

## Physical modification of Nylon-6 for improving dyeing quality of selected acid dyes on fabrics and variation of their thermodynamic parameters

Bello, I.A<sup>1</sup>; Bello, K. A<sup>2</sup>; Giwa, A.A<sup>1</sup>; Owolabi, R.U<sup>3</sup> and Adebayo, G. B<sup>4</sup>

<sup>1</sup>Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso. Nigeria;

<sup>2</sup>Department of Textile Science and Technology, Ahmadu Bello University, Zaria. Nigeria; <sup>3</sup>Fountain University, Osogbo Nigeria; <sup>4</sup>Department of Chemistry, University of Ilorin, Ilorin. Nigeria.

### Abstract

Nylon-6 fabric was chemically modified with one agent  $(\text{NH}_4)_2\text{SO}_4$ . The dyes applied to nylon 6 were synthesized by acetylating the amino group of H-acid and the products, coupled to different diazo coupling components. The percentage exhaustion (%E) of the nylon with each dye were determined spectrophotometrically, using both unmodified fabric and the modified fabric at constant temperature of 95°C. The results showed that higher % exhaustion, which is a measure of increase in dye up- take by the fabric, occurred with fabric treated with  $(\text{NH}_4)_2\text{SO}_4$  while there was no change in the % exhaustion of nylon that was not modified. We gave reason for the profile to be due to hydrolysis. Treatment of the fabric with a condensing agent, dicyandiamide also showed that washing fastness of the treated fabric is higher than that of the untreated fabric.

**Keywords:** Nylon-6, modification, dye quality, fabrics, acid dyes, thermodynamic parameters

### Introduction

There are considerable complaints against the locally produced textiles regarding poor fastness of the colored materials. About 50% of the complaints made by consumers on the quality of made in Nigeria textile goods are on the poor fastness aspects of the products, and in fact, this is why the illegal business of smuggling continues to grow. It is a fundamental requirement that colored textiles should withstand the conditions encountered during processing, following coloration and during their subsequent useful life. However, when a colored textile is subjected to particular conditions, e.g. light, washing, milling, bleaching, one or more of several things may happen. For example, during washing, adjacent white material may become colored and colored material may acquire new color due to the transfer of the dye from the original dyed material. This is generally described as staining or marking off. The color fastness of a colored textile is therefore defined as its resistance to these changes when subjected to a particular set of conditions (Nunn, 1979).

This paper aims at examining the effects of modification and after treatments for improving the exhaustion and washing fastness and fixation of some azo dyes on textile fibres. To do this end, selected dyes were synthesized, then applied to nylon-6 fabrics and their exhaustion and washing fastness on fabrics examined before and after dyeing.

---

Correspondence author: E-mail: [belloia2003@yahoo.com](mailto:belloia2003@yahoo.com)

Science Focus; An International Journal of Biological and Physical Sciences

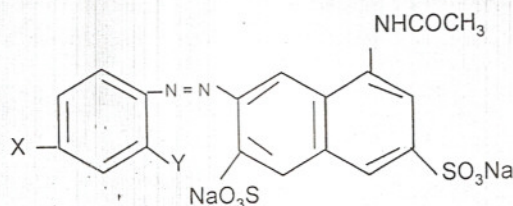
ISSN: 1596 – 7026

[http:// www.sciencefocusngr.org](http://www.sciencefocusngr.org)



## Materials and methods

Five red dyes were used for this investigation. The dyes are derivatives of N-acetyl H-acid and their chemical structures are as shown below.



(1) X = H, Y = H; (2) X = COOH, Y = H; (3) X = NO<sub>2</sub>, Y = H; (4) X = SO<sub>3</sub>H, Y = H; (5) X = Cl, Y = NO<sub>2</sub>

The dyes were made by coupling diazotised aniline, 4-aminobenzoic acid, 4-nitroaniline, sulphanilic acid and 4-chloro-2-nitroaniline respectively to N-acetyl H-acid under alkaline conditions (Fierz-David, 1985). The samples of nylon 6 fabrics used were bought in Zaria market, and the condensing agent used is dicyandiamide and was supplied by RDH chemicals to University of Leeds, U.K from where it was obtained.

## Materials and methods

### Experimental

Five red dyes were used for this investigation. The dyes are derivatives of N-acetyl H-acid and their chemical structures are as shown below.

### Dyeing

Dyeing was carried out in a Rotadyer machine using a liquor ratio of 50:1 at pH of 2.5. The optical density of the original dyebath solution was measured before dyeing. Dyeing was conducted at 95°C for 1 hour. After dyeing, the residual dyebath solution was filtered and made up to 50ml in a volumetric flask, and the optical density measured at the wavelength of maximum absorption of each dye, using a spectrophotometer Unicam SP-150. The optical density of the original dyebath solution was similarly measured before dyeing. The amount of dye absorbed by the fabric was determined. This is repeated for unmodified fabrics and the results obtained are summarized in Table 1.

Table 1: Percent dye exhaustion on nylon-6 fabrics and percent fixation before and after the after treatment with dicyandiamide.

Dye no.	% exhaustion		Partition coefficient K (lt kg <sup>-1</sup> )	Standard affinity (kJ mol <sup>-1</sup> )	Dye fixation	
	A	% E (b)			A	B
1	52	68.3	107.73	-14.434	32.0	45.3
2	50	65.8	96.20	-14.09	28.0	61.0
3	56	70.2	117.78	-14.71	37.5	55.0
4	46	80.0	200.0	-16.34	25.0	40.0
5	58	75.3	150.0	-15.46	45.0	63.0



### Wash fastness test

The wash fastness test was determined using a "Linitest" wash-wheel machine. The ISO No. 3 washing procedure was strictly followed (Bello, 1984). The results obtained are summarized in Table 2.

Table 2: Wash fastness rating of dyes on nylon-6 fabrics before and after the treatment with dicyandiamide.

Nylon -6				
	Change in shade		Staining of white	
	a	b	a	b
1	3-4	5	5	5
2	3-4	5	5	5
3	4	5	5	5
4	3-4	5	5	5
5	4	5	5	5

a, before the treatment; b, after the treatment.

### After treatment of the dyeing with dicyandiamide

The dyed fabric obtained were treated with  $5\text{g/dm}^3$  of dicyandiamide using a liquor ratio of 100:1 for 1 hour under exhaustion dyeing method. After the treatment, the amount of dye fixed on the fabrics were determined as described above. In the same manner, the effect of varying the temperature, time and concentration of dicyandiamide were also studied and the effects of these on fixation determined. The results are shown in Table 2. Also the wash fastness test was repeated for the treated samples and the results obtained are shown in Table 4 along with the untreated materials for comparison.

### Results and discussion

The results of the spectra characteristics of the dyes summarized in Table 3 show that dye (1) absorbs at 502 nm with molar extinction coefficient of  $2.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . This molar extinction coefficient is relatively low compared with other dyes in this series. This may be due to lack of any substituent in the acceptor half of the chromogen. Dye (2) obtained by coupling 4-aminobenzoic acid with N-acetyl H-acid absorbs at 507 nm with molar extinction coefficient of  $4.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  in water. This dye is more bathochromic than dye (1) due to the incorporation of the electron withdrawing carboxylic group at the para position of the acceptor half of the dye molecule.

Table 3: Spectra characteristics data of the dyes

Dye no.	$\lambda_{\text{max}}$ (nm) (in water)	Absorbance	Molar extinction Coefficient ( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) in water
1	502	1.08	$2.7 \times 10^4$
2	507	1.57	$4.5 \times 10^4$
3	506	1.26	$3.3 \times 10^4$
4	502	1.62	$4.9 \times 10^4$
5	503	1.18	$3.5 \times 10^4$



Replacement of the carboxylic group in dye (2) with nitro group gives dye (3) with absorption wavelength at 506nm. In this case, the electron withdrawing effect of both the nitro group and the carboxylic group at the para position are about the same with the carboxylic group absorbing with only a difference of 1nm. Dyes (4) and (1) absorb at the same wavelength, thus the sulphonic group incorporated at the para position has no effect on the visible absorption wavelength, however, the solubility property of dye (4) is more enhanced due to the presence of more sulphonic groups. Dye (5) has two electron withdrawing groups incorporated in the meta and para positions relative to the azo linkage and absorbs at 503nm. This dye is not as bathochromic as expected and the visible absorption is about the same as dye (1) without any substitution in these positions. This may be due to steric crowding of the nitro and the chlorine substituent which may prevent complete planarity of the dye molecule. Dye (1) exhaust better on nylon than dye (2) but dye (2) gives a deeper shade. However, dye (2) exhausts better on nylon. This variation in dye exhaustion might be due to the number of sulphonic groups and the relative molecular size of the dyes. For example, dye (4) has more sulphonic groups leading to increased solubility and high exhaustion while dye (1) has a lower molecular weight and size and is able to penetrate the more crystalline regions of nylon fibre.

The results of the washing fastness test summarized in Table 2 show that all the dyes gave dyeing of excellent wash fastness on nylon 6. The excellent wash fastness obtained on nylon 6 with all the dyes investigated may be due to the more crystalline nature of polyamide fibre. The results of the wash fastness test after the materials have been treated with dicyandiamide show that dyeing obtained with nylon fabrics show greater improvement in fastness to washing which might suggest that some forces other than the mechanical attachment might have come into play, for example, salt electrostatic links.

The results of the treatment of the dyed fabrics with dicyandiamide summarized in Table 2 also show increases in fixation for all the dyed fabrics with the dyes containing carboxylic group showing higher fixation on nylon 6 fabrics. This certainly shows that some forces other than mechanical retention of the dyes are responsible for this high fixation as pointed out by Nkeonye (1988) in a related study. It is interesting to note from the results summarized in Table 2 that dye (5) with nitro and chloro groups also show higher fixation. The fixation of this dye is higher on nylon 6 than for the carboxylic acid dye (2). This result may be ascribed to the chloride and nitro substituents. Further studies with dicyandiamide as shown in Table 2 reveal that dye exhaustion increases with increase in temperature, time and concentration of the condensing agent.

### Thermodynamic parameters

From thermodynamic point of view, the exhaustion of these dyes on nylon fabric showed that Dye 4 has the highest with 80.3% closely followed dye 5 and dye 3 with 75.3% and 70.2 % exhaustion respectively. Dye 1 marginally has lower exhaustion of 68.3 % compared with dye 3. The partition coefficients of the dye followed the same trend. For the standard affinities Dyes 1, 2, and 3 are in the same range of 14.71kJ mol<sup>-1</sup> to 14.09.kJ mol<sup>-1</sup>, meaning that the ease of dyeing using these three dyes almost remain the same. Dye 2 has the least affinity for the fabric while dye 4 has the highest affinity for nylon among the five dyes. The effect of (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub> on dyeing is reflected by an increase in % exhaustions as shown in Table 2. For instance, Dye 1 has exhaustion of 52.0 (untreated) while it has 68.3% when treated, an increase in exhaustion of 16.3%. The same thing is applicable to other dyes. The dyes used here are all acid dyes and can only dye material under acidic condition. The modifying agent applied here (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub>, is a salt formed from a weak base (NH<sub>4</sub>OH) and a strong acid H<sub>2</sub>SO<sub>4</sub>, so it undergoes hydrolysis thus:



The hydrogen (hydroxonium) ions H<sup>+</sup> so produced attack the amino group of nylon (Ny - NH<sub>2</sub>) thereby protonating the nylon, and this now attracts the (SO<sub>3</sub><sup>-</sup>) anions of the dye covalently and the material is dyed. It is therefore not surprising that dye 4 which has the highest number of SO<sub>3</sub><sup>-</sup> group has the highest exhaustion of 80% and has the least dye fixation of 25% before treatment and 40% after treatment with condensing agent.



## Conclusion

All the dyes synthesized exhaust well on nylon 6 and with good leveling properties. However the wash fastness rating on nylon 6 was higher, i.e. improved when treated with dicyandiamide and this shows that treatment is very important for improving the quality of textile materials. Likewise, the equilibrium % exhaustion (%E) increases with modification of the fabric. It was noticed that the increment of % E is directly proportional to the number of  $-SO_3^-$  attached to the dye molecules, hence increase in the standard affinity ( $\Delta\mu^0$ ) of all the dyes on modified fabrics and followed the same trend. The modifying agent used here, which is a hydrolyzing agent supplies the  $H^+$  ions needed to protonate the nylon fabric. It therefore acted as a source of acid in a sliding manner which allows for non-patch dyeing.

## References

- Bello, K.A. (1985). Reaction of colored carboxylate with polyamide. M.Sc. Thesis, University of Leeds.  
 Bello, I.A., Peters O.A., Nkeonye, O.P., sunmonu, O.K. (2002) Kinetics and Thermodynamic studies of an acid dye on modified nylon 6 fabric Science Forum 5, 2, 309-316.  
 Fierz-David, H.E. (1985). Fundamental Processes of Dye Chemistry. 1<sup>st</sup> Edition New York, Interscience. 50-56.  
 Nkeonye, P. O. (1988). Infrared studies of the reaction products of phosphonated and carboxylated reactive dyes with cellulose", Textile Research Journal 58, 57 – 59.  
 Nunn, D.M. (1979). The dyeing of Synthetic Polymer and Acetate Fibres. 1<sup>st</sup> Edition. Dyers Company Publication Trust, Bradford, U.K. pp 53-54.

## Conclusion

All the dyes synthesized exhaust well on nylon 6 and with good leveling properties. However the wash fastness rating on nylon 6 was higher, i.e. improved when treated with dicyandiamide and this shows that treatment is very important for improving the quality of textile materials. Likewise, the equilibrium % exhaustion (%E) increases with modification of the fabric. It was noticed that the increment of % E is directly proportional to the number of  $-SO_3^-$  attached to the dye molecules, hence increase in the standard affinity ( $\Delta\mu^0$ ) of all the dyes on modified fabrics and followed the same trend. The modifying agent used here, which is a hydrolyzing agent supplies the  $H^+$  ions needed to protonate the nylon fabric. It therefore acted as a source of acid in a sliding manner which allows for non-patch dyeing.

## References

- Bello, K.A. (1985). Reaction of colored carboxylate with polyamide. M.Sc. Thesis, University of Leeds.  
 Bello, I.A., Peters O.A., Nkeonye, O.P., sunmonu, O.K. (2002) Kinetics and Thermodynamic studies of an acid dye on modified nylon 6 fabric Science Forum 5, 2, 309-316.  
 Fierz-David, H.E. (1985). Fundamental Processes of Dye Chemistry. 1<sup>st</sup> Edition New York, Interscience. 50-56.  
 Nkeonye, P. O. (1988). Infrared studies of the reaction products of phosphonated and carboxylated reactive dyes with cellulose", Textile Research Journal 58, 57 – 59.  
 Nunn, D.M. (1979). The dyeing of Synthetic Polymer and Acetate Fibres. 1<sup>st</sup> Edition. Dyers Company Publication Trust Bradford, U.K. pp 53-54.

## Conclusion

All the dyes synthesized exhaust well on nylon 6 and with good leveling properties. However the wash fastness rating on nylon 6 was higher, i.e. improved when treated with dicyandiamide and this shows that treatment is very important for improving the quality of textile materials. Likewise, the equilibrium % exhaustion (%E) increases with modification of the fabric. It was noticed that the increment of % E is directly proportional to the number of  $-SO_3^-$  attached to the dye molecules, hence increase in the standard affinity ( $\Delta\mu^0$ ) of all the dyes on modified fabrics and followed the same trend. The modifying agent used here, which is a hydrolyzing agent supplies the  $H^+$  ions needed to protonate the nylon fabric. It therefore acted as a source of acid in a sliding manner which allows for non-patch dyeing.

## References

- Bello, K.A. (1985). Reaction of colored carboxylate with polyamide. M.Sc. Thesis, University of Leeds.  
 Bello, I.A., Peters O.A., Nkeonye, O.P., sunmonu, O.K. (2002) Kinetics and Thermodynamic studies of an acid dye on modified nylon 6 fabric Science Forum 5, 2, 309-316.  
 Fierz-David, H.E. (1985). Fundamental Processes of Dye Chemistry. 1<sup>st</sup> Edition New York, Interscience. 50-56.  
 Nkeonye, P. O. (1988). Infrared studies of the reaction products of phosphonated and carboxylated reactive dyes with cellulose", Textile Research Journal 58, 57 – 59.  
 Nunn, D.M. (1979). The dyeing of Synthetic Polymer and Acetate Fibres. 1<sup>st</sup> Edition. Dyers Company Publication Trust Bradford, U.K. pp 53-54.