

## Improvement in Wash Fastness of Dyed Silk by Aftertreatment with Commercial Syntan/Metal Salts

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### ABSTRACT

**S**ilk yarns were dyed by using commercial basic, reactive and pre-metallised acid dyes. An aftertreatment with a commercial synthetic tanning agent (syntan) was applied to the dyeings and the aftertreated dyeings were further treated with metal salts in an attempt to improve wash fastness properties. When all samples (untreated, syntanned and syntanned/backtanned specimens) were subjected five times to a repeated wash testing (ISO 105C01), it was found that the fastness, to repeated wash testing, was improved, as expected by an aftertreatment with the commercial syntan. Further, significant, the two-stage, syntan/metal salts aftertreatment raised the level of wash fastness of the syntanned samples. Prog. Color Colorants Coat. 1(2008) 27-36. © Institute for Colorants, Paint and Coatings.

## 1. Introduction

Silk fiber as a protein fiber that is produced from silk worm *Bombyx mori* and consists of 97% protein, and the rest are wax, carbohydrate, pigments, and inorganic compound [1]. Because natural silk, as a protein fiber of animal origin, resembles wool in its chemical structure, it can be dyed with most of the classes of dyes used for wool. The choice of dyes depends essentially on the fastness properties required. The occasionally inadequate wash fastness of these dyeings can be substantially improved by a proper aftertreatment, such as: potassium antimony tartrate (tartar emetic) or synthetic tanning agents (syntan) [2].

The word tannin is very old and reflects a traditional

technology. "Tanning" (water proofing and preserving) was the word used to describe the process of transforming animal hides into leather by using plant extracted from different plant parts (bark, wood, fruit, leaves) of different plant species (oak, birch, willow, pine) and Basically, tannins are phenolic compounds which can complex with protein, starch, cellulose and minerals [3].

Nowdays, the high wash fastness has become increasingly an improved goal for the silk dyers, in order to meet consumer's requirements [4]. However, tannic acid and its derivatives are often used for silk dyeing [5]. Thus, it can be expected that wash fastness of acid dye on silk fiber will be increased by the aftertreatment with tannic acid and tartar emetic (fullbacktan) [6].

But, in recent years, the use of fullbacktan which traditionally comprised treatment with tannic acid and the subsequent application of potassium antimony tartrate (tartar emetic) have been replaced by that of synthetic tanning agents (syntans) owing to the several disadvantages inherent with the two-stage process [7]:

- Potassium antimony tartrate is poisonous.
- Treatment can impart a harsh handle and reduce the light fastness of dyeings;
- The treatment can impart a shade change to the dyeing and also can be discoloured during repeated washing owing to oxidation of the high  $M_n$  gallotannin component.

But, syntans are mainly composed of condensates of formaldehyde with phenolsulphonic or naphtholsulphonic acid. Some contain polar groups (carbonamide, sulphonamide and ureides) and they can be divided into several types such as: phenolic, thiophenolic and dihydroxy diphenyl sulphone (DOS) [8].

However, syntans have the advantage of being applied in a single process compared with the common, two-bath, backtanning process and do not suffer from disadvantages displayed by their natural counterparts [9]. Also, syntans do not require a fixing treatment with tartar emetic and are therefore easier to be applied than natural tannins [10]. However, aftertreatment of the dyeing using the commercial syntan alone, improved the wash fastness of the dyes and sequential application of a cationic compound to the syntanned dyeings and enhanced the effectiveness of the syntan in improving wash fastness [11].

Also, it has been proposed that in this sequential aftertreatment process, a large molecular size and low aqueous solubility complex are formed between the anionic syntan and the cationic compound within the fiber [12, 13].

The enhanced effectiveness of the syntan, achieved using the sequential application technique, is attributed to lowering of the syntans aqueous solubility, and the increasing trend of the rate in its effective molecular size, by means of which the propensity of the syntan is desorbed from the dyed fiber, reduces during the washing [14].

## 2. Experimental

### 2.1. Materials

Raw silk yarn (2 filaments, 10.45  $N_m$ ) was kindly supplied by Iran Silk worm Rearing Co., Ltd. The used commercial dyes (Table 1), which were kindly supplied

by Avocet Dye & Chemical Co. Ltd, were selected on the basis that they display high to poor fastness on silk to the repeated washing. Also, a commercial syntan (Cetafix AFA) was kindly provided by Avocet Dye & Chemical Co. Ltd And Alapol A-130/M19-9025 (Anionic detergent for degumming process) was supplied by Alvan Sabbet Co. Anionic-nonionic detergent (Gata Pon 250 ANP) used for washing test which was purchased from Catan Co. Ltd. The chemical grade of the metal salts ( $CuSO_4$ ,  $SnSO_4$ ,  $K_2Cr_2O_7$ ), laboratory grade, were purchased from Merck.

### 2.2. Degumming and bleaching

All samples (2g) were degummed (Figure 1) according to the adjusted method [14]. Then, they were treated with 3g/l sodium dithionite solution (Figure 2) [15].

### 2.3. Dyeing

#### 2.3.1. Basic and pre-metallised acid dyes:

The dyeing methods are shown in Figure 3; the pH 5-6 was adjusted using a little acetic acid [16]. The dyeings were rinsed thoroughly in soft water and allowed to be dried in the open air.

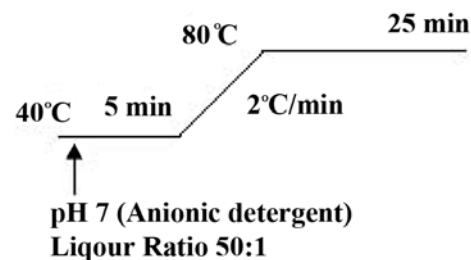


Figure 1: Degumming method.

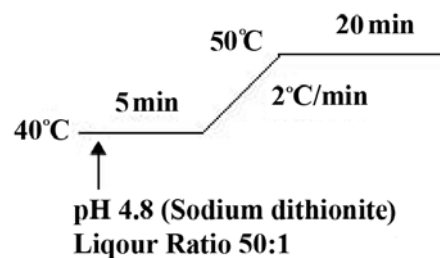


Figure 2: Bleaching method.

Table 1: Dyes used.

Commercial name	Chemical base	C.I. generic name
Irgalan Yellow 2GL	Azo	C.I. Acid Yellow 59
Irgalan Black BGL	Mono azo	C.I. Acid Black107
Procion Brilliant Purple H-3R	Azo	C.I. Reactive Violet 1
Procion Blue MX-3G	Mono azo	C.I. Reactive Blue 1
Astra Chrysoidine R	Mono azo	C.I. Basic Orange 2
Magenta	Tri aryl methane	C.I. Basic Violet 14

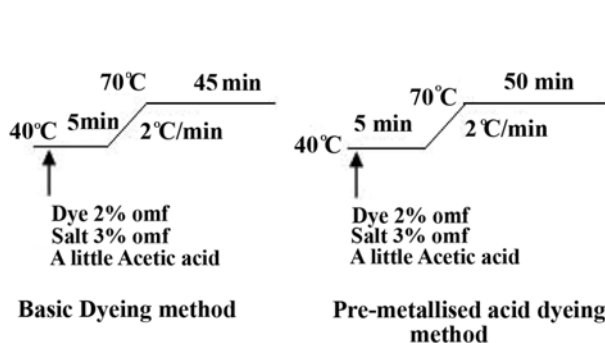


Figure 3: Basic and Pre-metallised dyeing methods.

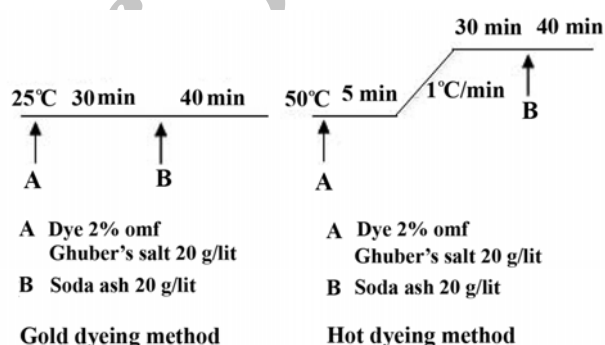


Figure 4: Reactive dyeing method.

### Reactive dyes

C. I. Reactive Violet 1 and C. I. Reactive Blue 1 were hot and cold reactive dyes, respectively. The dyeing methods are given in Figure 4. Finally, the dyeings were rinsed thoroughly in cold water, and then 'soap' (for 10 mins at 70°C) in a bath containing 2g of Lissapol NC, 5g of Glauber's salt, and 1g of soda ash per liter [16].

### 2.4. Syntan aftertreatment

Samples of dyed silk were aftertreated according to a recommended method [17] with syntan (2% omf: on the mass of fiber) at pH 3.5 (adjusted using acetic acid) for 30 min at 70°C. The aftertreated samples were removed, rinsed thoroughly in soft water and allowed to be dried in air.

### 2.5. Treatment with metal salts

Syntanned silk yarns were aftertreated with metal salts (2% omf:  $\text{CuSO}_4$ ,  $\text{SnSO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ) at pH 3.5 (adjusted using acetic acid) for 20 min at 60°C [18]. The treated dyeings were then rinsed thoroughly in soft water and allowed to dry in air.

The degumming, bleaching, dyeing, syntan aftertreatment, backtanning with metal salts processes and washing test were carried out in sealed stainless steel dye pots of 150 ml housed in an Ahiba-polymath laboratory scale dyeing machine using a liquor ratio of 50:1.

## 2.6. Colour measurement

All measurements were carried out using a Datacolor Texflash spectrophotometer interfaced to a PC using D<sub>65</sub> illumination, 10° standard observer with UV component were included and specular component were excluded. For reflection measurement, we should to use fabric substrate. Therefore, the silk yarns were weaved. Then, each fabric (dimension: 10 × 4 cm<sup>2</sup>) was folded once to give two thickness and an average of two readings was taken each time.

The extent of the staining of adjacent fabric (cotton fabric) was expressed in the appropriate staining grey scale whereas the change in shade of the sample after washing was expressed in CIE L\* a\* b\* units.

## 2.7. Wash fastness

The wash fastness of the dyed samples was determined

using the ISO 105-CO1 test method [19]. The samples of dyed silk (treated/untreated) were washed five times in a well agitated, aqueous solution of sodium carbonate 1 (g/l) and anionic-nonionic detergent 4 (g/l) at 50 °C and maintained at this temperature for 30 mins. The end of each wash test,  $\lambda_{\max}$  and absorbance of the residual wash solution was measured using a Varian Cary 300 spectrophotometer, and the absorbance (A) was converted to concentration (C) using the Beer's–Lambert Law.

$$A = K \times C \quad (1)$$

Also, the reduction in depth of shade that occurred as a result of washing was calculated using Eq. (2) where  $f_{ku}$  and  $f_{kw}$  are the weighed k/s function of the unwashed and washed samples, respectively

$$\text{Reduction in colour strength} = (1 - f_{ku} / f_{kw}) \quad (2)$$

**Table 2:** Colorimetric data for pre- metallised acid dyes\*.

Aftertreatment	No. of. washes	C.I. Acid Yellow 59						C.I. Acid Black 107					
		L*	a*	b*	C	h°	f <sub>k</sub>	L*	a*	b*	C	h°	f <sub>k</sub>
Untreated	0	56.3	16.5	63.5	65.6	75.4	109.2	18.8	0.6	-5.9	5.9	275.8	286.1
	5	58.2	14.0	64.0	65.5	77.7	88.7	19.3	0.5	-3.1	3.1	279.2	280.4
Syntan	0	57.3	14.8	63.7	65.4	77.0	98.2	18.4	0.6	-3.0	3.1	281.3	282.1
	5	57.6	13.3	62.6	64.0	78.0	94.0	18.8	0.4	-2.4	2.4	279.5	278.3
Syntan/SnSO <sub>4</sub>	0	57.6	16.0	66.3	68.2	76.4	89.9	18.1	-0.4	-4.3	4.3	264.7	281.7
	5	58.8	15.8	66.6	68.4	76.1	87.5	18.7	-0.6	-4.3	4.3	262.1	279.4
Syntan/CuSO <sub>4</sub>	0	57.5	9.7	62.7	63.4	81.2	95.2	18.3	-0.1	-3.0	3.0	268.1	284.9
	5	58.6	9.1	62.0	62.7	81.7	93.6	18.9	-0.3	-3.0	3.0	264.3	282.1
Syntan/K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0	57.5	15.1	63.5	65.3	76.6	93.0	18.3	0.2	-2.5	2.5	274.6	285.2
	5	57.9	15.2	63.8	65.6	76.6	91.4	19.0	0.1	-2.7	2.7	272.1	283.7

\*  $L^*$ , vertical axis (lightness);  $a^*$ , axis in plane normal to  $L^*$  (redness-greenness quality of the colour);  $b^*$ , axis in plane normal to both  $L^*$  and  $a^*$  (yellowness-blueness quality of the colour);  $C$ , chroma;  $h^\circ$ , line angle.

Table 3: Colorimetric data for Reactive dyes\*.

Aftertreatment	No.of. washes	C.I.Reactive Violet 1						C.I.Reactive Blue 1					
		L*	a*	b*	C	h°	f <sub>k</sub>	L*	a*	b*	C	h°	f <sub>k</sub>
Untreated	0	41.5	15.7	-19.2	24.8	309.3	81.3	41.8	-7.1	-26.1	27.0	254.8	65.3
	5	44.0	15.3	-18.7	24.2	309.3	75.6	43.0	-6.6	-25.5	26.3	255.5	57.9
Syntan	0	42.2	15.6	-18.8	24.4	309.7	69.6	42.3	-7.6	-25.1	26.1	253.8	64.7
	5	45.8	15.2	-18.5	23.9	309.4	66.1	44.7	-7.1	-24.9	25.9	254.1	60.0
Syntan/SnSO <sub>4</sub>	0	42.0	15.3	-18.6	24.1	309.4	54.5	42.0	-8.4	-24.7	26.0	251.8	63.7
	5	45.7	15.1	-18.8	24.1	308.8	52.7	44.5	-8.0	-24.4	25.7	251.8	61.2
Syntan/CuSO <sub>4</sub>	0	42.5	13.9	-18.9	23.5	306.3	74.9	42.2	-7.8	-24.5	25.7	252.4	63.6
	5	46.4	13.6	-18.7	23.1	306.0	72.8	45.9	-7.4	-23.9	25.0	252.8	61.9
Syntan/K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0	41.5	14.8	-18.4	23.6	308.8	60.5	43.2	-8.2	-22.0	23.5	249.5	62.4
	5	46.6	15.0	-18.5	23.8	309.0	58.5	45.7	-8.1	-22.8	24.2	250.4	60.2

\*  $L^*$ ,  $a^*$ ,  $b^*$ ,  $C$  and  $h^\circ$  as in Table 2.

Table 4: Colorimetric data for Basic dyes\*.

Aftertreatment	No.of. washes	C.I. Basic Orange 2						C.I. Basic Violet 14					
		L*	a*	b*	C	h°	f <sub>k</sub>	L*	a*	b*	C	h°	f <sub>k</sub>
Untreated	0	50.2	44.1	76.2	88.0	59.9	364.5	32.1	64.2	12.3	65.4	10.8	194.6
	5	53.5	42.4	72.4	83.9	59.7	318.4	37.5	62.3	12.7	63.6	11.5	156.0
Syntan	0	51.3	43.8	71.2	83.6	58.4	285.4	37.6	56.0	10.3	56.9	10.4	189.2
	5	52.7	41.3	69.0	80.4	59.1	271.5	38.3	53.8	9.8	54.7	10.3	181.6
Syntan/SnSO <sub>4</sub>	0	52.3	30.0	49.7	58.1	58.9	172.0	43.8	64.5	4.6	64.7	4.1	119.8
	5	53.7	28.0	50.2	57.5	60.8	165.0	47.1	63.1	3.9	63.2	3.5	114.7
Syntan/CuSO <sub>4</sub>	0	54.9	32.1	67.5	74.7	64.6	203.3	47.0	53.5	-6.2	53.6	353.4	134.8
	5	56.2	29.0	66.7	72.7	66.5	198.7	47.8	54.2	-6.9	54.6	352.7	129.5
Syntan/K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0	54.3	39.9	68.8	79.6	59.9	203.4	42.2	58.0	5.6	58.3	5.5	105.1
	5	55.5	38.8	68.9	79.1	60.6	197.8	44.0	58.4	4.8	58.7	4.7	99.7

\*  $L^*$ ,  $a^*$ ,  $b^*$ ,  $C$  and  $h^\circ$  as in Table 2.

### 3. Results and discussion

In this work, the six dyes which were suitable for silk used. The high to poor fastness of these dyes to repeat washing was clear. Thus, it was decided to investigate the effectiveness of the aftertreatments in improving the wash fastness of the dyes. In the context of the wash fastness change which the dyeings underwent different aftertreatments with metal salts, wash fastness was determined by the reduction in colour strength equation. The advantage of this approach for determination of wash fastness was that even low degree of variation in wash fastness changes could be measured.

Figures 5 to 10 show the reduction in colour strength that occurred for the dyeings, as a result of the five consecutive ISO 105 CO1 wash tests. It is apparent that

the reduction in colour strength achieved for the dyeings increased with increasing number of washes; thus, showing that dye loss occurred in a progressive manner. Clearly, each of the two aftertreatments reduced the extent of dye loss that occurred during repeated washing; and the effectiveness of the two aftertreatments in reducing dye loss followed the order: syntan < syntan/metal salts. The corresponding assessments of the extent of staining on adjacent fabric (cotton fabric) achieved for the dyeings after five washes (Table 5) support the findings shown in Figures 5 to 10 so far. Aftertreatment lowered the extent of staining on the adjacent cotton fabric and the effectiveness of the two aftertreatments in reducing staining followed the order; syntan < syntan/metal salts.

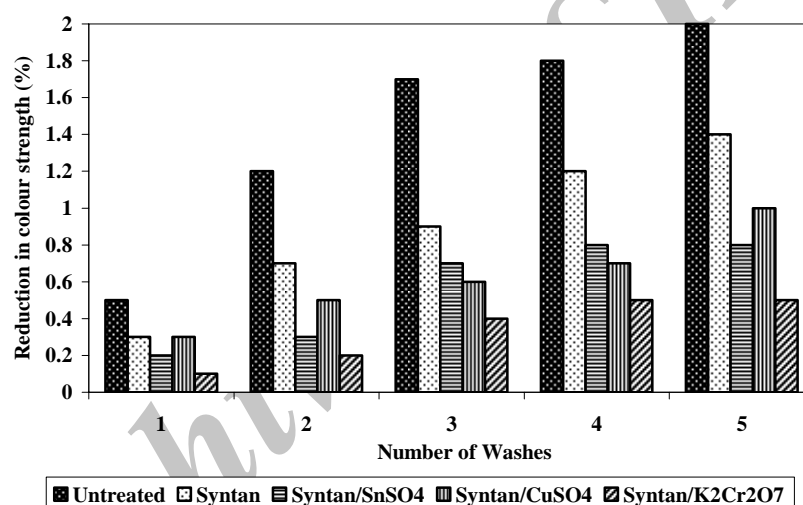


Figure 5: Reduction in colour strength of C.I. Acid Black 107.

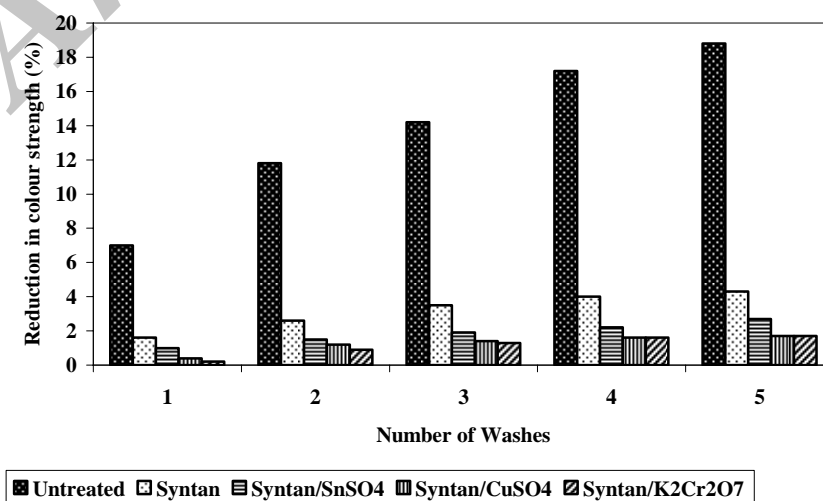


Figure 6: Reduction in colour strength of C.I. Acid Yellow 59.

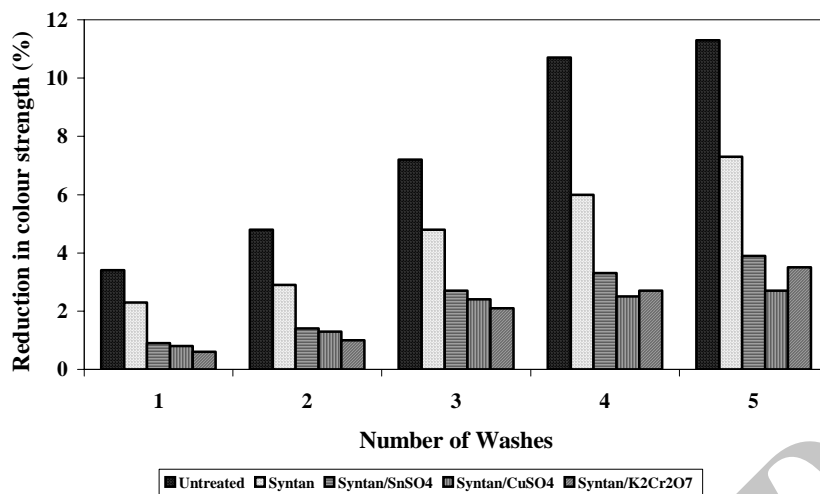


Figure 7: Reduction in colour strength of C.I. Reactive Blue 1.

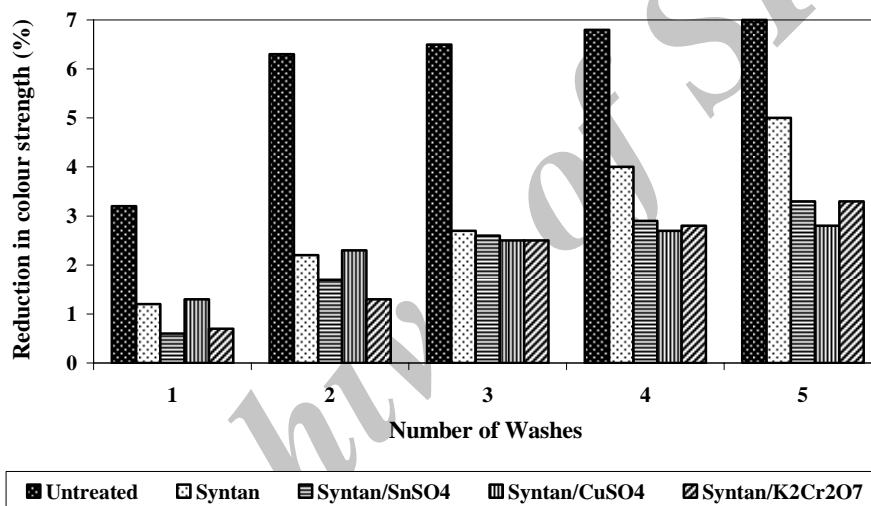


Figure 8: Reduction in colour strength of C.I. Reactive Violet 1.

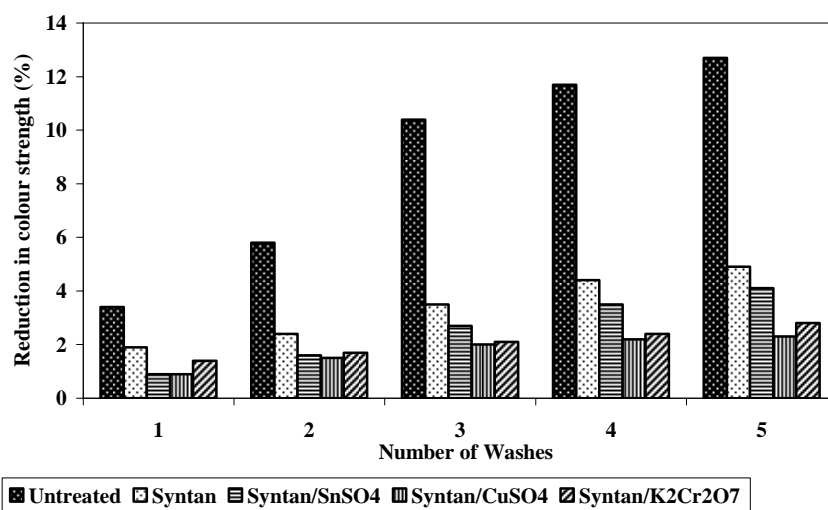


Figure 9: Reduction in colour strength of C.I. Basic Orange 2.

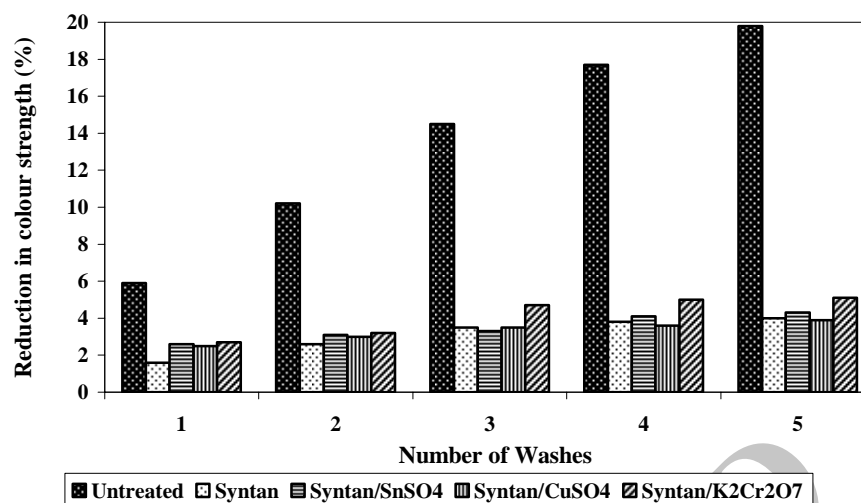


Figure 10: Reduction in colour strength of C.I. Basic Violet 14.

As mentioned, syntans are, typically, water-soluble, anionic polycondensates (of formaldehyde with arylsulfonates and sulfonates of dihydroxydiaryl sulfones) which are adsorbed on to dyed nylon by virtue of ion-ion forces of interaction operating between anionic (sulfonate) groups in the syntan and the terminal amino groups in the nylon substrate; other forces of interaction, such as H-bonding and ion-dipole forces also will contribute to syntan-fiber substantivity. Thus, similarities exist in terms of the manner by which syntan and tannic acid are adsorbed by the dyed nylon 6,6 fiber. The adsorption of the large  $M_n$  syntans follows a BET mechanism which results in the formation of multi-layers of adsorbed syntan molecules situated at the periphery of the dyed nylon 6,6 [6]. Although, the same mechanism exists in terms of the manner by which syntan and tannic acid are adsorbed by the dyed silk fiber. Their ability to improve the wash fastness of the dyes on silk is attributed to the resulting 'layer' of syntan molecules at the fiber surface reducing the diffusion of dye molecules out of the dyed material during washing; thus, similarities exist between the way in which the syntan and the tannic acid improve the wash fastness of the applied dyes on silk.

Interestingly, Figures 5 to 10 show that the additional treatment of the syntanned dyeings with metal salts enhanced the ability of the syntan to improve fastness to repeated washing. Previous works revealed that the purpose of the metal salts (potassium antimonyl tartrate) in the traditional fullbacktan aftertreatment can form a

low solubility complex with the adsorbed tannic acid in situ at the surface of the dyed nylon 6,6 [6]. Consequently, in the case of the syntanned dyeings with metal salts can be due to form a low solubility complex between the adsorbed anionic syntan in situ at the surface of the dyed silk and cationic metal salts which provides a physical barrier to the diffusion of dye from the dyed silk during washing.

Also, Tables 2 to 4 show the colorimetric data obtained for dyeings which had been subjected to the ISO 105CO1 wash test, data are shown for dyeings which had received no aftertreatment (untreated), for dyeings which had been treated with the syntan and also for dyeings which had been treated with the syntan/metal salts system. In the case of the unwashed dyeings, it is evident that for each of the six dyes used, the colour strength ( $f_k$ ) of untreated dyeings was greater than treated dyeings. The lower colour strength observed for treated dyeings is attributable to removal of the amount of dye during the aftertreatments.

However, the use of the syntan in conjunction with the cationic fixing agents (metal salts) was far more effective in reducing the extent of dye loss that occurred during washing.

The aftertreatments employed had very little or no effect upon the shade of the dyeings. This can be seen from the colorimetric parameters given in Tables 2-4 which show variation only within a small range. The only great difference noted was between the lightness ( $L^*$ ) values, which increased with washing, but this was



expected as colour strength reduced following the ISO 105CO1 wash test, thus the dyeings became lighter.

### Staining test

Table 5 shows the extent of staining of the adjacent cotton fabric achieved for the six dyes used. The aftertreatments were effective in reducing the extent of staining of the adjacent fabric during the washing test. Comparison of the data for the staining achieved for the untreated/treated dyeings shows clearly that, syntan/ $\text{SnSO}_4$  and syntan/ $\text{CuSO}_4$  were most effective in reducing the extend of staining of the adjacent fabric during the washing test.

Also, the handle of the syntanned/metal salts dyed fabrics was judged to be harsher than the dyed samples which had been aftertreated with the syntan system.

## 4. Conclusions

This is the first report on application of pre-metallise, reactive and basic dyes on silk using the syntan. Although aftertreatment of the dyeings using the commercial syntan alone improved the wash fastness of the applied dyes on the silk yarns, the sequential application of metal salts to the syntanned dyeings enhanced the effectiveness of the syntan in improving wash fastness. This, which is due to form a low solubility complex between the absorbed anionic syntan at the surface of the dyed silk and cationic metal salts, provides a physical barrier to the diffusion of dye from the dyed silk during washing.

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