

## **A STUDY ON THE AFTER – TREATMENTS OF METALLISED ACID DYE ON NYLON 6, 6 BY USING REACTIVE FIXING AGENT**

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### **ABSTRACT**

*Dyed nylon6,6 with non-metalized acid dyes show poor wet fastness at ISO C06/D1S (70 °C) wash test. Sodium 2-(4-(4,6-dichloro-1,2,3-triazin-2-ylamino)phenylsulfonyl) ethanesulfonate an fixing agent was synthesized and applied as an after-treatment on nylon6,6 dyeing in order to improve poor wet fastness. The after-treatment was done at various concentrations of reactive fixing agent on mass of fabric (omf) and application pH. It was found that fixing agent attached with fiber by virtue of covalent nature, therefore effectiveness of fixing agent in improving wet fastness was achieved. Wet fastness improvements were gained on applying fixing agent at pH 8 and 5% concentration (omf). Furthermore, colour coordinate values were also analyzed during this study.*

**Keywords:** *After-treatments; Nylon6,6; Non-metalized acid dye; Reactive fixing agent; Wash fastness.*

### **INTRODUCTION**

Nylon6,6 (polyamide) is widely used synthetic polymer in textile and also commercially available. Nylon and nylon blends were touted for their amazing “wash and wear” qualities, meaning they could be washed and worn without ironing. Nylon6,6 fabric has low absorbency rate, which makes it ideal for swimwear and sport wear, by accounting such properties polyamide plays an important role in the textile

industry. However nylon6,6 dyeing with many acid dyes including some pre-metallised acid dyes show poor or moderate wet fastness to repeated washing (Burkinshaw 1995 and Burkinshaw et al, 2000) and much improvements have been gained by after treating dyeing of nylon6,6 with different complexing agents like potassium antimony tartrate and tannic acid in conjunction with metallic salts in classical full backtanaftertreatments results in the formation of high  $M_r$ gallotannin, which is adsorbed onto the dyed nylon6,6 surface through protonated amino end groups and during washing resist the desorption of dye molecules from nylon6,6 fabric due to the formation of high molecular weight hydrophobic complex (Burkinshaw et al, 2003 and Burkinshaw and Kumar, 2008 c).

And tannic acid in conjunction with ferrous sulfate used as after-treatments shows comparable wash fastness results at 60°C than previous research (Burkinshaw et al, 2003, 2008 c). Tannic acid and ferrous sulfate form iron tantate complex which imparts a slight grayish colour to dyeing, although it does not affect the  $\lambda_{max}$  of dyeing, yet increase the colour strength of dyeing (Burkinshaw and Kumar, 2008 c). Despite the effectiveness of potassium antimony tartrate/tannic acid, and tannic acid/ferrous sulfate after-treatments (Burkinshaw et al, 2003 and Burkinshaw and Kumar, 2008 c). Polyvinyl alcohol (PVA) had also been used as an after-treatments, which is low cost, readily available polymer had been proved a good after-treating agent, but polyvinyl alcohol (PVA) imparts a yellow colouration and also reduce the chroma of red as well as lightness ( $L^*$ ) (Burkinshaw and Kumar, 2008 a).

Nylon6,6 fabric can be dyed using dyes belonging to different classes, however the wet fastness of non-metallised acid dyes on substrate is often unsatisfactory while pre-metallised acid dyes using Cd, Cr, Ni and Pb display superior wet fastness but their use has attended serious environmental concern to marine life in recent years (Kristin et al 2010). Similarly among other metals, widespread use of Cu exhibits high toxicity to aquatic life (Jin-Seok and Harold, 2007). So on focusing the running race of improving wash fastness along minimum disadvantages like imparting some hue to fabric and toxicity a reactive fixing agent was decided to synthesize and use as an after-treatments for dyed nylon 6,6with non-metallised acid dyes and investigate its effectiveness over nylon6,6 and discussed properties as well.

## 2) EXPERIMENTAL

### 2.1) Materials

The scoured and knitted nylon6,6 fabric was supplied by INTERLOOP private Ltd (Faisalabad) , that was used in this work and commercial sample of Acid Black 1 and fixing agent (Sodium 2-(4-(4,6-dichloro-1,2,3-triazin-2-ylamino) phenylsulfonyl) ethanesulfonate) was supplied by SANDAL DYESTUFF private Ltd Faisalabad, Pakistan. The other chemicals were laboratory grade reagents.

### 2.2) Procedure

#### 2.2.1) Dyeing

The dyeing was done in 300cm<sup>3</sup> capacity stainless steel dye pots housed in laboratory scale infrared dyeing machine using liquor ratio 40:1 at pH 4.5-5 adjusted with acetic acid was describe in figure 1. Two dye shades one lighter (0.5% omf) and other darker (4% omf) was selected to use. After dyeing samples were rinsed in tap water thoroughly.

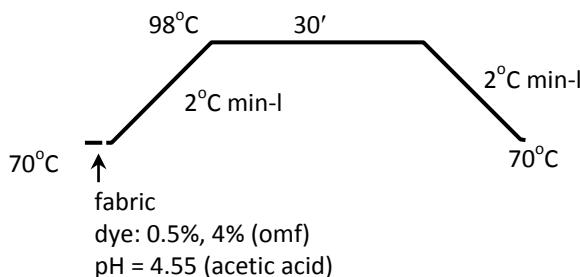
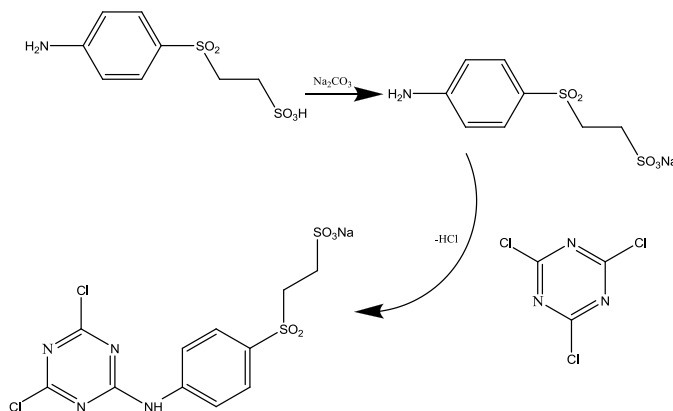


Figure 1: Dyeing method.

#### 2.2.2) Synthesis of fixing agent

The Sodium 2 - (4 - (4, 6 - dichloro - 1, 2, 3 - triazin - 2 - ylamino) phenylsulfonyl) ethanesulfonate was synthesized by the method described by Kim et al., (2004). 0.05M solution of 2-(4-aminophenylsulfonyl) ethane sulfonic acid<sup>1</sup> was neutralized by 0.016M solution of Na<sub>2</sub>CO<sub>3</sub> in water and then solution was cooled to 0-5°C (solution 1). Then the already 0.05M prepared solution in acetone of 2,4,6-trichloro-1,3,5-triazine<sup>3</sup> was poured in distilled water and adjusting

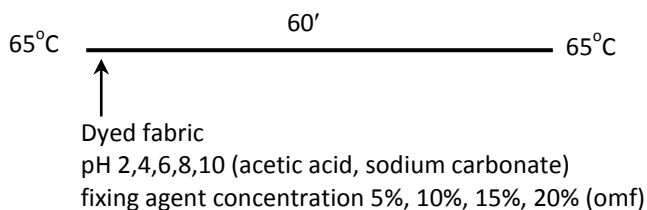
the pH 1-2 using 2N HCl (solution 2). Now the solution 1 was added very slowly to solution 2 and adjusting the pH to 6 by using sodium carbonate. The reaction mixer was stirred continuously for 1 hour at 0-5°C. At the end of the reaction light brown precipitated solid<sup>4</sup> was filtered and wash with acetone, dried in vacuum at room temperature (scheme Fig. 2)



**Fig. 2: Synthesis of Sodium 2-(4-(4,6-dichloro-1,2,3-triazin-2-ylamino)phenylsulfonyl)ethanesulfonate.**

### 2.2.3) Fixing agent after-treatments

Dyed nylon6,6 substrates were after-treated with fixing agent at various pH as well as concentration (omf). The pH was adjusted by using acetic acid and sodium carbonate. The after-treating method is described in figure 3.



**Figure 3: After-treatment method.**

### 2.2.4) Colour measurements

All measurements (colour coordinates value) were carried out using spectrophotometer. Values were taken by folding samples once to two thicknesses and averages of three values were taken.

### 2.2.5) Washing fastness

Wash fastness tests were performed, using ISO-105C06/D1S (70°C) wash test method and staining was obtained by using multifibre strip.

## 3) RESULTS AND DISCUSSIONS

Regarding popularity, black shades are commonly used for dyeing every type of fibre. Nylon 6,6 can be dyed by using variety of anionic dye classes including acid, mordant, direct and reactive but from two types of acid dyes, premetallised and non-metallised acid dyes, the earlier type of dyes are proved to be excellent resisters to wet fastness treatments but metals which use for metallization, pose number of serious environmental concerns. Premetallised acid dyes are superior than non-metallised acid dyes regarding wet fastness (Burkinshaw et al 2000) but such dyeing of nylon6,6 with non-metallised acid dyes is a problematic matter regarding level of wash fastness (Burkinshaw and son 2008). So it was decided to use black non-metallised acid dye (Acid Black 1) for dyeing nylon6,6. Figure 4 shows the extent of reduction in K/S on subjecting untreated dyeing at ISOCO6/D1S (70°C) wash test.

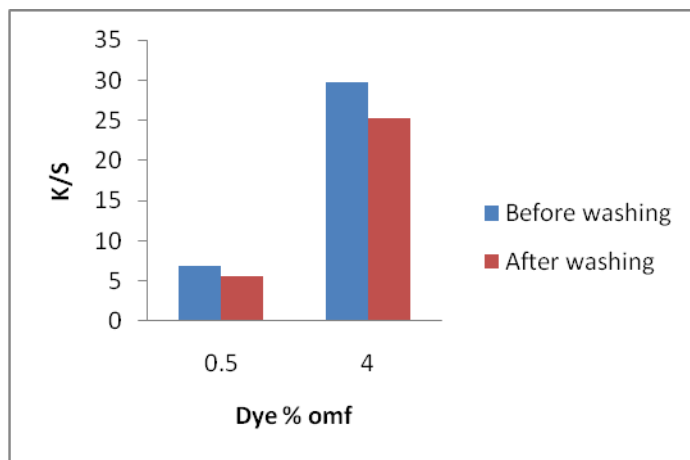


Figure 4: Comparison of K/S values of untreated dyeing before and after washing

*Table 1: Staining of adjacent multifibre strip achieved for untreated dyeing*

Percentage dye shade	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
0.5%	4-5	4	3	5	5	3-4
4%	3-4	3	3	4-5	5	3

It is found that the extent of reduction in K/S of untreated dyeing of nylon 6,6 increased with increasing depth of shade and this corresponding colorimetric data also presents that the shade changes observed were attributed to loss of dye from substrate during washing rather than to changes the colour of dyeing (Table 2).

*Table 2: Colorimetric data for untreated dyeings.*

Percentage dye shade	Washing	L*	a*	b*	C*	h°
0.5%	Nil	38.24	-5.38	-7.48	9.22	234.29
	1	43.43	-8.99	-12.48	15.38	234.25
4%	Nil	17.97	-3.04	-6.14	6.86	243.67
	1	23.50	-7.90	-11.96	14.34	236.55

In order to improve level of wet fastness, after-treatments had been done by using a reactive fixing agent (Sodium 2-(4-(4,6-dichloro-1,2,3-triazin-2-ylamino) phenylsulfonyl) ethanesulfonate) at various concentrations omf and application pH.

### **3.1) Effect of concentration of fixing agent on dyeings**

Both lighter (0.5% omf) and darker (4% omf) samples were after-treated with fixing agent (name) at various concentrations (5%.10%,15%,20% omf) with pH 8 for 60 minutes at 65°C temperature according to fig. 2. The after-treated samples were washed thoroughly and the effectiveness of fixing agent was determined by measuring the reduction in K/S of after-treated samples. Figure 5 & 6 present the decrease in colour strength values (K/S) of both lighter (0.5% omf) and darker (4% omf) after-treated samples.

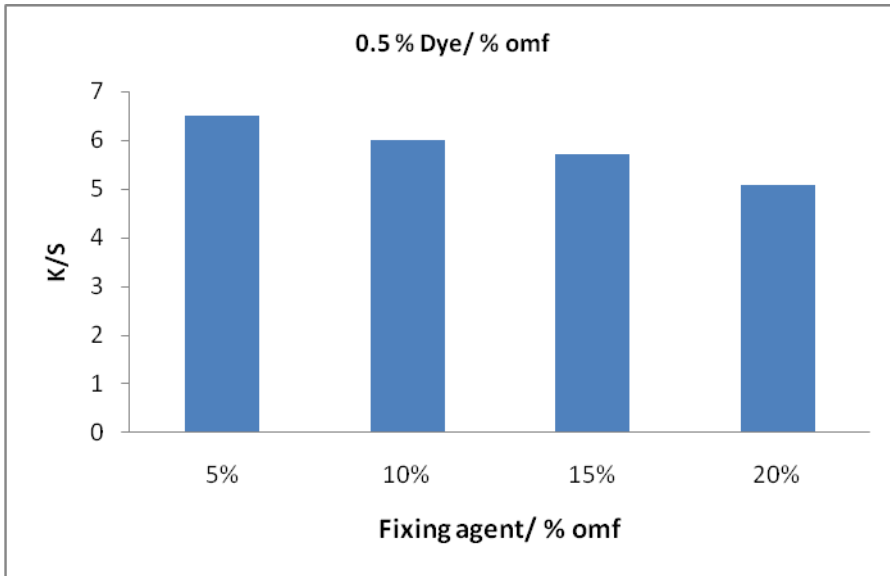


Figure 5: Comparison of reduction in K/S values of before and after-treated dyeing.

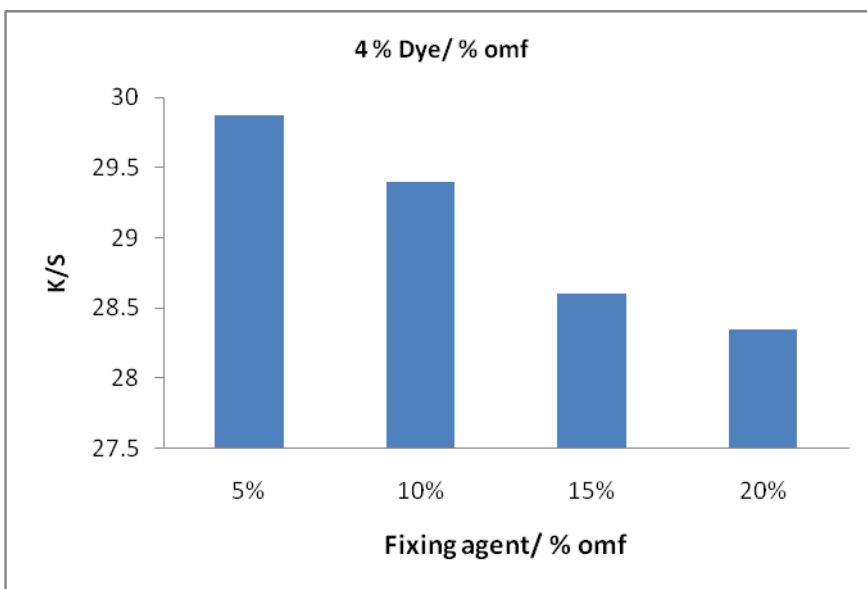


Figure 6: Comparison of reduction in K/S values of before and after-treated dyeing.

Results illustrate that the reduction in K/S values were more enhanced with increasing the concentration of applying fixing agent omf. In both cases of lighter and darker dye shades, the reduction in K/S values were minimum at 5% concentration of applying fixing agent omf and close to untreated dyeing which can be attributed as the corresponding

concentration is effective and such effectiveness results in better fixation of fixing agent along with less loss of dye molecules from substrate surface during its application. This corresponding concentration was employed to study the effect of application pH of fixing agent, which describe below.

### **3.2) Effect of application pH of fixing agent on dyeing**

Effect of application pH of fixing agent on nylon6,6 dyeing in terms of K/S value was determined at its optimized concentration omf. Fixing agent was applied at various pH values (2,4,6,8,10) at 65°C temperature and pH was adjusted by using laboratory grade acetic acid and sodium carbonate. Fig 7 & 8 represents the change in K/S value observed by applying the fixing agent at different pH values. K/S value became increased than the untreated dyeing at pH 2-6 which can be attributed as the shade change and it became close to the values of untreated dyeing at pH 8-10 for both shades (0.5% & 4% omf). This finding can be explained on the adsorption behaviour of fixing agent nylon6,6 dyeing. Under acidic conditions (pH 2-6), only electrostatic interactions existed between fixing agent and protinated amino as well as terminal hydroxyl groups of nylon6,6 however on the other hand, it is believed that in basic media (pH 8-10) the availability of lone pair at NH<sub>2</sub>- group in nylon 6,6 increases and that NH<sub>2</sub>- group attack on reactive Cl of fixing agent nucleophilicalyand covalently attach with nylon6,6. Vinyl sulphone group that is present in fixing agent whose reactivity increase with increasing temperature and pH, while the double bond of vinyl sulphone group becomes activated under the alkaline conditions and it can under goes electrophilically addition reaction with hydroxyl and amino groups (Hunter and Renfrew, 1999) of nylon 6,6, that leads to the formation of network cross linking across the dyeing. This network cross linking acts as a physical barrier around the dyed nylon6,6 substrate and decrease the leaching of dye molecules during washing. So the optimized pH for getting better wet fastness and maximum fixing of Sodium 2-(4-(4,6-dichloro-1,2,3-triazin-2-ylamino) phenylsulfonyl) ethanesulfonate is 8.



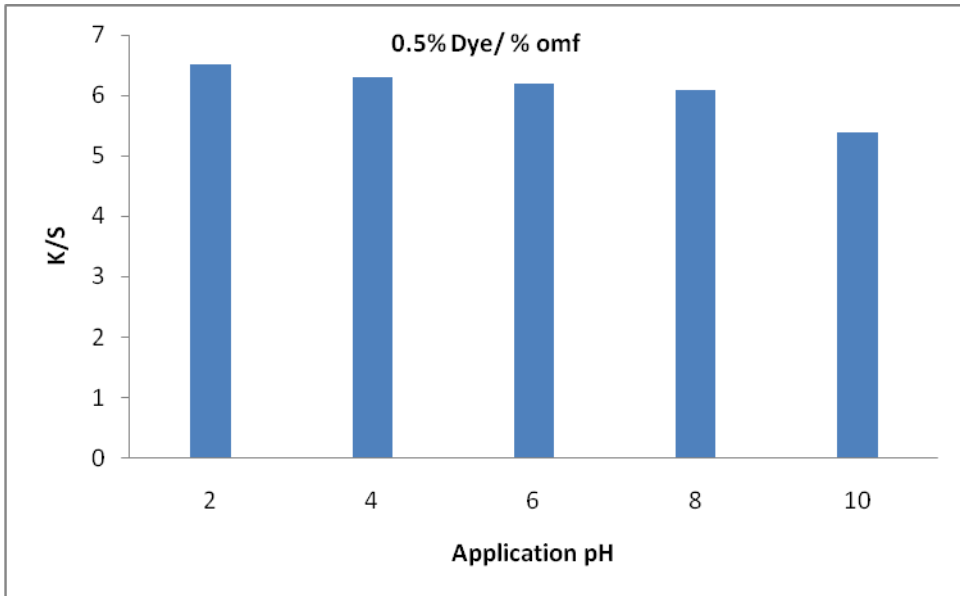


Figure 7: Effect of application pH on K/S values of after-treated dyeing

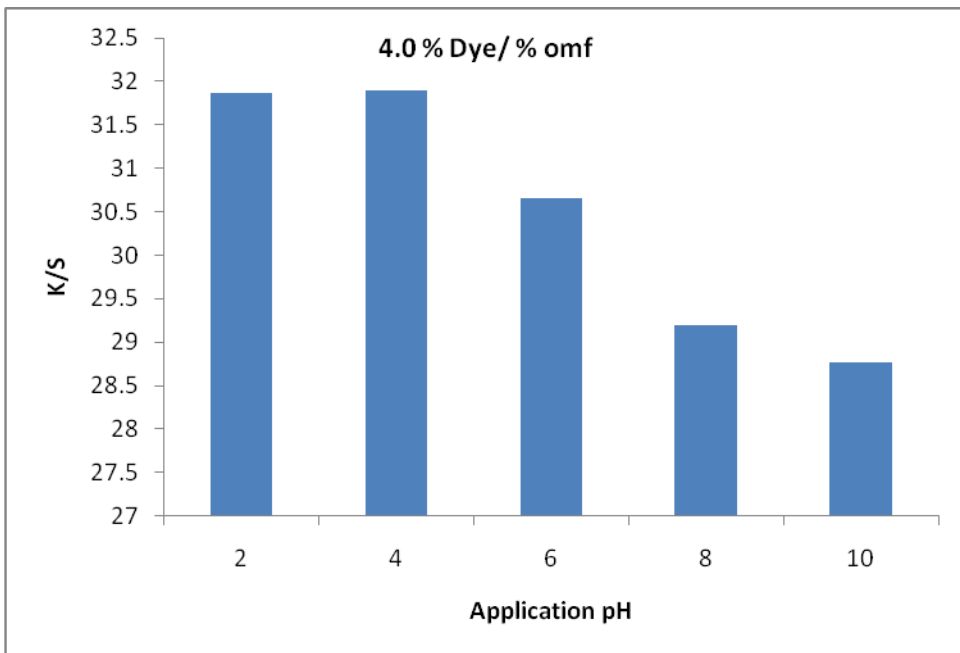


Figure 8: Effect of application pH on K/S values of after-treated dyeing

### Washing of after-treated dyeing at optimized conditions

As the low level of wet fastness of nylon6,6 dyeing with non-metallised acid dye is discussed previously (Figure 4) which is also become cleared by comparatively studying the staining achieved by the untreated dyeing on multifibre strip, which can be attributed to the loss of dye molecules during washing. So in order to enhance wet fastness, the after-treatments had been done by using a reactive fixing agent (Sodium 2-(4-(4,6-dichloro-1,2,3-triazin-2-ylamino)phenylsulfonyl)ethanesulfonate) at its optimized conditions regarding minimum disadvantages like polyvinyl alcohol imparted yellow colouration to dyeing (Burkinshaw and Kumar, 2008 a) and premetallised acid dyes which are environmental non friendly. Table 3 shows the staining obtained over multifibre strip of after-treated nylon6,6 dyeing, which was considerably reduced than the staining observed for untreated dyeing. This reduction in staining can be considered the effectiveness of after-treatments. Similarly by comparatively consulting the reduction in K/S values of both before and after-treated dyeing (Figure 9) also show that considerable improvements regarding wet fastness had been achieved.

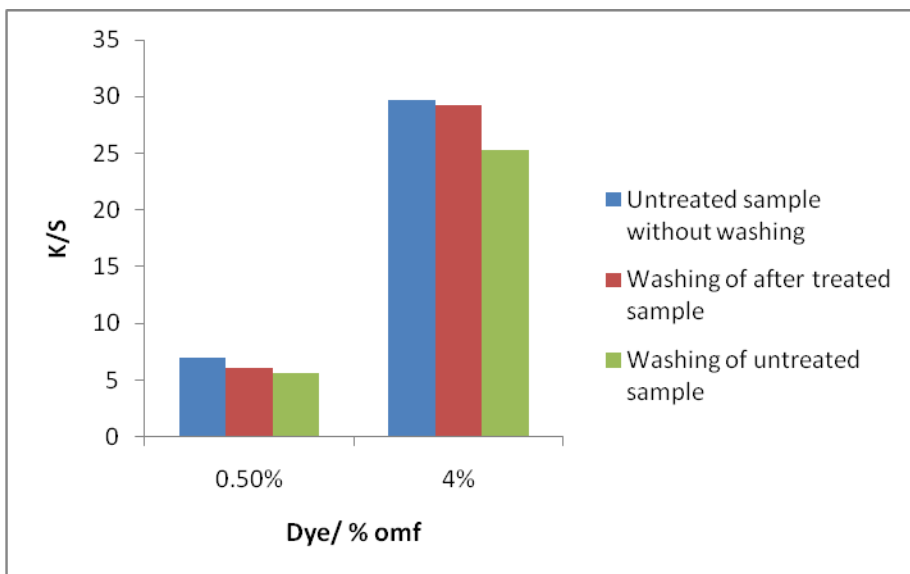


Figure 9: Comparison of reduction in K/S values of before and after-treated dyeing

Table 3: Staining of adjacent multifibre strip achieved for after-treated dyeing

Percentage dye shade	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
0.5%	5	4	4	5	5	5
4%	4	4	4	5	5	4

In previous studies, the reactive crosslinking agents were used to improve the exhaustion of dyes molecules towards fibre and improve their fixation as Lewis and Ho (1996) used 2-Chloro-4, 6-di (aminobenzene-4'-vinylsulphone)-s-Triazine. Similarly Burkinshaw and Kumar (2008 b) studied PVA-based aftertreatments in order to enhance washing fastness at 60°C. In the present study the use of Sodium 2- (4-(4, 6-dichloro-1, 2, 3- triazin-2-ylamino) phenylsulfonyl) ethanesulfonate as an aftertreatment not only enhanced the fixation of dye molecules over fibre surface but also improved level of washing fastness at 80°C as mentioned in Fig 9. So from the results it appears that the fixing agent improved the level of wet fastness by reducing the leaching of dye molecules from substrate during washing after making a physical barrier around the substrate.

## CONCLUSION

Findings of the present investigation clearly illustrate the improvement in washing fastness by applying the fixing agent onto dyed nylon 6,6 with non-metallised acid dye. Generally the fixing agents are sensitive to pH and their efficiency is significantly dropped at elevated pH. The evaluated fixing agent was applied under harsh conditions of pH. It was ascertained from the colorimetric data that the efficiency of fixing agent in terms of washing fastness increases with the pH of media in which fixing agent was applied and with its 5% concentration (omf). The washing fastness properties increases gradually and become maximum at basic pH i.e. 8. The investigated fixing agent has shown its importance as reactive fixing agent in the finishing of textile fabrics regarding washing fastness properties.

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