〔보 문〕

Journal of the Korean Society
of Clothing and Textiles
Vol. 25, No. 10 (2001) p.1763~1769

Dyeability of Saxon Blue Derived from Polygonum Tinctorium
Polygonum Tinctorium을 이용한 Saxon Blue 염색

Dept. of Clothing and Textiles, Seoul National University
Ji-Yun Kang · Hyo-Seon Ryu

서울대학교 의류학과
강 지 연 · 유 효 선

(2001. 9. 29 접수)

Abstract

본 논문에서는 쪽의 발효염색이 잿물과 같이 강 알칼리 매체 하에서 사용해야 하고 또한 자연 발효의 경우 온도 조절이 제한되어 있어 단백질 섬유 특히 양모에는 적합하지가 않은 점등을 해결하기 위해 우리나라에서 주로 현재 재배되고 있는 polygonum tinctorium을 사용하여 Saxon blue 법으로 단백질 섬유를 염색하여 염색성을 살펴보았다.

그 결과 Saxon blue로 염색할 때의 등온흡착곡선은 Langmiur형임을 보였으며 색상은 주로 B 영역에서 나타났다. Saxon Blue로 염색한 견직물과 양모 직물 모두 우수한 항균성을 나타내었으며 드라이크리닝과 마찰에 대해서는 좋은 견뢰도를 보여 주었다.

Key words: Indigo, Saxon blue, Silk, Wool, Dyeability, Antimicrobial activity, Colorfastness; 인디고, 색슨블루, 견, 양모, 염색성, 항균성, 견뢰도

I. Introduction

Indigo is one of the oldest dyes used throughout the history of mankind. There are many indigo dye precursor-containing plants all over the world, but the most common ones are Indigofera tinctoria, Isatis tinctoria, and Polygonum tinctorium. Indigofera has more than 800 different types of its own kinds and it spreads from India to tropical regions of Southeast Asia. Polygonum tictorium is most widely grown in the far east region like China, Japan, and Korea.[1]

There are mainly two methods of dyeing with natural indigo in Korea. One of them is to grind the leaves of Indigo containing plants, mix with water, and filter this mixture to get the dye bath. The dye bath prepared by this method contains indican which is taken up by the fiber through multiple dippings and oxidized in the air to give the blue color. This method is simple and easy to use but the dyeing is limited to harvesting period of the plants. The dyeing method using fresh indigo leaves should be carried out at a temperature below 40℃ to prevent the discoloration of the dye

※ This Research was partly Supported by a Grant from the Research Institute of Human Ecology in Seoul National University and by the Brain Korea 21 Project in 2001

bath by the formation of indigo red and indigo brown. In some cases ash water is poured directly into the fresh leaf dye bath and fermented to make the indigo into its reduced form.[3]

Another traditional dyeing method used in Korea is to make the indigo paste. The leaves of indigo plant is soaked in water for couple of days to extract indican. The leaves are then eliminated and the indican containing solution is mixed with lime water and stirred vigorously to oxidize the dye which becomes insoluble in water and settles at the bottom of the vessel. The water is then poured out to finally obtain the indigo paste. The carbonyl group in the insoluble dye is reduced in alkaline state to make the leuco dye.[3] The fiber is dyed in this solution and the dye is oxidized to indigotin to give the blue color.

Although the colors obtained from indigo vat dyeing is usually quite fast, it also has some disadvantages such as the possibility of ring dyeings.[4,5] Also, excess amount of hydrosulphites can hinder the dye uptake while insufficient amount can result in rapid oxidation of dyes which causes decrease in color fastness to abrasion.[6]

Care should be taken in adjusting the dye bath pH in vat dyeing for the reproduction of colors and to increase the dye efficiency. Since dyeing is usually carried out in alkaline media, dyeing protein fibers always require attention. Excess amount of alkalis not only damages the wool fiber but also results in dimensional shrinkage due to felting. Over-use of alkalis may increase the dye solubility in the dye bath, so the color build-up will not be satisfactory even after several repeated dyeings. Due to the difficulties mentioned above, it is critical to set the conditions for dyeing protein fibers with vat dyeing method using natural indigo.

During the 1740's with the discovery of sulfuric acid, a new method of natural indigo dyeing, called Saxon blue, was discovered.[7-8] The insoluble indigo obtained from indigo plant is dissolved in sulfuric acid to make indigo sulfonate, which becomes soluble in water. The dye is an acid dye which makes dyeing protein fibers much easier. Although this method has many advantages for indigo dyeing of protein fibers, it is not well known in Asia and the dyeing procedure has not yet been practiced with Poligonum tinctorium.

This study was conducted to investigate the dyeability, color, antimicrobial activity as well as the color fastness of Saxon blue on protein fibers using Polygonum tictorium for the purpose of proposing the optimum condition for this dyeing method, thus broadening the usage of this one of the most popular natural dyes in the world.

II. Experiment

1 Materials

1) Fabrics

The silk fabric used for the experiment was commercial habutae. The wool fabric used was manufactured by Kyung-Nam. Scouring of silk was done by boiling the fabric in sodium carbonate solution(5% owf) at 90°C with the liquor ratio of 1:30 for 2hours followed by sufficient rinsing with distilled water and air drying. Wool fabric

Table 1. Characteristics of fabrics

	Silk Fabric	Wool Fabric
Fiber Content	Silk 100%	Wool 100%
Weave	Plain	3/1 Twill
Yarn Number	Warp(Denier): 17.4×2 Weft(Denier): 55.2	Warp(Nm): 2/72.3 Weft(Nm): 37.0
Fabric Count (ends x picks/5cm)	192×108	92×88
Thickness(mm)	0.11	0.42
Weight(g/m²)	63.3	197.1
Tensile Strength(Kg)	20.9	19.8

underwent soxlet extraction using dichloromethane followed by repeated cleaning in distilled water and ethanol and air drying.

The characteristics of fabrics after scouring are shown in Table 1.

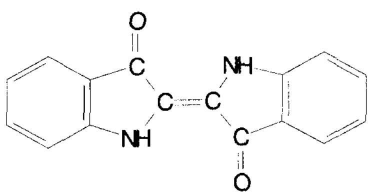
2) Method for dye making

(1) Formation of indigo powder[9]

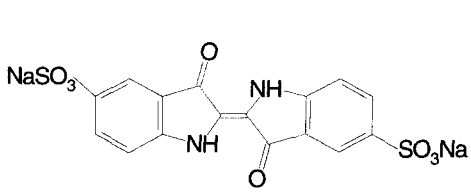
The stems were cut off from fully grown indigo plants and the leaves were separated from the stems. 1Kg of leaves were soaked in 20L of distilled water for 48 hours. Then the leaves were taken out of the water and strained with a fine mesh. 2.5g/L of calcium hydroxide was added to the solution followed by vigorous stirring with rotary stirrer for 20 minutes. When the oxidized dye settles at the bottom of the container, the water is poured out and excess water is filtered. The remaining sediment is dried in the oven at 50℃ for 24hours. The dried lump is then crushed to make powder.

(2) Formation of Saxon blue[7,8]

50ml of sulfuric acid was slowly poured to 10g of indigo powder while stirring the mixture. After the bubbles settled and solution stabilized, the lid of the container was covered and the solution was left for 1 week. The solution is disodium 5,5'-indigotin disulfonate and the structure is shown in scheme 2.



Scheme 1. Structure of Indigo.[10]



Scheme 2. Structure of disodium 5,5'-indigotin disulfonate.[11]

2 Experimental methods

1) Dyeing methods using Saxon blue

The dyes were dissolved in several different concentrations and the dye bath pH was adjusted to 2.5 using10% Na_2CO_3 solution. The dyeing was carried out at various dyeing times and temperature, using IR Dyeing machine(DL 6000, Dae Lim Starlet) at the liquor ratio of 1:50.

2) Evaluation of dyeability and other properties

(1) K/S values

Reflectance of dyed fabrics was measured at every 10nm between 400 to 700nm using Spectrophotometer (CM 3500D, Minolta). The K/S values were calculated using Kubelka-Munk equation.

$$K/S = (1-R)^2 / 2R$$

R: Surface reflectance at wavelength of maximum absorption

K: Absorption coefficient

S: Difussion coefficient

(2) Color

The colors of dyed fabrics were evaluated using Spectrophotometer(CM 3500D, Minolta) by measuring the L* a* b* values. H V/C was obtained using Munsell' s conversion system.

(3) Antimicrobial Activity

The antimicrobial activities of dyed fabrics were investigated according to KS K 0693, by measuring the reduction number of Staphylococcus aureus colonies.

(4) Color fastness

Colorfastness to washing was investigated according to KS K 0430 and A-1 using Launder-ometer(Atlas Electrics Co.) by washing at 40°C for 30 minutes and comparing with the standard grey scale.

Colorfastness to drycleaning was investigated according to KS K 0644 using Launder-o-meter(Atlas Electrics Co).

Colorfastness to abrasion was investigated according to KS K 0650 using Crockmeter(Atlas Elecrtric Co.).

Colorfastness to light was investigated according to KS K 0700 using Fade-Ometer(Atlas Electric Co.).

III. Results and Discussions

1. Dyeability

1) In relation to dyeing time and temperature

Vat dyeing of indigo holds the risk of damaging the protein fibers apart from the complicated dyeing process. But sulfonation of indigo opens another possibility of dyeing with indigo in a much easier way. Fig.1 and Fig. 2 illustrate the K/S values of silk and wool fabrics dyed with Saxon blue at different dyeing time and temperatures.

For silk, highest K/S value was obtained at 40°C and the K/S values decreased as the temperature increased. In case of wool, satisfactory dyeing could not be achieved at lower temperature due to the hydrophobicity of the fiber outerlayer. Highest K/S value was obtained at 60°C and the K/S values decreased noticeably above 80°C. This shows that the dye is quite unstable at high temperatures. In case of silk, K/S values as a function of dyeing time showed that K/S values increased for the first 10 minutes, but showed little change after that. At 70°C, K/S values showed a slight decrease after 10 minutes. In case of wool, K/S values increased until the dyeing time reached 30 minutes for 50, 60, and 70°C but decreased after the dyeing time became longer than 20 minutes for 100°C.

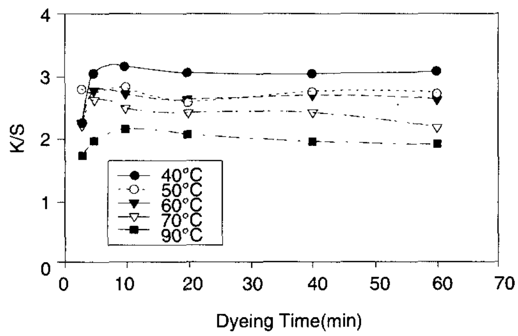


Fig. 1. K/S values of silk fabrics dyed with Saxon blue dyes as a function of time at various dyeing temperatures.(Dye conc.: 6g/l, Dyebath pH: 2.5)

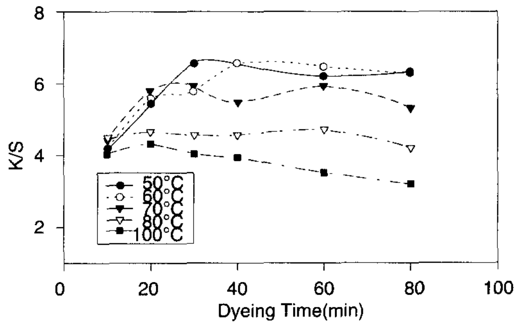


Fig. 2. K/S values of wool fabrics dyed with Saxon blue dyes as a function of time at various dyeing temperatures.(Dye conc.: 6g/l, Dyebath pH: 2.5)

Optimum dyeing temperature for silk was 40°C while that for wool was 60°C.

2) Build up of color

Fig. 3 and Fig. 4 show the build up of color according to the dye concentration. K/S values increased until the dye concentration reached 16g/L for silk and 20g/L for wool but showed little increase at a higher concentration. Dark colors are usually achieved through multiple dippings for vat dyeing, however, it can be achieved by dipping

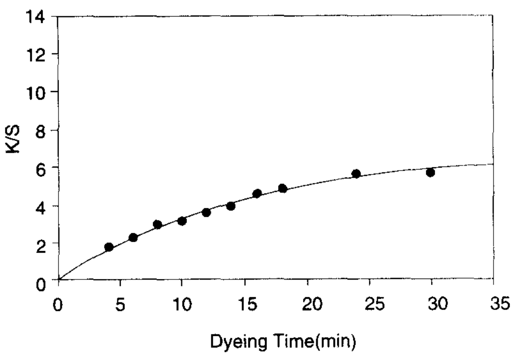


Fig. 3. *Effect of dye paste concentration on K/S* values of Saxon blue dyed silk fabrics. ((max: 620nm, *Dyeing Temp:* 40℃ , Dyeing Time: 60min, Dyebath pH: 2.5)

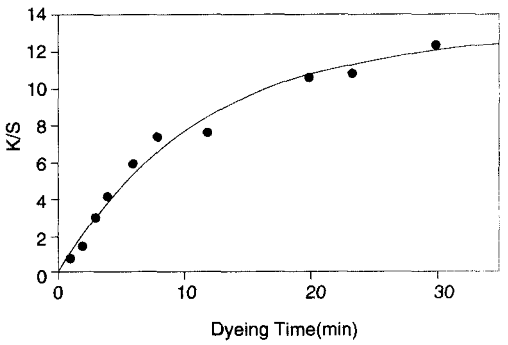


Fig. 4. Effect of dye paste concentration on K/S values of Saxon blue dyed wool fabrics. (max: 620nm, Dyeing Temp: 60℃ , Dyeing Time: 60min, Dyebath pH: 2.5)

once at a high concentration for Saxon blue. The adsorption isotherm curve shows the Langmuir type which follows the pattern of an acid dye.

2. Color

1) Colors of fabrics dyed with Saxon blue

The colors of Saxon blue dyed silk fabrics are shown in Table 2. As the dyeing temperature increased, the greenness as well as the blueness decreased, especially at 90℃ . The colors of Saxon blue dyed wool fabrics are shown in Table 3. The results also show that there was a decrease in greenness as well as blueness as the dyeing temperature increased. Munsell values show that the color moved from PB to B as the dyeing temperature increased. For wool, the color was PB at 50℃ and the value of both a* and b* decreased as the dyeing temperature increased.

Saxon blue dyed fabrics showed quite different colors from the indigo vat dyed fabrics. When fabrics were dyed with hydrosulphite vat of indigo, the colors were PB[12] compared to B for the fabrics dyed with Saxon blue and the value of b* increased even more at higher temperatures.

3. Antimicrobial Activity

Fig. 5 shows the antimicrobial activity of the

Table 2. Effect of dyeing temperature on L*, a*, b*, and Munsell values(Hue) of Saxon blue dyed silk fabric(Dye paste conc.: 8g/L, Dyebath pH: 2.5, Dyeing time: 60min.)

Dyeing Temp(℃)	L*	a*	b*	Munsell Values
40	53.6847	−12.1232	−12.7699	7.7 B 5.1/4.1
50	55.8673	−11.8529	−12.9299	8.1 B 5.3/4.1
60	54.9113	−11.4257	−11.8702	7.8 B 5.3/3.8
70	56.5146	−10.8432	−10.9029	7.7 B 5.4/3.6
90	57.584	−10.3763	−8.8419	6.7 B 5.5/3.1

Table 3. Effect of dyeing temperature on L*, a*, b*, and Munsell values(Hue) of Saxon blue dyed wool fabric(Dye paste conc.: 6g/L, Dyebath pH: 2.5, Dyeing time: 60min.)

Dyeing Temp(℃)	L*	a*	b*	Munsell Values
50	41.2127	−11.7671	−22.2903	0.9 PB 3.9/6.0
60	39.9021	−11.6721	−19.0002	10.0 B 3.8/5.2
70	40.9876	−11.5225	−15.9458	9.1 B 3.9/4.5
80	42.7711	−10.5858	−11.5829	7.7 B 4.1/3.5
100	46.3516	−9.35	−7.4278	5.9 B 4.4/2.6

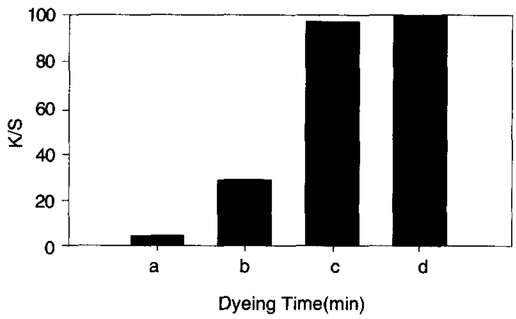


Fig. 5. Antimicrobial activity of fabrics dyed with Saxon blue.
a. Silk; untreated
b. Wool; untreated
c. Silk; dye conc. 8g/l; pH 2.5; 40°C
d. Wool; dye conc. 6g/l; pH 2.5; 70°C

fabrics dyed with Saxon Blue. Both silk and wool fabrics showed excellent microbial activity compared to untreated fabric when dyed with Saxon blue at the dye concentration of 8g/L and 6g/L respectively.

4 Color fastness

Table 4 shows the colorfastness to washing of

Table 4. Colorfastness to washing of fabrics dyed with natural indigo using Saxon Blue

		Slik	Wool
Color Change		1	2-3
Stain	Cotton	4-5	4-5
	Wool	-	4-5
	Silk	4-5	-

Table 5. Colorfastness to dry cleaning of fabrics dyed with natural indigo using Saxon Blue

		Slik	Wool
Color Change		4-5	4-5
Stain	Cotton	4-5	4-5
	Wool	-	4-5
	Silk	4-5	-
Test Solvent		4-5	4-5

Saxon blue dyed silk and wool fabrics. Silk fabrics showed more color change than wool. The staining to adjacent fabrics showed scale of 4-5 for both fabrics.

Colorfastness to dry cleaning of Saxon blue dyed silk and wool are shown in Table 5. Both fabrics showed little color change and staining, which proved the color was quite fast to dry cleaning.

Table 6 shows the colorfastness to abrasion and light of silk and wool fabrics dyed with Saxon blue dyes. As can be seen by the scale of 4-5, they both showed good fastness to abrasion.

The colorfastness to light was poor for both fabrics which showed the scale of 1 for silk and 2 for wool.

Table 6. Colorfastness to abrasion and light of fabrics dyed with natural indigo using Saxon Blue

		Slik	Wool
Colorfastness to Abrasion	Dry	4-5	4-5
	Wet	4-5	4
Colorfastness to Light		1	2

V. Conclusion

Silk and wool fabrics were dyed with Saxon blue using Polygonum tinctorium. Dyeablity, color, antimicrobial activity and colorfastness were investigated at various dyeing conditions such as time and temperature. Dyeability was measured using K/S values and the color was investigated by using CIE L*, a*, b* and Munsell Values. The results obtained were as follows:

1. When protein fibers are dyed with Saxon blue dyes, adsorption isotherm curve showed Langmuir type.

2. The colors of silk and wool fabrics dyed with Saxon blue dyes were in the range of B in most cases, However, the color was in PB range for wool

dyed at 50°C.

3. Both silk and wool fabrics dyed with Saxon blue showed excellent antimicrobial activity.

4. Saxon blue dyed fabrics showed good colorfastness to dry cleaning and abrasion but showed poor colorfastness to light.

References

1. Balfour-Paul, J., "Indigo", British Museum Press, P91-96, 1998.
2. Park, J. S., "Dyeing with Indigo" Taehakwon, 33–118, 1998.
3. Hughey, C.S. "Indigo dyeing: An ancient art", *Textile Chem. Colorist*, **15**(6), 103, 1983.
4. Etters, J. N., Reproducibility in Indigo dyeing *Amer. Dyest. Rep.*, **83**(6), 26, 1994.
5. Etters, J. N., Advances in indigo dyeing: Implications for the dyer, apparel manufacturer, and environment, *Textile Chem. Colorist*, **27**(2), 17, 1995.
6. Liles, J. N. "The Art of Indigo Dyeing. Traditional Recipes for Modern Use" Univ. of Tennesse Press, p. 65, 1990
7. Liles, J. N. op. cit p. 58, 97-98
8. Van Stralen, T., "Indigo, Madder, and Marigold", Interweave Press, 113–115, 1993.
9. Chung,I. M. Korean Patent No. 0264675, 2000.
10. Kim, N. S., "Chemistry of Dyeing", Kyomunsa, p. 294, 1996.
11. The Merck Index 4856, Merck & Co. Inc., 1989.
12. Kang, J. Y. and Ryu H. S., Natural Indigo Dyeing on Wool Fibers(I), *J. Korean Soc. Dyers & Finishers*, **13**(4), 15, 2001.