Dyeability Improvement of Proteinic and Polyamide Fabrics Pretreated with Saccharin Sodium Salt: A Kinetic Approach

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ABSTRACT: Improvement of the dyeability of wool, silk, and polyamide fabrics with cationic dye was achieved by their pretreatments with saccharin sodium salt. The acquired color values of the dyed materials were significantly enhanced by the aforementioned treatment. Kinetic investigations of the dyeing process were performed by determining the half dyeing time, specific dyeing rate constant, and diffusion coefficient. Fastness properties to crocking (dry and wet) and washing of the pretreated dyed fabrics were significantly improved. J Appl Polym Sci 114: 3034–3040, 2009

Key words: wool; silk; polyamide; saccharin sodium salt; treatments; dyeing; cationic dye; kinetic investigation; fastness properties

INTRODUCTION

Considerable amounts of proteinic and polyamide fibers are used in textiles carpets and floor covering.[1] Polyamide and some synthetic fibers can be used in carpeting because of their resilience, good coloration, and aesthetics.[2] Interaction of some compounds with the textile substrates results in some changes in the polymeric structure and in the mechanical properties of the fibers. These effects on the properties can be expected to affect strongly the dye diffusion characteristics and the equilibrium uptake of the dyestuffs.[3]

Coloration of wool, silk, and polyamide fibers is satisfactorily performed with acid dyestuffs. Energy saving as well as high fastness performance and reduction of costs can be reasonably gained by applying cationic dyes to the fibers used in the carpet manufacture (cf. Chem Abstr 1975, 82, 74350 d).[4] The dyeability can be altered by treating the polyamide fiber to be inert to acid dyes and stable under normal acid dyebath conditions. A variety of compounds have been reported including the use of carboxylic acid (cf. Chem Abstr 1972, 77, 115455 j),[5] chlorides,[6] and anhydrides.[7] These reagents cause hydrolysis of the polyamide chain imparting some weakening of the fibers. The application of sulphamic acid onto proteinic fibers reveals a possibility of cationic dyeing.[8] The dye uptake results in higher dye exhaustion with level and good penetration of dye molecules into proteinic fibers. The affinity of wool fibers to cationic dyes can be induced by chemical modifications[4] or by adding additives to the dyeing bathes (cf. Chem Abstr 1971, 75, 41913 p; cf. Chem Abstr 1972, 77, 166063; cf. Chem Abstr 1972, 75, 7339 z).[9–11] Addition of some compounds that may behave as a dyeing carrier to the dyebath with cationic dye was given. Sodium benzenesulfonate acetic acid mixture,[11] -napthol (cf. Chem Abstr 1973, 78, 73578 q),[12] and zinc thiocyanate[11] are typical examples. It has been reported that saccharin (*o*-sulphobenzoic imide) was used to improve the polyamide fiber dyeability with cationic dyes.[13–15] This work aims to study the possibility of promoting the affinity of wool, polyamide, and silk fabrics to cationic dyes by pretreatment with saccharin sodium salt, providing such improvement without causing fabrics damages. A kinetic characterization of the dyeing process is also carried out.

EXPERIMENTAL

Materials

Fabrics

Wool, polyamide, and silk fabrics were supplied by Misr El Mahalla Company and El Shorbagy Company. The fabrics were washed with a solution of nonionic detergent (2 g/L) for 45 min at 60°C, thoroughly rinsed, and dried at room temperature.

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Chemicals

Saccharin (2-sulphobenzoic acid imide sodium salt) of technical grade was used (PK d. by: Oxford Laboratory Mumbai-400002).

Dyestuff

The used dye is a commercial sample; C. I. Basic Red 18 used (Remacryl® Red TGL from Hoechst Germany).

Treatments

The fabrics were treated with the specific concentration of saccharin sodium salt aqueous solutions in stoppered glass bottles using a liquor ratio of 1 : 50 at 90°C for 1 h.

Dyeing

The dyebath was prepared by first pasting the needed amount of the dyestuff with small amount of water. This paste was then diluted by adding boiling water and was thoroughly stirred. The dyeing bath was adjusted to pH 4.5 using acetic acid solution, liq. ratio 1 : 50. Dyeing was performed by exhaustion technique using a laboratory shaking apparatus (Julabo-Germany). The dye bath containing the prescribed amounts of the dye was heated to 75–90°C. The dyeing was carried out for varying times (5–120 min). The dyed samples were then withdrawn, thoroughly washed with hot and cold water, and air dried.

Measurements

Color value

Spectral reflectance measurements of the dyed fabrics were carried out using a recording Spectrophotometer (Hunter lab, Ultra Scan Pro, USA). The color values expressed as K/S values of the dyed samples were determined by applying the Kubelka–Munk equation.[16]

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_o)^2}{2R_o}$$

where R is the decimal fraction of the reflectance of the dyed substrate, R_o is the decimal fraction of the reflectance of the undyed substrate, S is the scattering coefficient, and K is the absorption coefficient.

Dye exhaustion

Measurement of the amount of residual dye in the dyeing bath was determined spectrophotometrically using 6405 UV–visible Spectrophotometer (JENWAY, U.K.)

Time of half dyeing ($t_{1/2}$)

Dyeing of the fibers was performed on a 1-g sample using 1% dye (o.w.f). Each set included dyeing for 5–120 min. Samples from the dyebath were withdrawn immediately after the prescribed dyeing time, and the amount of the dye remaining in the liquor was determined spectrophotometrically.[17] For each dyeing temperature, the percentage exhaustion was plotted versus dyeing time. The time of half dyeing was determined from these plots.

Specific dyeing rate constant (K')

The specific dyeing rate constant (K') was further estimated using the equation.[13]

$$K' = 0.5\, C_\infty (d.t_{1/2})^{1/2}$$

where d is the fiber diameter (cm) and C_∞ is the percentage of dye taken-up by the fibers at equilibrium conditions.

Apparent diffusion coefficient (D)

The fabric (1 g) was dyed in a dye solution (100 mL) for 12 h. The dye taken-up by the fabrics (C_∞) was determined spectrophotometerically. In another experiment, dyeing of the fabrics was performed for a short period (10 min) and C_t was similarly determined. The values of C_t/C_∞ were calculated and the apparent diffusion coefficient (D) was then calculated using Hill's equation.[17]

$$D = \frac{C_t}{C_\infty} \times \frac{d^2}{T} \times 100$$

Color fastness

Crocking fastness

The color fastness to crocking was determined according to the AATCC test method 8, 1993. A colored test specimen fastened to the base of a crockometer (Auto Preset Counter Control Box-Hungary. TA Instrument Co.) was rubbed with a white crock cloth under controlled conditions.[14]

Dry crocking. The test specimen was placed flat on the base of the crockometer. A white testing cloth was mounted, and then the covered finger was lowered onto the test specimen and caused to slide back and forth 20 times by making complete turns at a rate of one turn/second. The white test samples were then removed for evaluation using the Gray Scale Staining.

Wet crocking. The white test sample was thoroughly wetted out with distilled water to 65% pick up. The procedure was run as before. The white test samples were then air-dried before evaluation.

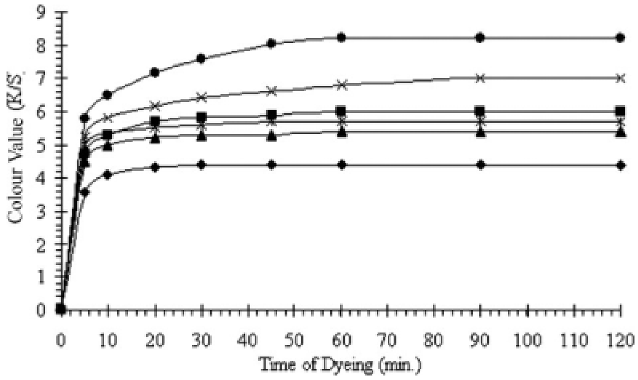


Figure 1 Dependence of the color value of the dyed saccharin sodium salt-pretreated wool on the time of dyeing. Pretreatment: 10 g/L saccharin sodium salt at 90°C, 1 h, liq. ratio 1 : 50. Dyeing conditions: C. I. Basic Red 18 (1% shade o.w.f), pH 4–5, liquor ratio 1 : 50. Dyed untreated wool at 75°C (—◆—), 85°C (—▲—), and 90°C (—✳—). Dyed pretreated wool at 75°C (—●—), 85°C (—✕—), and 90°C (—■—).

Washing fastness

Color fastness to washing was determined according to the AATCC test method 61–1075 using a laundrometer (ATLAS–Germany) (5 g/L, liq. ratio 1 : 50) and 2 g/L sodium carbonate (o.w.f) for 45 min at 40°C.[14]

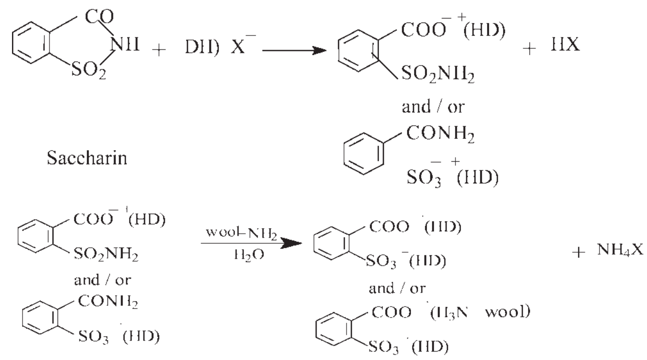
RESULTS AND DISCUSSION

During dyeing of the various investigated fabrics, some steps can be envisaged. (i) Adsorption, absorption of the dye moiety within the fabrics, (ii) transfer across the surface, (iii) diffusion within the fabrics to the interior, and (iv) bonding of the dye moieties to appropriate groups in the fabrics structure. Various mathematical derivations have been estimated depending on Fick's law as an attempt to trace the experimental dyeing rates.[15]

Saccharin sodium salt treatments

Wool fabrics were treated with saccharin sodium salt solutions (10 g/L); the treatment was carried out at 90°C for 1 h. Figures 1 and 2 show the effect of treatment of wool with saccharin sodium salt (10 g/L, 90°C, liq. ratio 1 : 50) on its dyeing ability with C. I. Basic Red 18 (1% shade) for various time intervals at 75–90°C. It can be observed that the pretreatment with saccharin sodium salt had enhanced the color value of the dyed wool fabrics. The increase in color value was found to be dependent on the temperature and the time of dyeing.

The increased affinity of the saccharin sodium salt-treated fabric to the cationic dye can be attributed to the possibility of breakdown of saccharin sodium salt molecules liberating either carboxylic acid and/or sulfonic acid groups. These functional groups are able to trap both cationic moiety as well as the $-H_2N-$ group of the fabrics. Similar mechanisms are cited elsewhere.[18–20]



Polyamide and silk fabrics were treated with saccharin sodium salt under the prescribed chosen optimum conditions. The pretreated fabrics were further dyed with a cationic dye and the attained color values are illustrated in Figure 3. The attained corresponding exhaustion % was also given in Figure 4. It can be observed that pretreatment of polyamide, silk, and wool fabrics with saccharin sodium salt enhanced the color value upon dyeing with cationic dye as well untreated ones. The increases in the color value as well as the exhaustion % were found to depend on the time of dyeing (Figs. 3 and 4).

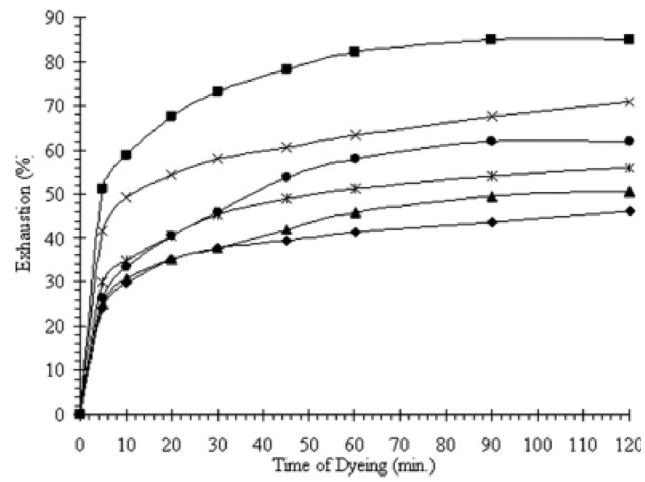


Figure 2 Dependence of the exhaustion % of the dyed saccharin sodium salt-pretreated wool on the time of dyeing. Pretreatment: 10 g/L saccharin sodium salt at 90°C, 1 h, liquor ratio 1 : 50. Dyeing conditions: C. I. Basic Red 18 (1% shade o.w.f), pH 4–5, liq. ratio 1 : 50. Dyed untreated wool at 75°C (—◆—), 85°C (—▲—), and 90°C (—✳—). Dyed pretreated wool at 75°C (—●—), 85°C (—✕—), and 90°C (—■—).

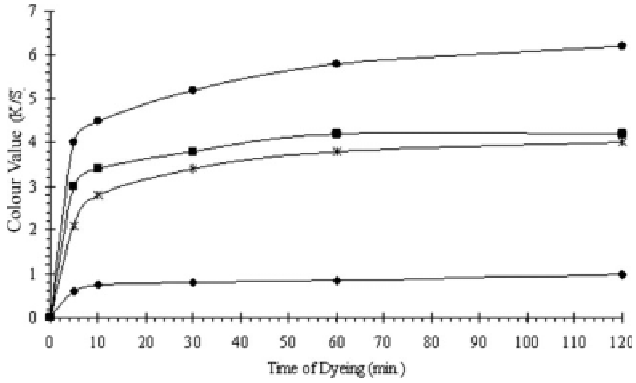


Figure 3 Dependence of the color value of the dyed saccharin sodium salt-pretreated polyamide on the time of dyeing. Pretreatment: 10 g/L saccharin sodium salt at 90°C, 1 h, liq. ratio 1 : 50. Dyeing conditions: C. I. Basic Red 18 (1% shade o.w.f), pH 4–5, liq. ratio 1 : 50. Dyed untreated polyamide at 90°C (—◆—) and dyed pretreated polyamide at 90°C (—■—), dyed untreated silk at 90°C (—✳—) and dyed pretreated silk at 90°C (—●—).

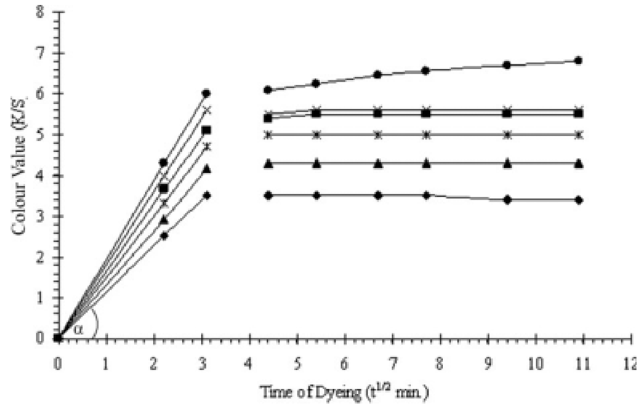


Figure 5 Dependence of the color value acquired by the dyed wool and saccharin sodium salt-pretreated wool fabrics on the square root of time of dyeing. Pretreatment: 10 g/L saccharin sodium salt at 90°C, 1 h, liquor ratio 1 : 50. Dyeing conditions: C. I. Basic Red 18 (1% o.w.f), pH 4–5, liq. ratio 1 : 50. Dyed untreated wool at 75°C (—◆—), 85°C (—▲—), and 90°C (—✳—). Dyed pretreated wool at 75°C (—■—), 85°C (—✕—), and 90°C (—●—).

Kinetic investigation

Figures 5–8 show the relation between the acquired color value and exhaustion % of the dyed saccharin sodium salt-pretreated substrates (wool, silk, and polyamide) versus the square root of the dyeing time (min). The slopes of the given lines were calculated expressed as tan α (where α is the inclination of the straight line on the *x*-axis)[11] and were then plotted against the dyeing temperature.

The rates of the first parts of the lines seem to be faster than that of the second ones, and it seems to be the rate determining step. Combination of saccharin with amino groups of the wool, silk, and polyamide fabrics can lead to an increase in the rate of dyeing at the early stages of dyeing

The influence of variation of temperature of dyeing on the extent of dyeing was studied by plotting tan α against the dyeing temperature (Fig. 9).The given plots increased moderately at low temperature up to 85°C and then the increase of tan α was slowed down by increasing the temperature up to

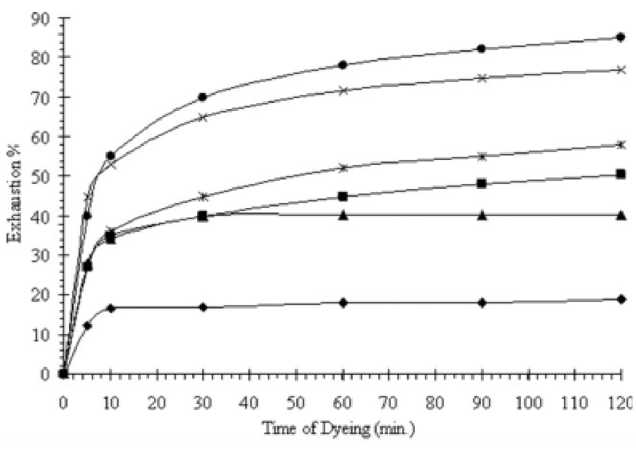


Figure 4 Dependence of the exhaustion % of the dyed saccharin sodium salt-pretreated polyamide, silk, and wool fabrics on the time of dyeing. Pretreatment: 10 g/L saccharin at 90°C, 1 h, liq. ratio 1 : 50. Dyeing conditions: C. I. Basic Red 18 (1% shade o.w.f), pH 4–5, liq. ratio 1 : 50. Dyed untreated polyamide (—◆—) and dyed pretreated polyamide (—■—), dyed untreated silk (—▲—) and dyed pretreated silk (—✕—), and dyed untreated wool (—✳—) and dyed pretreated wool (—●—).

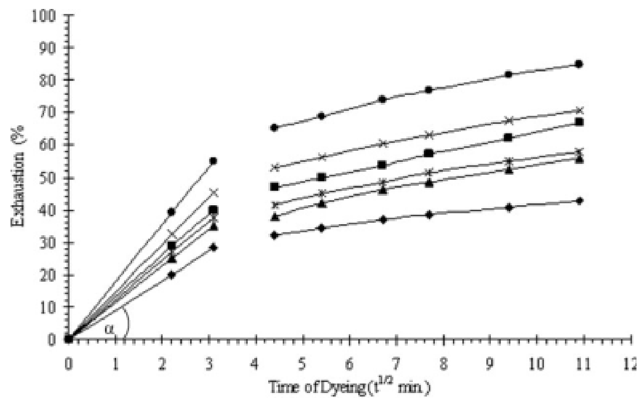


Figure 6 Dependence of the exhaustion % acquired by the dyed wool and saccharin sodium salt-pretreated wool fabrics on the square root of time of dyeing. Pretreatment: 10 g/L saccharin sodium salt at 90°C, 1 h, liq. ratio 1 : 50. Dyeing conditions: C. I. Basic Red 18 (1% o.w.f), pH 4–5, liq. ratio 1 : 50. Dyed untreated wool at 75°C (—◆—), 85°C (—▲—), and 90°C (—✳—). Dyed pretreated wool at 75°C (—■—), 85°C (—✕—), and 90°C (—●—).

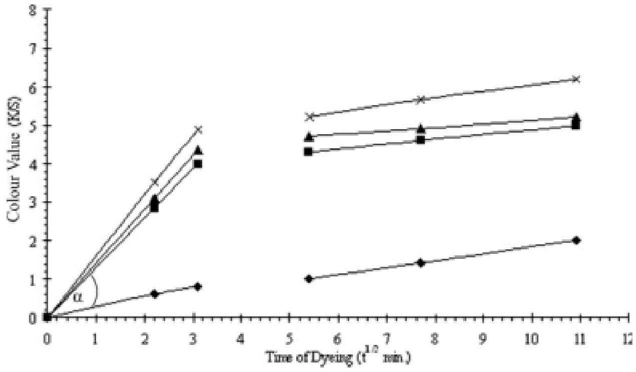


Figure 7 Dependence of the color value acquired by the saccharin sodium salt-pretreated fabrics on the square root of time of dyeing. Pretreatment: 10 g/L saccharin sodium salt at 90°C, 1 h, liq. ratio 1 : 50. Dyeing conditions: C. I. Basic Red 18 (1% o.w.f), pH 4–5, liq. ratio 1 : 50. Dyed untreated polyamide at 90°C (—◆—) and dyed pretreated polyamide at 90°C (—■—). Dyed untreated silk at 90°C (—▲—) and dyed pretreated silk at 90°C (—×—).

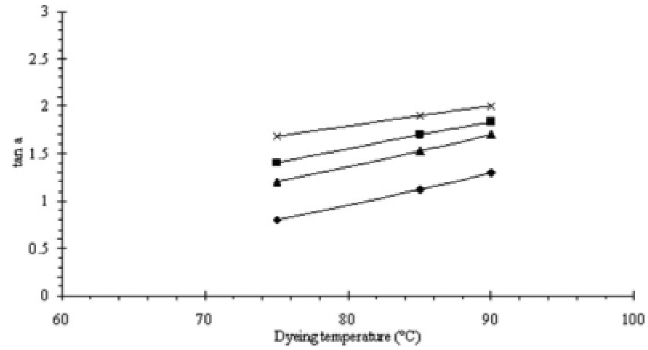


Figure 9 Dependence of the tan α values acquired by the dyed wool and saccharin sodium salt-pretreated wool fabrics on the dyeing temperature. Pretreatment: 10 g/L saccharin sodium salt at 90°C, 1 h, liquor ratio 1 : 50. Dyeing conditions: C. I. Basic Red 18 (1% o.w.f), pH 4–5, liquor ratio 1 : 50. Dyed untreated wool with 0.5% shade (—◆—) and dyed pretreated wool with 0.5% shade (—■—). Dyed untreated wool with 1% shade (—▲—) and dyed pretreated wool with 1% shade (—×—).

90° C for both intact and pretreated wool. The assumed equations are shown below:

$$Y = -2.8x + 2.5x \text{ for untreated dyed wool}$$

$$Y = -6.8x + 5.3x \text{ for saccharin sodium salt pretreated dyed wool}$$

Differentiating the aforementioned equations to get (y'), which represent the tangent of the curve at any point, it can be deduced that $y'_{x=0.1} = 1.82$, $y'_{x=0.2} = 1.4$ for the untreated sample. The corresponding values for the saccharin sodium salt-pretreated wool are 3.6 and 2.7. This means that the rate of tan α decreased on increasing the dyeing temperature up to 85°C. The same trend was previously mentioned.

The half dyeing time ($t_{1/2}$ min.), specific dyeing rate constant (K'), and diffusion coefficient (D)

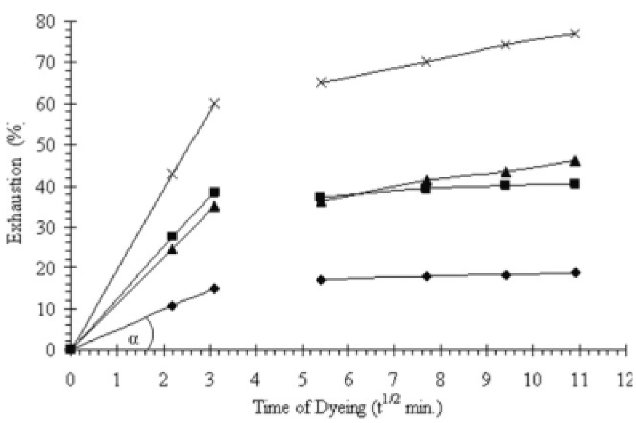


Figure 8 Dependence of the exhaustion % acquired by the saccharin sodium salt-pretreated fabrics on the square root of time of dyeing. Pretreatment: 10 g/L saccharin sodium salt at 90°C, 1 h, liq. ratio 1 : 50. Dyeing conditions: C. I. Basic Red 18 (1% o.w.f), pH 4–5, liq. ratio 1 : 50. Dyed untreated polyamide at 90°C (—◆—) and dyed pretreated polyamide at 90°C (—■—). Dyed untreated silk at 90°C (—▲—) and dyed pretreated silk at 90°C (—×—).

TABLE I
Time of Half Dyeing ($t_{1/2}$), Specific Dyeing Rate Constant (K'), and Diffusion Coefficient (D) of the Dyed Untreated and Saccharin Pretreated Dyed Fabrics

Treatment	Dyeing temp (°C)	$t_{1/2}$ (min)	K'	$D \times 10^{-3}$ ($cm^2\ s^{-1}$)
Dyed untreated wool	90	4	0.01870	0.2685
Pretreated and dyed wool		4	0.04210	0.2758
Dyed untreated polyamide		4	0.00708	0.3065
Pretreated and dyed polyamide		4	0.02508	0.2734
Dyed untreated silk		4	0.02425	0.2260
Pretreated and dyed silk		4	0.04229	0.2616
Dyed untreated wool	85	4	0.02790	0.2544
Pretreated and dyed wool		4	0.03600	0.2660
Dyed untreated wool	75	4	0.02900	0.1877
Pretreated and dyed wool		4	0.02900	0.2000

Pretreatment: 10 g/L saccharin (w/w) at 90°C, 1 h, liq. ratio 1 : 50.

Dyeing conditions: C. I. Basic Red 18 (1% o.w.f), pH 4–5, liq. ratio 1 : 50.

TABLE II
Crocking and Washing Fastness for Untreated and Pretreated Dyed Fabrics for 30 min

	Crocking fastness		Washing fastness	
Substrate	Wet	Dry	St.	Alt.
Dyed untreated wool	3–4	3–4	3	3
Pretreated and dyed wool	3–4	4	4	4
Dyed untreated polyamide	4	4	4	4
Pretreated and dyed polyamide	4–5	5	4–5	4–5
Dyed untreated silk	4	4	4	4
Pretreated and dyed silk	4–5	5	5	5

Pretreatment: 10 g/L saccharin (w/w) at 90°C, 1 h, liq. ratio 1 : 50.
Dyeing conditions: C. I. Basic Red 18 (1% o.w.f), pH 4–5, 90°C, Liq. ratio 1 : 50.
St, staining; Alt, alternation.

TABLE III
Crocking and Washing Fastness for Untreated and Pretreated Dyed Fabrics for 60 min

	Crocking Fastness		Washing Fastness	
Substrate	Wet	Dry	St.	Alt.
Dyed untreated wool	3–4	3–4	3	3
Pretreated and dyed wool	4	4–5	4–5	4–5
Dyed untreated polyamide	4	4	4	4
Pretreated and dyed polyamide	4–5	4–5	5	5
Dyed untreated silk	4	4	4	4
Pretreated and dyed silk	4–5	5	5	5

Pretreatment: 10 g/L saccharin (w/w) at 90°C, 1 h, liq. ratio 1 : 50.
Dyeing conditions: C. I. Basic Red 18 (1% o.w.f), pH 4–5, 90°C, Liq. ratio 1 : 50.
St, staining; Alt, alternation.

during dyeing of wool fiber were determined and summarized in Table I. It can be seen that the dyeing rate constant and the diffusion coefficient increased by the saccharin pretreatment, whereas the half dyeing time was found to decrease.

Fastness properties

Tables II–IV summarize the results of crocking and washing fastness of the dyed untreated and pretreated wool fabrics (dyed for 30–120 min). It can be

TABLE IV
Crocking and Washing Fastness for Untreated and Pretreated Dyed Fabrics for 120 min

	Crocking fastness		Washing fastness	
Substrate	Wet	Dry	St.	Alt.
Dyed untreated wool	3–4	3–4	3	3
Pretreated and dyed wool	4	4–5	4–5	4–5
Dyed untreated polyamide	4	4	4	4
Pretreated and dyed polyamide	4–5	5	5	5
Dyed untreated silk	4	4	4	4
Pretreated and dyed silk	4–5	5	5	5

Pretreatment: 10 g/L saccharin (w/w) at 90°C, 1 h, liq. ratio 1 : 50.
Dyeing conditions: C. I. Basic Red 18 (1% o.w.f), pH 4–5, 90°C, Liq. ratio 1 : 50.
St, staining; Alt, alternation.

seen that the rating of crocking fastness of the pretreated dyed wool fabrics was increased in comparison with the untreated dyed wool. The data of the fastness measurements showed that the washing fastnesses of the pretreated dyed wool fabrics were found to be higher than the untreated dyed one.

CONCLUSIONS

Wool, silk, and polyamide fabrics can be successfully dyed with basic dyes after pretreating the fabrics with saccharin sodium salt.

Saccharin sodium salt molecule behaves as a bridge between both basic dye and the studied fabrics. Kinetic investigation of the dyeing process was carried out to study the effect of the pretreatment. Some enhancements in fastness to crocking and washing are showed for the dyed pretreated fabrics.

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