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Tencel Dyeing by Natural Indigo Prepared from Dyer's Knotweed

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천연인디고를 이용한 텐셀직물의 염색

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Abstract

Natural indigo dye in powder form was prepared by modifying traditional Niram method, using $Ca(OH)_2$ instead of baked oyster powder for precipitating indigo dye. The prepared dye was applied to dyeing Tencel fabrics to investigate the effect of experimental conditions for the optimization of dyeing process. The indigo dye powder contained 15.2%(w/w) of indigo content and 0.757%(w/w) of indirubin content on the basis of HPLC analysis. Maximum dye uptake was obtained at 60°C for 20min. Almost saturated dye uptake was obtained at 2g/L of sodium hydrosulfite concentration up to 4g/L of indigo dye and then slowly increased for further increase of sodium hydrosulfite. Whereas at higher indigo dye concentration(8g/L) more than 3g/L of reducing agent concentration was required for obtaining the maximum dye uptake. At the same indigo dye and reducing agent concentration, K/S value of the sample dyed without sodium hydroxide(pH 5.75) was 15.19, much higher than one dyed in alkaline condition(K/S 5.76). There was no difference in colorfastness ratings among samples with different color strength. However, more fading was occurred for the sample with low color strength.

Key words: Natural indigo, Tencel, Indigo, Indirubin, Colorfastness; 천연인디고염료, 텐셀, 인디고, 인디루빈, 염색견뢰도

I. Introduction

Natural indigo is universally used and oldest blue dye. Recently, increasing concern for sustainability and consumer preference trend for eco-friendly products made a revival of natural dyes. In Europe, a research project of natural indigo production was completed successfully and natural indigo dye is produced commercially for laser printing ink and textile products. Indigo used mainly dyeing denim jeans in textile industry.

Due to better touch and drape properties and more versatile usage than cotton, Tencel(Lyocell) is now being used for denim jean material by top designers and major jean company. Tencel is being made of wood pulp cellulose by eco-friendly technology and biodegradable. If natural dyes are to be commercialized into market place, then indigo can be the most

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promising candidate with immediate commercial potential because there is already an existing demand in the market for the final product, namely, its use in dyeing denim jeans(Gilbert & Cooke, 2001).

Natural indigo dye in powder form was prepared by modifying traditional Niram method, using $Ca(OH)_2$ instead of baked oyster powder for precipitating indigo dye. The prepared dye was applied to dyeing Tencel fabrics to investigate the effect of experimental conditions on dye uptake and colorfastness for the optimization of dyeing process.

II. Experimental

1. Materials

A scoured and bleached 100% Tencel fabric was used and its characteristics are listed in <Table 1>. Indigo plant material(Dyer's knotweed) was cultivated in Naju(Korea) and sampled in August 8, 2007. Chemicals used were reagent grade.

2. Preparation of Natural Indigo Dye

Plants with leaves and stems(40kg) were put into a tank and water(27°C) was poured over the plants(10L of water to 1 Kg of plant material). The steeping plants were weighted down with stone blocks to hold plants under water to exclude air for maintaining anaerobic conditions. After steeping for 2.5 days, the extraction liquid(370L) was pumped into a settling tanks and added $Ca(OH)_2$(2.0g/L) in the tank, and aerated for 30min using a compressor to help oxidation of indigo precursors and precipitation of indigo. The indigo was settled down for 12 hrs and the supernatant was siphoned off. The sediment was collected, filtered through two layers of cotton fabric, dried in a laboratory dryer at 50°C, and pulverized for analytical tests and dyeing experiments. The total mass of obtained indigo dye powder was about 670.8g.

3. Analysis of Natural Indigo Dye

Indigo and indirubin contents of the prepared indigo dye powder were determined by HPLC-UV (high performance liquid chromatography with ultraviolet detector) analysis(Liau et al., 2007). It was carried out on an Agilent 1200 liquid chromatography system(Agilent technologies Inc., Waldbronn, Germany) equipped with two pumps, a MWD UV detector and Rheodyne injector(50mL loop). Chromatographic conditions for the above system were the same as follows: the LC column was a Zorbax Eclipse XDB-C18(4.5mm×150mm, 5μm)(Palo Alto, CA, USA) column. Two mobile phases A and B were used at flow rate of 1.0mL/min. The mobile phase was filtered through a 0.45m filter. Mobile phase A consisted of water with 0.1% trifluoroacetic acid(TFA) and mobile phase B was acetonitrile containing 0.1% TFA. Separation was carried out at room temperature. A gradient was used, starting at 40% B, changing to 85% B linearly in 15min. For each sample measurement was done in triplicate. Synthetic indigo(Vat. Blue 1, Aldrich) and indirubin(Alexis Biochemical, USA) were used as standard dyestuffs for calibration.

4. Dyeing

Reduction and dyeing was carried out as one-step process using an automatic laboratory dyeing machine (Ahiba Nuance, Datacolor International, USA). To optimize dyeing process, dye uptake was studied varying reduction/dyeing temperature(30-80°C) and time(5-80min), dye concentrations(1-12g/L), and reducing agent (sodium hydrosulfite) concentration(0.5-5g/L) at liquor ratio of 1:50. Samples were placed in a 20°C dyebath containg indigo dye and sodium hydrosulfite and temperature was raised to varied temperature and hold for varied time. The samples impregnated with reduced indigo dye solution were removed from the dyeing machine and allowed to oxidize in the open air for 15min, rinsed in tap water, and dried. For compari-

Table 1.Characteristics of the Tencel fabric used

Weave	Density(wxf/5cm^2)	Weight(g/m^2)	Thickness(mm)
3/1Twill	216 × 145	235	0.36

son, Samples were dyed by conventional method using sodium hydroxide at room temperature, 20°C. Sodium hydroxide concentration was varied by 1-8g/L with fixed dye(4g/L) and reducing agent(4g/L) concentration at 20°C for 20min. And the same procedure described above was followed except neutralization in 0.1% acetic acid solution.

5. Color Measurement

Color strength(indigo dye uptake on the fabric) was determined according to the Kubelka-Munk equation from the reflectance at 640nm(λmax) and expressed as K/S values using a Macbeth Coloreye 3100 spectrophotometer. CIELab coordinates(Illuminant D_{65}/10°Observer) was measured with a Macbeth Coloreye 3100 spectrophotometer at 640nm. H V/C values were obtained from L*a*b* data using CIE Munsell conversion program.

6. Fastness Tests

Fastness to washing of the dyed samples was evaluated by AATCC method 61-1989. Light fastness was assessed in terms of color difference(ΔE) and color change against the appropriate Gray scale according to AATCC method 16-1998 with Fade-Ometer(Atlas Electric Devices Co, USA). Color differences after irradiating for 5, 10, 20, and 40 hours was measured to get fading curve. Dry and wet rubbing fastness also evaluated by AATCC method 8-2005.

III. Results and Discussion

1. Characterization of Natural Indigo Dye

During the formation of indigo from indican in indigo plants via indoxyl, indirubin which is an isomeric with indigo and red shade colorant is also produced as shown in <Fig. 1>. So, the contents of indigo

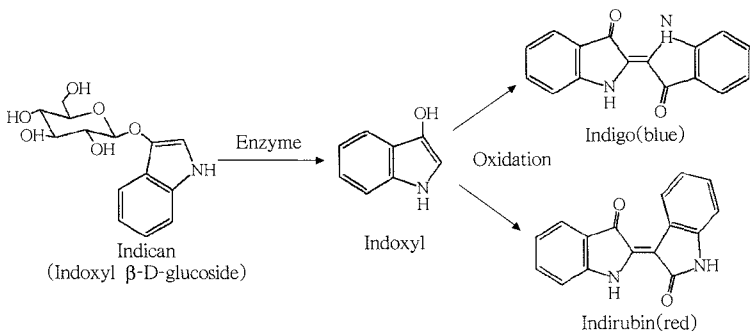


Fig. 1. The formation of indigo and indirubin from indican via oxidative coupling of indoxyl.

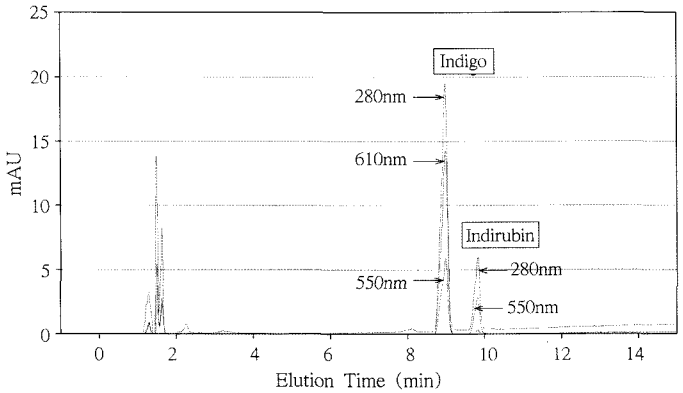


Fig. 2. HPLC profile of natural indigo dye prepared.

and indirubin in the prepared dye were determined by HPLC analysis. <Fig. 2> shows the HPLC profile of natural indigo dye prepared in this study. Indigo component was eluted at 9.18min, showing peaks at 280, 610, and 550nm. Whereas indirubin was eluted at 10.02min, showing peaks at 280 and 550nm. They were well separated and all the peaks had good shape. For the quantification of indigo and indirubin contents of the prepared indigo dye, the peak at 280nm was used because the peak signal was strong and also it was a common peak for two components. The peak areas at 280nm were determined and calculated the concentrations of indigo and indirubin, respectively, from the standard calibration curves. It was found that the prepared natural indigo dye contained 15.2%(w/w) of indigo and 0.757%(w/w) of indirubin. The factors affecting indirubin formation

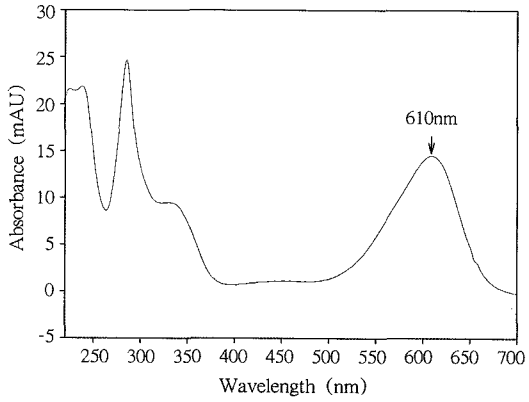


Fig. 3. UV/Visible spectrum of indigo.

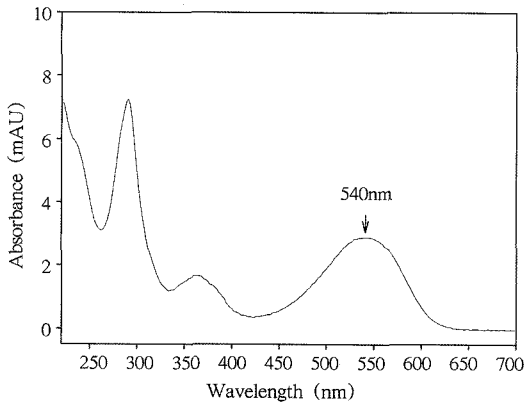


Fig. 4. UV/Visible spectrum of indirubin.

are not completely understood, but weak alkaline conditions and elevated temperatures tend to favor its formation(Cardon, 2007). <Fig. 3-4> show Uv/vis spectra of indigo and indirubin eluted at 9.18 and 10.02min, showing maximum wavelengths at 610 and 550nm in visible range, respectively. The spectra were matched consistently with the spectrum of synthetic indigo and indirubin. The quantification analysis was verified as appropriate from the result.

2. Effect of Dyeing Conditions on Dye Uptake and Color

<Fig. 5> shows reflection spectra of the indigo in the Tencel fabrics with different dye concentration. The maximum wavelength of the indigo in the Tencel fabrics was 640nm. This is apparently different from 610nm obtained for the indigo dissolved in TFA. The indigo molecules on the Tencel fabrics are oxidized form and they are associated together by intermolecular hydrogen bonds, resulting in a batho-chromic shift of reflection spectra(Kunttou et al., 2005).

<Fig. 6> shows the effect of temperature on the dye uptake of Tencel fabrics. Dye uptake was expressed by K/S value at the maximum absorption wavelength, 640nm. Maximum dye uptake was obtained at 60°C. Above 70°C, indigo dye seemed unstable and dye uptake was decreased. The optimum reduction/dyeing temperature was set at 60°C. <Fig. 7> shows the effect of reduction/dyeing time on dye uptake. Dye adsorption of the first 5min was very

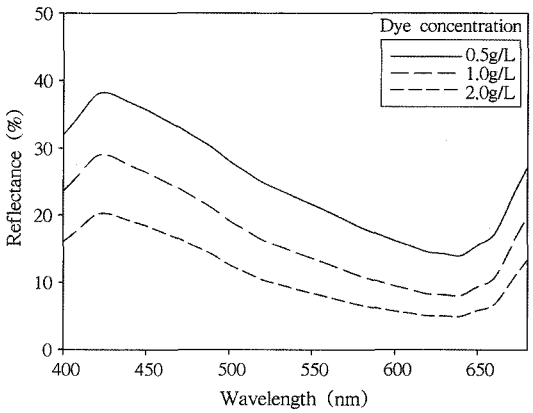


Fig. 5. Visible spectra of indigo in Tencel fabrics.

high and increased slowly up to 30min and decreased thereafter. On the basis of this result, it was found that dye adsorption occurred mainly within the first 20min during dyeing.

The chemical vat dyeing with sodium hydrosulfite is most commonly used worldwide for synthetic and natural indigo dye. Insoluble blue indigo is reduced to soluble, colorless, acid form of *leuco*-indigo, as shown in <Fig. 8>. The acid form of *leuco*-indigo penetrates into fabrics and oxidized in the air to bring back blue color on the fabrics. When sodium hydroxide exists, monophenolate and diphenolate ionic forms, sodium salts, are presented in the dyebath. Without sodium hydroxide in the dyebath, non-ionic, acid forms of *leuco*-indigo are produced. The ionic forms are more hydrophilic than non-ionic, and have a high affinity for hydrophilic fibers(Etters & Hou, 1991; Kunttou et al., 2005).

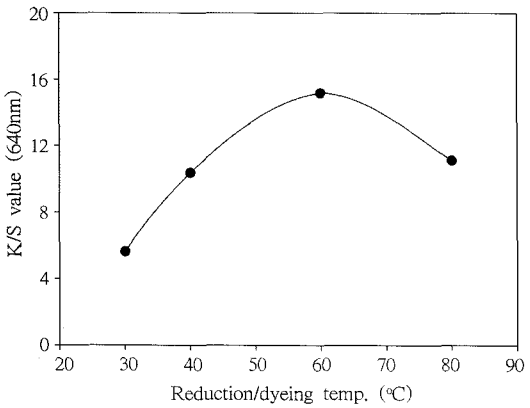


Fig. 6. Effect of reduction/dyeing temperature on the dye uptake(indigo dye 4g/L, sodium hydrosulfite 4g/L, 30min).

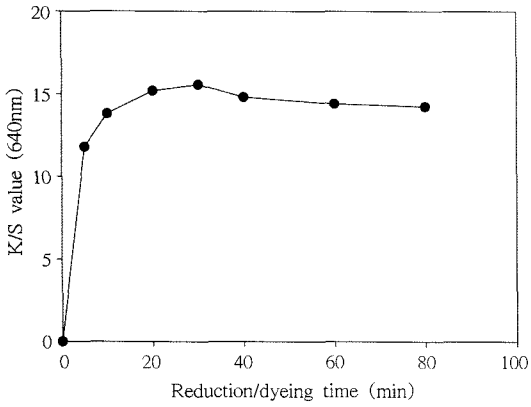


Fig. 7. Effect of reduction/dyeing time on the dye uptake(indigo dye 4g/L, sodium hydrosulfite 4g/L, 60°C).

The effect of sodium hydrosulfite concentration, without sodium hydroxide in the dyebath, on dye uptake was investigated and the results are presented in <Fig. 9>. At the same sodium hydrosulfite concentration, color strength increased with the increase of dye concentration, but at 1g/L of reducing agent concentration, dye uptake was negligible irrespective of dye concentration. Almost saturated dye uptake was obtained at 2g/L of sodium hydrosulfite concentration up to 4g/L of indigo dye and then slowly increased for further increase of sodium hydrosulfite. Whereas at higher indigo dye concentration(8g/L) more than

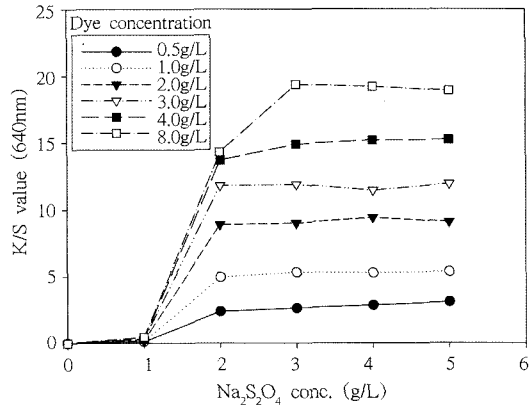
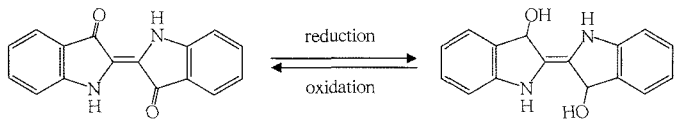


Fig. 9. Effect of sodium hydrosulfite concentration on the dye uptake(60°C, 20min).



Indigo(blue), insoluble

Acid form of *leuco*-indigo(colorless), soluble

Fig. 8. Reduction of indigo into soluble *leuco*-indigo.

3g/L of hydrosulfite concentration was required for obtaining the maximum dye uptake. More elaborate experiments are needed for getting accurate ratio of indigo dye versus reducing agent. It has been known that the adsorption of vat dye by cellulosic fibers is brought by hydrogen bonds and physical forces.

At constant indigo concentration(4g/L) and sodium hydrosulfite concentration(4g/L), sodium hydroxide concentration in the dyebath was varied by 1-8g/L and compared with the sample dyed without sodium hydroxide in the dyebath. The results are shown in <Table 2>. Unexpectedly, dye uptake was much lower with sodium hydroxide in the dyebath than without sodium hydroxide. At the same indigo dye and reducing agent concentration, K/S value of the sample dyed without sodium hydroxide(pH 5.75) was 15.19, which is more than two times compared with the samples dyed with sodium hydroxide in the dyebath. K/S value decreased with increasing alkali concentration. In the dyebath in the pH range of 11.0-11.5, a high amount of the monophenolate ion is produced. On the other hand, high dyebath pH in the range of 12.5-13.5 produces the biphenolate ion, which has lower affinity for cellulose, resulting in better penetration of denim yarn bundle(AATCC International Technical Paper, 1989). For better understanding it is needed to do further research on the effect of dyebath pH in indigo dyeing of Tencel.

The sample dyed without sodium hydroxide produced less blueish color than those dyed in alkaline condition, and they showed 3.4-3.9PB Munsell color. And the samples dyed in alkaline condition were slightly brighter and little more saturated, giving higher V and C values.

3. Colorfastness

<Table 3> shows the effect of repeat dyeing on dye uptake and colorfastness. Dye uptake increased little by little as dyeing was repeated. The reason is speculated that the indigo already fixed on the fiber is partly dissolved during repeated dyeing and so it is difficult to get darker tone of blue color on the fibers in this case. The color of samples dyed repeatedly was not changed due to little difference of K/S value. And colorfastness was fairly good and not much affected by the number of repeat dyeing. <Table 4> shows the effect of color strength on the colorfastness. There was no difference in colorfastness rating among samples with different color strength. How-

Table 2. K/S value and color properties according to the sodium hydroxide concentration(indigo dye 4g/L, sodium hydrosulfite 4g/L)

NaOH(g/L)	pH	K/S value(640nm)	H V/C	a*	b*	ΔE*
0	5.75	15.19	3.4PB 2.9/4.5	-3.53	-19.32	64.61
1	11.71	5.56	3.5PB 4.4/6.3	-4.73	-24.27	52.23
2	12.20	5.91	3.9PB 4.3/6.2	-3.89	-24.27	53.41
4	12.49	5.76	3.9PB 4.3/6.2	-3.97	-24.18	53.16
6	12.59	4.65	3.6PB 4.6/6.1	-4.48	-23.29	50.26
8	12.66	3.63	3.4PB 4.9/5.7	-4.72	-21.62	47.10

Table 3. Effect of repeat dyeing on K/S value, color, and colorfastness(60°C/20min, indigo dye 4g/L, sodium hydrosulfite 4g/L)

Repeat time	K/S value (640nm)	H V/C	Washing			Rubbing		Irradiation (20hr)
			Color change	Stain		Dry	Wet	
				First	Second			
1	15.18	3.4PB 2.9/4.5	4/5	5	5	4	3/4	4/5
2	16.51	3.4PB 2.9/4.6	4/5	5	5	4	3/4	4/5
3	17.91	3.4PB 2.9/4.5	4/5	4/5	5	4	3/4	4/5
4	18.19	3.5PB 2.9/4.5	4/5	4/5	5	4	3/4	4/5

Table 4. Effect of color strength of dyed fabrics on colorfastness

Color strength	K/S value (640nm)	H V/C	Washing			Rubbing		Irradiation (20hr)
			Color change	Stain		Dry	Wet	
				First	Second			
Low	2.62	2.2PB 5.4/5.0	4/5	5	5	4/5	4	4/5
Medium	11.88	3.2PB 3.3/4.7	4/5	5	5	4/5	4	4/5
High	19.36	3.9PB 2.4/4.3	4/5	4/5	5	3/4	3/4	4/5

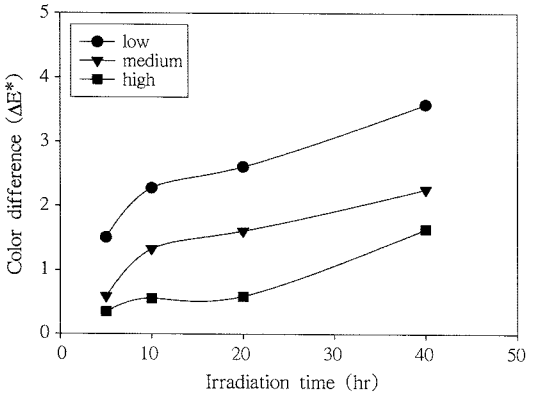


Fig. 10. Fading curves of the fabrics with different color strength.

ever, fading rate and color differences were slightly different with different color strength, as shown in <Fig. 10>. Less and slow fading was occurred in the samples with darker tone for 20 hours exposure. More fading was occurred in sample with low color strength. The light fastness is influenced by several factors: the chemical and physical state of dye, the dye concentration, the nature of fibers, the mordant type, etc. It has been known that the physical state of dye is more important than the chemical structure of dye. Fibers with large aggregates of dye show better light fastness due to less surface area of the fiber exposed to light(Cristea & Vilarem, 2006).

IV. Conclusions

Natural indigo dye was prepared from Dyer's knotweed based on the traditional Niram method. The prepared dye was applied for dyeing Tencel fabrics to investigate the effect of experimental conditions on dye uptake and colorfastness. The indigo dye prepared in this study was contained 15.2%(w/w) of indigo component and 0.757%(w/w) of indirubin component. Maximum dye uptake was obtained at 60°C. The optimum reduction/dyeing temperature and time were set at 60°C and 20min, respectively. Almost saturated dye uptake was obtained at 2g/L of sodium hydrosulfite concentration up to 4g/L of indigo dye and then slowly increased for further increase of sodium hydrosulfite. Whereas at higher indigo dye concentration(8g/L) more than 3g/L of reducing agent concentration was required for obtaining the maximum dye uptake. At the same indigo dye and reducing agent concentration, K/S value of the sample dyed without sodium hydroxide at pH 5.75, was 15.19 which is more than two times higher than the samples dyed in alkaline condition. There was no difference in colorfastness rating among the samples with different color strength. However, more fading was occurred in sample with low color strength.

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요 약

전통적인 니남쪽염료 제조법을 기준으로 굴껍질가루 대신 칼슘하이드록사이드를 사용하여 천연인디고분말염료를 만들었다. 제조한 인디고분말염료에 대한 텐셀의 염색성을 몇 가지 실험조건에서 조사하였으며 염색견뢰도를 측정하였다. 제조한 인디고분말염료는 약 15.5%의 인디고 성분과 0.757%의 인디루빈 성분을 함유하는 것으로 분석되었다. 환원과 염색을 자동염색기로 one-step으로 하였으며 환원제로 소디움하이드로설파이트를 사용하였다. 최대염착량은 60°C에서 얻었으며 초기 20분 동안에 염착이 거의 이루어졌다. 본 연구의 실험조건 범위에서는 염료농도 4g/L까지는 2g/L의 환원제 농도에서, 염료농도 8g/L에서는 3g/L의 환원제 농도에서 최대염착량을 보였다. 텐셀은 염욕에 가성소다를 넣지 않고 pH 5.75에서 염색할 때 훨씬 높은 염착량을 나타냈다. 염색견뢰도는 4/5-5등급으로 대체로 우수하였으며, 염착량이 낮을수록 더 높은 광퇴색을 보였다.