www.Americanscience.org>.
- [3] Ali, S., Hussain,T., and Nawaz, R. (2009) *Journal of Cleaner Production*, 17, 61.
- [4] Broadbent Authur D. (2001) Basic principles of textile coloration. Bradford: *Society of Dyers and Colourists*; p 268.
- [5] BS 1006: (1978), Color A02, A03 color fastness tests. Standard Methods for the Determination of the Colour Fastness of Textiles and Leather (A02, A03), Bradford: SDC, 4<sup>th</sup> ed.
- [6] Burkinshaw, S.M. and Son, Y.A. (2001). *Dyes Pigments*. 48:57 – 69.
- [7] Dalal, M. and Desai, K.R. (1996): **Dyeing effects of bifunctional reactive dyes on knitted cotton fabric**. Pp 23-24. <http://www.American science.org>.

- [8] Fan, Q., Sunil, H., and Yoejun, H. (2004). *Journal of Hazardous Materials*, 112,123.
- [9] Farouk, R., Mohammed, F.A., Youssef Y.A. and Mousa, A.A. ( 2012). **High Performance Thiophene- Based Bifunctional Sulphatoethylsulphone Disazo Reactive Disperse Dye on Silk and Nylon 6 Fabrics.** *Journal of American Science*;8(12):1101-1105]. (ISSN: 1545-1003). <http://www.jofamericanscience.org>. 148.
- [10] Giles, C.H. (1974) “**A Laboratory Course In Dyeing**”, The Society of Dyer and Colorist. Bradford, 3<sup>rd</sup> ed. Pp 35-128
- [11] Hunger, K. (2008). *Industrial dyes: chemistry, properties, applications.* Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; p 113 – 128.
- [12] Mohammed, F.A., Farouk, R., Youssef, Y.A. and Mousa, A.A. (2013). **Dyeing of Nylon 6 and Silk Fabrics with Novel Polyfunctional Disazo Reactive Disperse Dye.** *Journal of American Science* 9(1):34-39]. (ISSN: 1545-1003). <http://www.jofamericanscience.org>
- [13] Preston, C. (1986). *The dyeing of cellulosic fibres.* London: The Dyers’ Company Publications Trust; p142 -147.
- [14] Rattanaphani, S., Chairat, M., Bremner, J.B. and Rattanaphani, V. (2007). An adsorption and thermodynamic study of lac dyeing on cotton pretreated with chitosan, *Dyes and Pigments*, 72, 88 – 96.
- [15] Sadov, F., Korchagin, M. and Matetsky, A. (1967) “Chemical Technology of Fabrous Material”. MIR Publishers, Pp14, 512, 642.
- [16] Soleimani-Gorgani, A. and Taylor, J.A.. (2005). Dyeing of nylon with reactive dyes. Part 2. The effect changes in level of dye sulphonation on the dyeing of nylon with reactive dyes. *Dyes and Pigments* [www.elsevier.com/locate/dyepig](http://www.elsevier.com/locate/dyepig).
- [17] Trotman, E.R. (1984), *Dyeing and Chemical Technology of Textile Fabrics*, Nottingham; 6<sup>th</sup> ed;
- [15] Venkat, S.M., Indra, D.M., and Vimal, C.S., (2007). Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution, *Dyes Pigment.*, 73, 269 – 278.
- [16] Yoon, S.H., Kim, T.K., Lim, Y.J., Son, Y.A., and Korean, J. (2002). *Soc Dyers Finishers* 14:35 – 41.
- [18] Yoshida, H., Okamoto, A., and T. Kataoka, (1993) Adsorption of acid dye on crosslinked chitosan fibers – equilibria, *Chem. Eng. Sci.*, 48, 2267 – 2272.