# A Study on Dyeability with Chitosan and Silane treatment on Natural Dyeing

Park, Ji-Yang\* · Jeon, Dong-Won

Plural Prof. Dept. of Clothing and Textiles, Catholic University\* Prof. Dept. of Clothing and Textiles, Ewha Womans University

#### **Abstract**

In this study, one of disadvantages is to improve the durability of natural dyeing. In order to enhance linkage of Chitosan or Linkage of between Chitosan and cotton fabrics, effect of increasing amount of Silane on Chitosan durability and possibility of using Chitosan as natural mordant were reviewed. After treatment of chitosan with silane, color effect is similar to dyeability used metal mordant. And the durability's washing fastness and air permeability as using chitosan with silane is better than treatment of metal mordant. Chitosan with silane can perform the natural mordant.

Key Words: Natural dyeing, Chitosan, Silane, durability, Caesalpinia sappan, L.

#### I. Introduction

Due to development of science, problems of pollution became social issues and people intend to return to nature. 'Environmental engineering', 'Human sensibility engineering', and 'eco-friendly' were more emphasized and customers have wanted products distinguished from others. <sup>1)</sup> In order to make customers' satisfaction higher, efforts were made to distinguish not only design in textile industry but also dyeing in processing industry. So natural dyeing can offer deep color, not instant color, and different products enough to touch customers' emotions. <sup>2-3)</sup>

Advantage of natural dyeing were verified that they affected on various fields like medical and mental treatments. However, disadvantages of natural dyeing were difficulties to remake natural colors compared artificial dyes and there were too many variables like cultivating periods, kinds, lands, and dyeing situations even though they were same dyes. In order to overcome these difficulties, many researches have continuously been conducted. For reproducing and revealing colors, metal mordant (Al, Sn, Fe, Cu) were used. However, this study was made to increase dye uptake amount of natural dyes and find out necessity of eco-friendly natural mordant. After melting Chitosan which was considered as most

Corresponding author; Park, Ji-Yang, Tel.+82-2-880-9008, Fax.+82-2-878-7296 E-mail: jeeyang@hanmail.net suitable thing in acid, this solution was directly processed with textiles and fabrics. 4-5) Improvement of dyeing properties, change and improvement of cotton fabrics softness and change of rigidity were analyzed. Also, when Chitosan was processed, Silane was added in order to overcome washing durability. In order to enhance linkage of Chitosan or Linkage of between Chitosan and cotton fabrics, effect of increasing amount of Silane on Chitosan durability and possibility of using Chitosan as natural mordant were reviewed.

#### II. Methods and contents

#### 1. Sample

Standard cottons for testing color fastness on KS K 0905 were used.

#### 2. Dyes and reagents

Powdered type of Caesalpinia sappan made from Mi-Gwang International company as natural dyes were used. In addition, Glycidoxyproply-trimethoxysilane (SILQUEST A-187, OSI Specialties Inc.), Zirconium acetate(Aldrich Chemical Company, Inc.) and Triton X-100(DUKSAN PURE CHEMICAL CO., LTD.) were used as reagents. Chitosan made from Ewha precision chemical company was measured 95,600 for number-average molecular weight, 120,000 for weight-average molecular weight, Polydispersity 1.26 for molecular weight, and 100% for deacetylation.

#### 3. Making solution of Chitosan acetic acid

7g of Chitosan was added in 993g of Acetic acid solution at 1% (w/w) concentration and was mixed by using an electric mixer under normal temperature for 24 hours and obtained solution of Chitosan acetic acid at 0.7% concentration. In order to minimize risk that molecular weight could be decreased because folded chains of chitosan which was melted in solution of acetic acid were broken due to action of acetic acid, this solution was used right away after mixed for 24 hours.

#### Processing and spreading solution of Chitosan acetic acid and Silane on cotton fabrics

Silane was added in solution of Chitosan acetic acid in the ratio of 1:0.5, 1:1, and 1:2 comparing with weight of Chitosan respectively and Zirconium acetate was put with same amount with Silane as catalytic reactor and 3g of Triton X-100 was also added as a surfactant.

#### 5. Dyeing

Distilled water with 1:75 ratio was boiled and when it reached at  $35\,^\circ\text{C}$ , cotton fabrics were digested in distilled water and out of it in order to permeate solution when dyes were melted. When temperature of distilled water reached at  $40{\sim}50\,^\circ\text{C}$ , dyes were melted and cotton fabrics were digested. Regarding Caesalpinia sappan, 20% of sample weight was chosen as optimum concentration. Until  $60\,^\circ\text{C}$  was reached, it was

<Table 1> Characteristics of fabrics

	Fiber	Weave	Yarn counts		Density(threads/5cm)		Weight
	content (%)	vveave	Warp	Weft	Warp	Weft	(g/m²)
Cotton	100	Plain	31.4	41.7	132.0	148.8	96.9

heated for 30 minutes. When it reached at  $60^{\circ}$ C, it was kept for 60 minutes and cooled up to 3  $0^{\circ}$ C. And it was washed, dehydrated, and dried.

#### 6. Measuring color differences

Colors of dyed cotton fabrics were measured and obtained color differences from Standard cotton by using L (Whiteness), a (Redness), and b (Yellowness). Indirectly, amount of dye uptake was compared.

#### 7. Measuring air permeability

It was measured by using Textest FX 3300 Air Permeability Tester(Textest, Switzerland)under condition of  $125^{Pa}$ . Each sample was measured five times and used its average. The measuring unit was  $\lceil cm^2/cm^2/s \rfloor$ .

#### 8. Measuring color fastness to washing

The method which was most close to real life was used, not method of KS K0430. Color fastness to washing was measured by using wool course of household washing machine. After washing 20 times, color and air permeability were measured again to check color changes on surface of samples.

#### III. Results and inquiries

#### 1. Analyzing color differences

By using L (Whiteness), a (Redness), and b (Yellowness), color difference ( $\Delta E$ ) from Standard cotton was measured. The results included color differences of surface on samples of pre-dyeing and post-dyeing and showed indirectly amount of dye uptake and these amounts could be quessed.

Comparing with natural cotton fabrics weren't processed with Chitosan, it showed  $\Delta E$  of cotton fabrics had definite differences from cotton fabrics processed with only Chitosan and cotton fabrics processed with both Chitosan and Silane. The result of color difference of cotton fabrics processed with only Chitosan was higher than natural cotton fabrics and it meant color became clearer. It meant there is possibility that Chitosan can be used instead of metal mordant.

Next thing is color difference per proportion of processing Silane. In order to complement the problem of Chitosan durability, Silane was processed. however, the more concentration were, the more  $\Delta E$  increased. That meant amount of dye uptake also increased and dye properties were improved. As a result, the higher Silane concentration were, the more  $\Delta E$ increased. As the results were summarized on table, it could be seen differences with the naked eyes. It showed the state of stop on cotton fabrics processed with 7g of Chitosan. The reason was guessed when 7g of Silane were spread, either it wasn't spread equally or it wasn't saturation point.

## 2. Analyzing L, a, and b of processed samples after dyeing

L (Whiteness) of dyed cotton fabrics was decreased sharply comparing with Standard cotton fabrics. After dyeing process, it is the result of white cotton fabrics dyed white and color element of dyes.  $\Delta E$  of Standard cotton fabrics showed slight differences from that of cotton fabrics processed with only Chitosan and that of cotton fabrics processed with both Chitosan and Silane. Cotton fabrics processed with only Chitosan showed deeper color than Standard cotton fabrics. That meant it had more amount of dye uptake indirectly. There wasn't

<table 2=""> Co</table>	lor-change of t	the dved	cotton	vatious	natural-dves	with	Chitosan	and Silan
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	Condition	L	а	b	ΔΕ
	Natural	93.54	-0.24	1.67	_
	Chitosan	93.25	-0.52	2.88	_
Standard	Silane 3.5g	93.33	-0.43	2.50	_
	Silane 7g	84.23	-0.40	2.21	_
	Silane 14g	93.40	-0.50	2.33	_
	Natural	67.81	11.91	26.96	38.07
Cae*	Chitosan	53.54	19.41	29.11	51.60
	Silane 3.5g	42.61	26.79	19.54	60.03
	Silane 7g	38.18	31.35	18.76	58.34
	Silane 14g	33.79	33.66	17.09	70.28

<sup>\*</sup> Cae: Caesalpinia sappan. L.

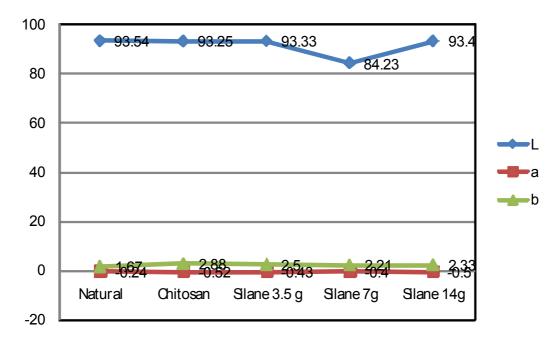
80
70
70.28
60
60.03
58.34
50
40
39.07
30
20
Natural Chitosan Slane 3.5 g Slane 7g Slane 14g

<Figure 1> Color of Caesalpinia sappan.L

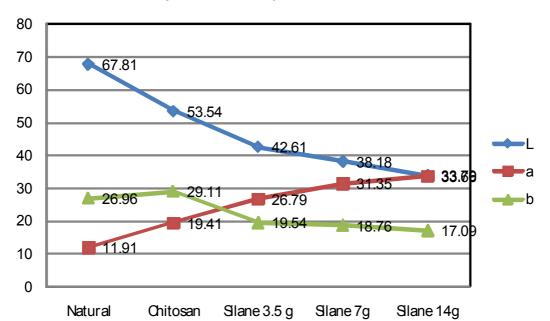
big difference between cotton fabrics processed with only Chitosan and cotton fabrics processed with both Chitosan and Silane. The higher Silane ratio was, the smaller L (Whiteness) of dyed cotton fabrics was. That meant Silane concentration—

affected on mixed amount of Chitosan and color got darker.

Regarding a (Redness), cotton fabrics dyed with natural dyes increased more than standard cotton fabrics. Differing from L (Whiteness), a



<Figure 2> L, a, b analysis of Standard Cotton



<Figure 3> L, a, b analysis of dyed Cotton with Caesalpinia sappan, L.

(Redness)increased per ratio of Silane. It was found out Silane affected on coherence with colors. Regarding b (Yellowness), it decreased on dyed cotton fabrics with natural dyes.

By analyzing L (Whiteness), a (Redness), and b (Yellowness) of dyed cotton fabrics, amount of dye uptake could be increased with Chitosan and the depth of color can be controlled by Silane ratio.

#### 3. Measuring air permeability and Analysis

After dyeing, in order to measure physical properties of fabrics, air permeability was measured and analyzed. Air permeability of cotton fabrics processed with 7g of Silane was 80.5 for the lowest and air permeability of natural cotton fabrics was 93.3 for the highest. It showed cotton fabrics processed with Chitosan had lower rate of air permeability than natural cotton fabrics. And also the cotton fabrics processed with both Chitosan and Silane had low rate of air permeability. However, it wasn't significant change on air permeability due to processing with Chitosan and Silane. It could be guessed air holes of cotton were blocked due to combinations of Chitosan and Silane, and

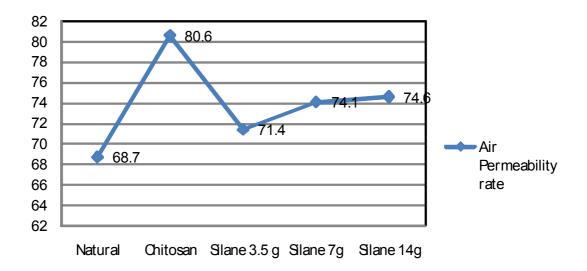
combinations of Silane and cotton fabrics, and combinations of Chitosan and cotton fabrics because cotton fabrics were process with mixture of Chitosan and Silane. Generally, more than 75 of air permeability rate was kept and it couldn't be concluded there were big differences of physical properties.

After dyeing, regarding change of air permeability, there was difference between Standard cotton fabrics anddyed cotton fabrics. Because there was effect which was made by physical power during process of heating up to 60°C, mixing, washing, and dehydrating.

Among dyed cotton fabrics, air permeability of cotton fabrics processed with Chitosan was higher than standard cotton fabrics. It was turned out there was slight differenceper Silane ratio, however, its air permeability was higher than that of cotton fabrics processed with both Chitosan and Silane and standard cotton fabrics. Approximately, range of air permeability of standard cotton fabrics was 60~70, however, range of air permeability of cotton fabrics processed with both Chitosan and Silane was 70~80. Therefore, cotton fabrics processed with both Chitosan and Silane had high its air permeability and increased comfort properties.

<Table 3> Air permeability(cm²/cm²/s)

	Condition	Air permeability(125Pa)		
	Natural	93.3		
	Chitosan	90.2		
Standard	Silane 3.5g	86.2		
	Silane 7g	80.5		
	Silane 14g	82.1		
	Natural	68.7		
Cae*	Chitosan	80.6		
	Silane 3.5g	71.4		
	Silane 7g	74.1		
	Silane 14g	74.6		



<Figure 4> Air permeability od Casesalpinia sappan, L.

#### 4. Change of color by washing

For this study, using household washing machine was chosen as a method of washing in consideration of practicality, not by using Color fastness to washing suitable for KS K0430. Generally, high qualified clothing was hand washable, however, it was hard to repeat procedures of washing, rinsing, and dehydrating in the same way, so wool course of household washing machine was chosen. Procedure of 「washing→rinsing three times→dehydrating→enough natural drying」 was one course and each sample was repeated same procedures by 20 times.

After measuring colors of samples,  $\Delta E$  was measured by using L (Whiteness), a (Redness), and b (Yellowness) of dyed cotton fabrics and those after washing them 20 times. Color fastness to washing was analyzed under the standard

of given sensitive expression by using the measured  $\Delta E$ . As summarized on Table, there were various color changes on dyed cotton fabrics per processing conditions after washing.

Generally, level of  $\Delta E$  was more than 10. When it was observed with the naked eyes, it showed definite color differences from colors before washing. It was considered color was changed by combination of heavy metals in tap water during washing. In the meantime, it was guessed easily falling elements came out of Caesalpinia sappan as multi-color dyes during washing and after washing, there was discoloration by left coloring elements.

Regarding natural dying, durability of washing was not excellent. Its color could be changed by washing, however, elegance of tender, soft and deep color of natural dyeing remained. In consideration of dyeing one time, not repeating, and washing 20 times, durability of washing

wasn't bad as a result. Also, comparing with standard cotton fabrics, there was little color change on cotton fabrics processed with both Chitosan and Silane. That meant Silane, Chitosan and cotton fabrics formed linkage and it made coherence strong.

#### 5. Change of air permeability by washing

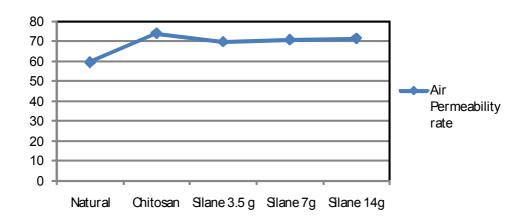
When clothing is worn, comfort property is one of the most important things. Air permeability is a good measurement indirectly to know comfort property. Air permeability of standard cotton

<Table 4> The difference of color betwenn cotton after dyeing and cotton after washing 20 times

	Condition	L	а	b	ΔΕ
	Natural	61.6	10.8	8.8	6.61
	Chitosan	44.2	17.6	10.4	21.09
Cae	Silane 3.5g	38.7	21.7	7.7	13.59
	Silane 7g	34.3	26.7	6.3	14.49
	Silane 14g	30.4	30.1	5.3	12.62

<Table 5> Air permeability after washing 20 times(arr/arr/s)

	Condition	Air permeability(125Pa)		
	Natural	59.2		
	Chitosan	73.8		
Cae*	Silane 3.5g	69.5		
	Silane 7g	70.5		
	Silane 14g	71.2		



<Figure 6> Air Permeability Caesalpinia sappan, L. after washing 20 times

fabric was decreased more than that before washing 20 times. On the other hand, air permeability of cotton fabrics processed with Chitosan wasn't almost changed. Also, there wasn't significant difference from air permeability before washing of cotton fabrics processed with both Chitosan and Silane. Chitosan durability was improved by forming linkage of Silane.

### IV. Results and Discussion

- 1. After dyeing, colors of cotton fabrics were measured and then compared with  $\Delta E$ . As a result,  $\Delta E$  of cotton fabrics processed with Chitosan was higher than that of standard cotton fabrics and  $\Delta E$ of cotton fabrics processed with both Chitosan and Silane was also high. This meant it was effective for Chitosan to increase amount of dye uptake.
- 2. The higher Silane concentration was, the more  $\Delta E$  was increased. This meant Silane improved Chitosan durability and increased amount of dye uptake. It could be controlled with keeping unique color of natural dyeing, not being affected by metal mordant.
- 3. As a result of analyzing L (Whiteness), a (Redness), and b (Yellowness) of dyed cotton fabrics comparing with standard cotton fabrics, L (Whiteness) was decreased and a (Redness) was increased. Processing both Chitosan and Silane affected on amount of dye uptake and wanted colors could be made by controlling Silane concentration.
- 4. Comparing with air permeability of standard cotton fabrics and cotton fabrics processed with Chitosan and Silane, air permeability of cotton fabrics processed with both Chitosan and Silane was higher than that of standard cotton fabrics and cotton fabrics processed with only Chitosan.

- 5. After washing 20 times, the result of observing color wasn't over 10 of  $\Delta E$ . Processing Silane was very important thing to improve the durability of Chitosan.
- 6. Regarding air permeability, in case of processing both Chitosan and Silane, after washing 20 times, the result was similar with air permeability before washing.

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