Improvement of Wash Fastness of Direct and Acid Dyes Applied to Silk by Aftertreatment with Syntan, Syntan/Cation, and Full Backtan Processes

Mahmoud Feiz and Zeinab Radfar

Textile Department, Isfahan University of Technology, Isfahan-84156/83111, Iran

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ABSTRACT

To examine the effect of different aftertreatments, on dyeing of silk fibres using acid and direct dyes the dyed samples were aftertreated using different commercial systems: such as full backtan, syntan, and syntan/cation processes. When all dyeings were subjected to ISO105C06 wash test, it was found that all three aftertreatments improved wet or wash fastness. However, aftertreatment of the dyeing using backtanning system showed greatest wash fastness improvement toward wash testing. A commercial syntan improved the wash fastness and the sequential application of a cationic compound to the syntanned dyeing caused further improvement in wash fastness. The effect of syntan in reducing dye removal was increased by decreasing the applied pH, which indicates that ion-ion interactions operating between the protonated end groups in the silk fibre and anionic syntan contribute towards syntan-fibre affinity. Also the effect of syntan in reducing dye removal increased with decreasing liquor ratio. Increasing the concentration of syntan that accompanied a decrease in liquor ratio can be expected to increase the degree of syntan aggregation in solution. It can be suggested that the aggregation of the syntan will occur in solution by virtue of both polar and non-polar forces operating between the large molecular size syntan molecules which in turn can be considered to result in greater uptake of the tanning agent. However, the aftertreatment with full backtan had markedly improved the fastness to washing of the six dyes used and showed greatest wash fastness improvement.

INTRODUCTION

High wet fastness has become increasingly an important goal for the silk dyers in order to meet consumer requirement. The mechanism of dyeing silk with acid dyes is likely to be similar to that of wool and nylon [1]. Aftertreatments are thus frequently used on dyed nylon to improve the wet fastness by either back tanning with natural tannins and tartar emetic or a syntan [2-6]. But in the case of silk, the above aftertreatments have not been used on dyed silk for improvement of...
wash fastness. Tannic acid and its derivatives are often used for dyeing silk. The fibres will be coloured dull brown if the tannic acid content in the fibres becomes too high, and also tannic acid form complex with silk and acid dyes [7]. Thus, it can be expected that wet fastness of acid dye on silk fibre will be increased by the aftertreatment with tannic acid and tartar emetic (full backtan).

In recent years the use of full backtan 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 [8]. Aftertreatment using a synthetic tanning agent (syntan) is generally considered to be less effective than aftertreatment using the natural tanning agent (full backtan) in improving the wet fastness of acid dyes [9]. Syntans do not require a fixing treatment with tartar emetic and are therefore easier to apply than natural tannins. However, they are less effective and may impair the light fastness of some dyeing [10].

The compounds regarded as syntans can be divided into several types, but they are mainly composed of condensates of formaldehyde with phenolsulphonic or naphtholsulphonic acids. Some contain polar groups such as carbonamide, sulphonamide and ureides. The main types are discussed as follows.

Phenolic
Aromatic compounds containing phenolic -OH groups, e.g. phenol, cresol, naphtol, and bisphenol are used as starting materials. Though compounds of this type enhance fixation, they tend to give reddish stains on treated fabric. Increasing the number of sulphonic acid groups in the molecule tends to increase its affinity for nylon.

Thiophenolic
Syntans of this type can be produced by the reaction of phenolic compounds with molten sulphur. Hydrophilic groups, such as sulphonic acid and methanesulphonic acid or its sodium salt, are introduced into the compound in order to confer solubility in water.

Dihydroxy diphenylsulphone (DOS)
Syntans from DOS have been developed commercially in recent years. DOS syntans resemble the condensates of the phenolic type which contain -OH and -SO₃H groups, but the -SO₂ group para to the phenolic -OH, although prevent discoloration by formation of p-quinone, lower light fastness. An improvement in fixation efficiency can be achieved by forming a complex between the -OH groups and metal ions [2].

Aftertreatment of the dyeing using the commercial syntan alone improved the wash fastness of the dyes and the sequential application of a cationic compound to the syntaned dyeings enhanced the effectiveness of the syntan in improving wash fastness [11].

It was proposed that in this sequential aftertreatment process, a large molecular size, low aqueous solubility complex was formed between the anionic syntan and the cationic compound within the fibre [12,13].

The enhanced effectiveness of the syntan achieved using the sequential application technique was attributed to a lowering of the syntans aqueous solubility and an increase in its effective molecular size, by means of which the propensity of the syntan desorbed from the dyed fibre was reduced during washing [13].

EXPERIMENTAL

Materials
Fibres
Degummed silk fibres was purchased from Iran Silk Worm Rearing Co., Gillan (36 filament, 63denier). Prior to dyeing the fibre were scoured by treatment at 70°C for 1 h in aqueous solution (50:1 liquor goods ratio) containing anionic detergent (2 g/L CEBATEX) followed by thorough rinsing in water.

Dyes
The following commercial dyes were used: Carmoisine (C.I. Acid Red 14), Acid red 88 (C.I. Acid red 88), Acid cyanine 5R (C.I. Acid blue 113), Durazed yellow FR (C.I. Direct yellow 50), Kayarus superblue FF2GL (C.I. Direct blue 106), and Direct Congo red (C.I. Direct red 28). These dyes were not purified prior to use.

Auxiliaries
The commercial syntan used was named Cetafix AFA and purchased from Avocet Dye & Chemical Co. Fixogen CD as cationic agent was used. Other chemical
were purchased from Merck.

**Procedures**

**Dyeing**

Samples of silk (2 g) were dyed in stainless steel dye pots in a Polymath AHIBA1000 laboratory-scale dyeing machine using a liquor ratio of 50:1. The dyeing method used for silk shown in Figure 1, according to the recommended method [14]. At the end of dyeing, the dyed samples were removed, rinsed thoroughly with tap water and allowed to dry in the open air.

**Aftertreatment of Dyed Silk with Full Backtan**

Samples of dyed silk were aftertreated in sealed, stainless steel dye pots in a Polymath AHIBA1000 laboratory-scale dyeing machine using a liquor ratio of 50:1 with tannic acid (2% on the weight of fibre) at pH 2.5 (adjusted using formic acid) for 30 min at 95°C. The silk was then treated in a fresh bath with potassium antimonyl tartrate (2% on the weight of fibre) at pH 2.5 (adjusted with formic acid) using a liquor ratio of 50:1 for 15 min at 95°C. Then the samples were removed, thoroughly rinsed in tap water and allowed to dry in the open air.

**Aftertreatment of Dyed Silk with Syntan**

Samples of dyed silk fibre was treated in sealed, stainless steel dye pots in a Polymath AHIBA1000 laboratory-scale dyeing machine using a liquor ratio of 50:1 with syntan (2% on the weight of fibre) at pH 4 (adjusted using formic acid) for 30 min at 80°C. The syntanned dyeing sample was then rinsed thoroughly with tap water and allowed to dry in the open air.

**Aftertreatment of Syntanned Dyed Silk with Cationic Agent**

Syntanned silk fibres were aftertreated with Fixogen CD carried out in sealed, stainless steel dye pots in a Polymath Ahiba 1000 Laboratory-scale dyeing machine. At the end of aftertreatment with syntan (2%...
on the weight of fibre), the syntanned dyed silks were rinsed thoroughly with tap water and treated with the cationic agent (2% on the weight of fibre) using a liquor ratio of 50:1 at pH 5 (adjusted using acetic acid) for 20 min at 50°C. The treated dyeing samples were then rinsed thoroughly with tap water and allowed to dry in air.

Effect of pH on the Aftertreatment with Syntan
Silk fibres (2 g) were dyed by Acid Cyanine 5R. The dyed samples were treated with syntan (2% on the weight of fibre) at pH value of 1, 3, 5, 7, and 9 (using sulphuric acid/sodium sulphate, acetic acid/sodium acetate buffers and sodium carbonate) at 80°C for 1 h using liquor ratio of 50:1 in sealed, stainless steel dye pots in a Polymath AHIBA 1000 laboratory-scale dyeing machine. The treated samples were then rinsed thoroughly with tap water.

Effect of Temperature on the Aftertreatment with Syntan
Samples (2 g) were dyed by Acid Cyanine 5R. The dyed samples were treated with syntan (2% on the weight of fibre) at pH 5 at room temperature, 40, 60, 80, 98 and 120°C for 1 h using a liquor ratio of 50:1 in stainless steel dye pots in a Polymath AHIBA1000 laboratory-scale dyeing machine. The treated samples were then rinsed thoroughly with tap water.

Effect of Liquor Ratio on the Aftertreatment with Syntan
Silk fibres (2 g) were dyed by Acid Cyanine 5R. The dyed samples were treated with syntan 2% (on the weight of fibre) at pH 5 at 80°C for 1 h, using liquor ratio of 10:1, 25:1, 50:1 and 100:1 in stainless steel dye pots in a Polymath AHIBA1000 laboratory-scale dyeing machine. The treated samples were rinsed thoroughly with tap water.

Measurement of Desorption of Dyes from Dyed Silk
Samples of dyed silk (treated/untreated) was immersed in a well agitated, aqueous solution of sodium carbonate 1 (g/L) and detergent 4 (g/L) CEBATEX at 50°C and maintained at this temperature for 30 min. \( \lambda_{\text{max}} \) and absorption of the dyes used in this work were measured at the above mentioned conditions for the desorbing media and plain water, no differences were observed. Therefore, the optical density of the desorbing media was measured. The concentration of washing liquor was calculated by eqn (1):

\[
A = K \times C
\]  

(1)
Where A, K, and C are absorbance, the constant coefficient of Beer-Lambert law, and concentration, respectively.

Volume of washing bath was 100 mL, therefore the amount of dye (milligram) lost during washing (M) was calculated by eqn (2):

\[ M = \frac{C}{10} \times 1000 \]  

Any reduction in colour strength that occurred as a result of washing according to the ISO105C06 wash test was calculated for percentage dye removed (DR) using eqn (3):

\[ DR = \left[ 1 - \frac{M_t}{M_{ut}} \right] \times 100 \]  

Where \( M_t \) and \( M_{ut} \) are the amount of dyes (milligram) removed during the wash test from treated and untreated dyeing samples, respectively.

**RESULTS AND DISCUSSION**

Tables 1-3 and Figure 2 shows that the aftertreatment with full backtan has markedly improved the wash fastness of the used six dyes. The backtanning system showed greatest wash fastness improvement toward...
wash testing. It is clear from Figure 2 that aftertreatment using syntan alone (2% on weight of fibre) reduced the amount of dye removal during washing for the used three acid dyes and three direct dyes. However, the use of the syntan in conjunction with the cationic agent was far more effective in reducing the extent of dye removal that occurred during washing. Other workers have also suggested that aftertreatment of the dyeings using the commercial syntan alone improves the wash fastness of 1:2 metal-complex acid dyes on conventional nylon 6,6 fabric, and the sequential application of a cationic compound to the syntanned dyeing enhanced the effectiveness of the syntan in improving the wash fastness [15].

Table 4 and Figure 3 clearly show that the effectiveness of syntan in reducing dye removal increases with decreasing the applied pH. The results in Table 4 indicate that ion-ion interaction between the protonated end groups in the silk fibre and absorbed syntan increased and therefore the wash fastness improvement is observed.

Table 5 and Figure 4 show that the effect of syntan in reducing dye removal increases with decreasing liquor ratio. The increase in the effectiveness of concentration of syntan which is accompanied by a decrease in liquor ratio can be expected to increase the degree of syntan aggregation in solution. It can be suggested that aggregation of the syntan will occur in solution by virtue of both polar and non-polar forces operating between the large molecular size of syntan molecules [16, 17] which in turn can be considered to result in greater uptake of the tanning agent.

Table 6 and Figure 5 demonstrate that the effect of syntan in reducing dye removal increases with increasing the applied temperature. These results can be attributed to the higher kinetic energy of the syntan molecules and their consequent greater diffusion power within the substrate, together with the higher extent of fibre swelling that accompanies the increase in applied temperature.

**CONCLUSION**

Aftertreatment of the acid and direct dyes on silk with full backtan improves their wash fastness. Backtanning system showed greatest wash fastness improvement toward wash testing. Aftertreatment of the dyes using a commercial syntan improves the wash fastness and the sequential application of a cationic compound to the syntanned dyeing fibres causes further improvement in wash fastness.
REFERENCES