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Effect of Chitosan Treatment Methods on the Dyeing of Cotton, Nylon, and PET using Cochineal (III)

– Light Fastness and Perspiration Fastness Characteristics –

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Abstract

Recently, problems related to the natural dyeing have been addressed. Severer problems have been posed by the elution of metallic ions and dyestuff from dyed fabrics. In order to prevent the elution from the dyed fabrics, it is needed to improve the fastness. Especially, it is the most important measure to improve the fastness to perspiration in terms of human body safety. In this study, we employed chitosan pretreatment method before the dyeing process, anticipating that the pretreatment might improve the fastness. We used Al, Sn, and Cu as mordants and investigated the fastness to light and perspiration of the chitosan treated and dyed fabric specimens. By the chitosan pretreatment, the fastness to perspiration improved, while the fastness to light did not.

Key words : chitosan, cochineal, mordants, light fastness, perspiration fastness

I. Introduction

Natural dyeing has been in the limelight due to its natural color and safety of the dyestuff for long. Especially, from the viewpoint of dyestuff safety, natural dyestuffs have been regarded as being beneficial since they have been used as herbal medicines and edible materials. Recently, however, the natural dyeing has no option but to be reconsidered in two types of human safety-related aspects. Firstly, issues related to the natural dyestuff itself are being raised. For example, the safety of madder has become an important issue. Recently, in Japan, the madder, which had been used as food coloring, is banned for usage as food additives.[1)] Besides the madder, many arguments may be raised in the future. Secondly, environmental problems may be induced by the natural dyeing process.

First of all, since natural dyestuffs are recognized as non-polluting organic materials, they are regarded as non-pollutants even when the wastewater from the process is discharged. The possibility of environment pollution is very high considering the fact that the natural dyestuffs are excellent nutriment to microbes. In the natural dyeing process, natural dyestuffs are employed together with metallic mordants. These mordants may also pollute the environment when discharged. Remaining tasks are to reduce the hazardousness to the human body by the mordants. Issues in the natural dyeing are raised by the experts in dyeing.[2] In order to prevent the metals used as mordants from being released out of dyed materials, the fastness should be improved. Especially, the method of improving perspiration fastness has won much recognition in order to reduce the metal release.

In this study, the lightfastness and the perspiration fastness of the mordanted fabrics by Al, Sn and Cu mordants in cochineal dyeing.

Chitosan-treated fabrics show less liability of metallic ions to be detached from the treated fabrics, since the ions are strongly bonded with the chitosan components. In the previous studies,[3,4] the effect of chitosan treatment methods on the color changes, wash fastness, abrasion resistance of the fabric according to laundering was reviewed.

Two experimental methods were designed based on the chitosan treatment.

Method 1: Direct dyeing after the chitosan pretreatment of the fabric.

Method 2: Dyeing after the acid salt form was destroyed by alkaline treatment when we consider the fact that metallic ion absorption is favorable mainly in the acidic range, the possibility of metallic ion detachment is low in the case of Method 1. In the case of Method 1, however, since the state of chitosan is acid salt form, it is likely for the chitosan to be soluble or detached in neutral water. On the contrary, in the case of Method 2, the possibility of the chitosan to be soluble in water is low since the chitosan maintains insoluble form.

II. Experiments

1. Specimens and chemicals

1) Fabric specimens

Cotton, PET, and nylon standard fabrics, conforming to the specifications of KS K 0905, for dye fastness test were employed in this test. 〈Table 1〉

2) Dyestuff

Powdered cochineal extract (Mikwang International Co.) dyestuff was used for dyeing fabric specimens.

3) Mordants

- Al mordant ($AlK(SO_4)_2 \cdot 12H_2O$)
- Sn mordant ($SnCl_2 \cdot 2H_2O$)
- Cu mordant ($CuSO_4 \cdot 5H_2O$)
- NaOH

4) Chitosan

High purity chitosan was prepared in our lab. The characteristics determined using a GPC(Gel Permeation Chromatography) were Mw(Molecular Weight) 174,500, degree of deacetylation(DA) 93.19%, and polydispersity (Pd) 2.18.

〈Table 1〉 Characteristics of fabrics

Specification \ Material		Cotton	Polyester	Nylon
Fiber Content(%)		100	100	100
Weave		Plain	Plain	Plain
Fabric count (threads/5cm)	warp	148	223.4	204
	weft	132	183	162
Yarn count	warp	31.4's	74.5 d	68.0 d
	weft	41.7's	74.2 d	68.0 d
Weight(g/m^2)		96.9	69.1	56.2

〈Table 2〉 Wet pick-up ratio

Fabrics	Cotton	Polyester	Nylon
Wet pick-up ratio	113%	35%	52%
Weight of Fabrics(g)	8.63	6.22	5.02

〈Table 3〉 Drying condition

Fabrics	Cotton	Polyester	Nylon
Temp (℃)	120	120	120
Dwelling time (sec)	60 × 2 cycles	60 x 1cycle	60x 1 cycle

5) Water for dyeing

Deionized water was used in this study since the metallic ions, chlorine ions for sterilization, and organic matters may affect the mordanting and dyeing behavior, if any usual tap water were used in the dyeing process.

2. Treatment Methods

1) Chitosan Treatment of Fabric Specimens

(1) Preparation of acetic acid solution of chitosan

10 g of chitosan were added into the 990g of

acetic acid solution of 0.7%(w/w), and solubilized for 24 hrs. at room temperature using a mechanical stirrer in order to prepare 1% concentration of chitosan in acetic acid.

(2) Pretreatment of fabric using chitosan solution

Fabric specimens of 30x30cm size were dipped in the chitosan solution for 72hrs. The specimens were padded using a mangle roller(Model DHE, Mathis Co.) to maintain wet pick up % of 113% for cotton, 35% for PET, and 52% for nylon fabric specimens.〈Table 2〉
Lab Tenter(Model Continuous Type, Daiho, Taiwan) was used to dry fabric specimens. 〈Table 3〉

(3) Alkali neutralization of chitosan pretreated fabric specimens

Alkaline solution was prepared by adding NaOH 75g in 20ℓ of deionized water. Chitosan pretreated fabric specimen was dipped in the alkaline solution one by one. After 2.5hrs. of dipping, the specimens were rinsed twice using deionized water and dehydrated. The fabric specimens were dipped in deionized water for 1hr. and dehydrated. The specimens were dried under room condition for 12hrs.

2) Mordanting

Liquor ratio was adjusted to 1:75, deionized water was heated up to 40℃, 2%(o.w.f.) of Al, Sn, and Cu mordants were added, and the bath was heated up to 60℃. The fabric specimen was mordanted for 1hr. at 60℃, cooled down to 30℃ slowly, and dehydrated followed by room temperature drying for 12hrs.

3) Dyeing

Liquor ratio was adjusted to 1:75, deionized water was heated up to 40℃, 2%(o.w.f) of cochineal dyestuff was added. The dye bath temperature was raised to 45℃, fabric specimen was dipped in the bath and the temperature was raised to 60℃. Dyeing at 60℃ was maintained for 60min. After dyeing, the bath was cooled down to room temperature for 24hrs, the fabric was rinsed twice with deionized water, dehydrated, and dried for 12hrs. at room temperature.

3. Measurement and analysis

1) Light fastness measurement

Weather-O-meter(Atlas Ci4000, Atlas Co., USA) was employed. Three specimens were mounted on the cardboard of 7x4cm, half of the specimen was blocked with a piece of paper to observe the change by light for 5hrs.

2) Perspiration fastness measurement

This test is used to determine the fastness of colored textiles to the effects of perspiration. Test fabric specimen of 4x5cm was mounted on a multi-fiber ribbon. Simulated perspiration solutions, alkaline/acid perspiration solution, were prepared to maintain pH values of 8.0 and 5.5, respectively.

The fabric specimens were placed in two

beakers, containing alkaline and acid perspiration liquid respectively, for 30min.

Subsequently, a compound test fabric, the fabric specimen mounted on a multi-fiber test strip, was inserted between two glass plates, which was mounted on the perspiration tester at 12.5kPa pressure. Then the perspiration tester was placed inside a drier of 37±2℃ for 4hrs. The compound test specimen was removed from the tester, and dried below 60℃.

III. Results and Discussion

1. Light fastness

Light fastness is related to the color change or fading by the exposure of dyed specimens under light, which has been one of the problems that must be solved in natural dyeing. As a whole, contrary to our expectations, the chitosan treatment did not improve light fastness. In the case of cotton fabric, only the non-mordanted chitosan untreated fabric specimen resulted in grade 2, all the others resulted in grade 1 with their colors changed within 5hrs. In the end, the same results were obtained for the chitosan untreated fabric specimens and for the chitosan treated fabric specimens. However, it was hard to conclude that the chitosan untreated fabric specimens were better than the chitosan treated fabric specimens in fastness on the reason that the chitosan untreated fabric specimens resulted in grade 2. Since the dye build-up on the chitosan untreated fabric was very low, it was difficult to recognized the difference even though the light fading had proceeded. Colorwise, chitosan treated fabric has shown excellent characteristics as the strong dyestuff build-up took place. Based on the fact that the light fastness did not improve, it was inferred that the bond strength of the fiber-dyestuff or chitosan-dyestuff was not the factor to determine the light fastness. Several experimental results supported the view that the light fastness was not determined by the bond strength of the dyestuff. First of all, when the mordanting procedure was introduced, the insoluble coordinate-bond complex formed between the dyestuff and fiber had a tendency to improve the color or fastness. However, from the results shown in 〈Tables 4, 5, 6〉, even though the dyestuff may form the coordinate-bond complex with the mordant or fiber molecules, it was inferred that the light fastness did not improve. Also, since the alkali neutralized fabric specimens showed the same results, it was estimated that the alkali neutralization did not make any contribution to the improvement of light fastness.

〈Table 4〉 The colorfastness to light of Cochineal dyed cotton fabrics

Fabric	Mordant	Treated	Level
Standard	Non	Non	5
Dye	Non	Non	2
		Chitosan	1
		Chitosan+Alkali	1
	Al	Non	1
		Chitosan	1
		Chitosan+Alkali	1
	Sn	Non	1
		Chitosan	1
		Chitosan+Alkali	1
	Cu	Non	2
		Chitosan	2
		Chitosan+Alkali	2

〈Table 5〉 The colorfastness to light of Cochineal dyed PET fabrics

Fabric	Mordant	Treated	Level
Standard	Non	Non	5
Dye	Non	Non	1
		Chitosan	1
		Chitosan+Alkali	1
	Al	Non	1
		Chitosan	1
		Chitosan+Alkali	1
	Sn	Non	1
		Chitosan	1
		Chitosan+Alkali	1
	Cu	Non	2
		Chitosan	1
		Chitosan+Alkali	1

〈Table 6〉 The colorfastness to light of Cochineal dyed nylon fabrics

Fabric	Mordant	Treated	Level
Standard	Non	Non	5
Dye	Non	Non	1
		Chitosan	1
		Chitosan+Alkali	1
	Al	Non	1
		Chitosan	1
		Chitosan+Alkali	1
	Sn	Non	1
		Chitosan	1
		Chitosan+Alkali	1
	Cu	Non	1
		Chitosan	1
		Chitosan+Alkali	1

2. Perspiration fastness

Perspiration fastness test was implemented using solutions of simulated acid and alkaline perspiration according to the KS K 0715.

In case of wearing apparels in our daily life, various actions induced by perspiration other than plain water are regarded as important. Especially in natural dyed fabrics, in case of the presence of metals used as mordants, the metals might be slowly dissolved out by perspiration. The perspiration fastness improvement is of prime importance in terms of human body safety.

The resulting grades for the chitosan untreated fabrics, the chitosan treated fabrics by Method 1 and Method 2 all alike. In effect, the chitosan treatment or alkali neutralization of chitosan did not affect the improvement of perspiration fastness. As a general trend, the grades of perspiration fastness to the simulated acid perspiration solution are 2~5 for the cotton fabrics, 3~5 for the PET fabrics, and 2~5 for the nylon fabrics. Since the chitosan untreated fabrics made very low dye uptake, it was concluded that the resulting value of fastness grade 5 did not make any sense. The fact that perspiration fastness grades of 2~5 range were maintained by the chitosan treatment was regarded as very favorable in terms of fastness.

Alkaline perspiration fastness grades were a little lower than the acid perspiration fastness. The fastness grades were maintained in the range of 1~5 for cotton fabrics, 3~5 for PET fabrics, 2~5 for the nylon fabrics.

Considering the fact that chitosan is soluble in the acid solution of pH4 or less while insoluble in water or alkaline solution, it had been postulated there would be difference in the fastness grades between the acid solution and alkaline solution. However, the difference was almost none, or the acid perspiration fastness grades were better. This implies that the chitosan coated on the surface of fabrics did not accompany serious durability degradation.

In 〈Tables 7, 8, 9〉 the result of fastness to the acid perspiration are presented. In 〈Tables 10, 11, 12〉 the result of fastness to the alkaline perspiration are presented.

〈Table 7〉 The colorfastness to perspiration of cochineal dyed cotton fabrics (simulated acid perspiration solution)

Mordant	Multifibre	Treated		
		Non	Chitosan	Chitosan+Alkali
Standard	Acetate	5	–	–
	Cotton	5	–	–
	Nylon	5	–	–
	Polyester	5	–	–
	Acryl	5	–	–
	Wool	5	–	–
Non	Acetate	5	4–5	4
	Cotton	5	2	3
	Nylon	5	2	2–3
	Polyester	5	4	3
	Acryl	5	4	3
	Wool	5	1–2	2
Al	Acetate	4–5	4	3
	Cotton	3	2–3	1–2
	Nylon	2–3	2	1–2
	Polyester	4–5	4–5	4
	Acryl	4	4	3–4
	Wool	3–4	1–2	1–2
Sn	Acetate	4	4	4
	Cotton	2–3	1–2	1–2
	Nylon	3	2	2–3
	Polyester	3–4	4	4–5
	Acryl	3–4	3–4	4
	Wool	2	1–2	2
Cu	Acetate	4–5	4	4
	Cotton	2	1	1
	Nylon	2–3	2	2
	Polyester	4–5	4–5	4–5
	Acryl	4	4	4–5
	Wool	2–3	2	1–2

〈Table 8〉 The colorfastness to perspiration of Cochineal dyed PET fabrics (simulated acid perspiration solution)

Mordant	Multifibre	Treated		
		Non	Chitosan	Chitosan+Alkali
Standard	Acetate	5	–	–
	Cotton	5	–	–
	Nylon	5	–	–
	Polyester	5	–	–
	Acryl	5	–	–
	Wool	5	–	–
Non	Acetate	5	4–5	4–5
	Cotton	5	3	3
	Nylon	5	2–3	2–3
	Polyester	5	4–5	4–5
	Acryl	5	4	4
	Wool	5	2	2
Al	Acetate	5	4	3–4
	Cotton	4	3	2
	Nylon	4	2	2
	Polyester	5	3–4	2–3
	Acryl	5	3–4	3
	Wool	4–5	1–2	2
Sn	Acetate	4–5	3–4	4
	Cotton	3–4	2–3	2–3
	Nylon	3	3–4	3–4
	Polyester	4–5	4	4
	Acryl	4–5	4	4
	Wool	3	2	2
Cu	Acetate	4–5	4	3–4
	Cotton	2–3	1–2	1–2
	Nylon	3–4	2	3–4
	Polyester	5	4–5	4–5
	Acryl	4–5	3	4
	Wool	3	1–2	2

〈Table 9〉 The colorfastness to perspiration of cochineal dyed nylon fabrics (simulated acid perspiration solution)

Mordant	Multifibre	Treated		
		Non	Chitosan	Chitosan+Alkali
Standard	Acetate	5	–	–
	Cotton	5	–	–
	Nylon	5	–	–
	Polyester	5	–	–
	Acryl	5	–	–
	Wool	5	–	–
Non	Acetate	4–5	4–5	4–5
	Cotton	3	2	3
	Nylon	3–4	2–3	2–3
	Polyester	4–5	4–5	4–5
	Acryl	4	3–4	4
	Wool	2–3	2	2–3
Al	Acetate	3–4	4	2–3
	Cotton	2	2	1–2
	Nylon	1–2	2	2
	Polyester	3–4	3	3
	Acryl	3–4	2–3	3–4
	Wool	2	2–3	2
Sn	Acetate	3–4	4–5	4–5
	Cotton	2	1	2
	Nylon	2	2	2–3
	Polyester	3–4	3–4	4–5
	Acryl	3–4	3	3–4
	Wool	2	2	1–2
Cu	Acetate	3–4	3–4	2–3
	Cotton	2–3	1–2	1
	Nylon	4	2–3	2
	Polyester	4–5	3	3–4
	Acryl	4–5	2–3	3
	Wool	2–3	2	1–2

〈Table 10〉 The colorfastness to perspiration of Cochineal dyed cotton fabrics (simulated alkaline perspiration solution)

Mordant	Multifibre	Treated		
		Non	Chitosan	Chitosan+Alkali
Standard	Acetate	5	–	–
	Cotton	5	–	–
	Nylon	5	–	–
	Polyester	5	–	–
	Acryl	5	–	–
	Wool	5	–	–
Non	Acetate	5	4	4
	Cotton	5	2	1
	Nylon	5	2–3	2–3
	Polyester	5	4	3–4
	Acryl	5	4	1–2
	Wool	5	3	1
Al	Acetate	4–5	3	1–2
	Cotton	3–4	1	1
	Nylon	4	3	1–2
	Polyester	4–5	3–4	3
	Acryl	4	3	2
	Wool	3–4	2–3	1
Sn	Acetate	4	4	2–3
	Cotton	2–3	1–2	1–2
	Nylon	3–4	2–3	3–4
	Polyester	4–5	3–4	5
	Acryl	3–4	3–4	4–5
	Wool	2–3	3	3
Cu	Acetate	5	4	4–5
	Cotton	2–3	1	1
	Nylon	4–5	3	4–5
	Polyester	5	3	5
	Acryl	4–5	2–3	3–4
	Wool	3	2	2–3

〈Table 11〉 The colorfastness to perspiration of Cochineal dyed PET fabrics (simulated alkaline perspiration solution)

Mordant	Multifibre	Treated		
		Non	Chitosan	Chitosan+Alkali
Standard	Acetate	5	–	–
	Cotton	5	–	–
	Nylon	5	–	–
	Polyester	5	–	–
	Acryl	5	–	–
	Wool	5	–	–
Non	Acetate	5	5	5
	Cotton	5	4–5	3
	Nylon	5	4–5	3–4
	Polyester	5	5	4–5
	Acryl	5	4	4
	Wool	5	3	3
Al	Acetate	5	4	4
	Cotton	4	3	3
	Nylon	5	4	3–4
	Polyester	5	4–5	4–5
	Acryl	5	3–4	4
	Wool	5	2–3	3
Sn	Acetate	4–5	5	4
	Cotton	2–3	3–4	2–3
	Nylon	4	4–5	4–5
	Polyester	4–5	5	4–5
	Acryl	4	4–5	4–5
	Wool	3	2–3	2–3
Cu	Acetate	4–5	4	4–5
	Cotton	2–3	1–2	1
	Nylon	4–5	4–5	4–5
	Polyester	5	4–5	5
	Acryl	4	4	4–5
	Wool	2–3	3	3

〈Table 12〉 The colorfastness to perspiration of Cochineal dyed Nylon fabrics (simulated alkaline perspiration solution)

Mordant	Multifibre	Treated		
		Non	Chitosan	Chitosan+Alkali
Standard	Acetate	5	–	–
	Cotton	5	–	–
	Nylon	5	–	–
	Polyester	5	–	–
	Acryl	5	–	–
	Wool	5	–	–
Non	Acetate	5	4	4–5
	Cotton	3–4	2–3	2
	Nylon	4–5	3	3
	Polyester	5	4	4
	Acryl	4–5	3–4	3–4
	Wool	4	1–2	2–3
Al	Acetate	4	3–4	3
	Cotton	3	2–3	2
	Nylon	4–5	4–5	3–4
	Polyester	5	4–5	4
	Acryl	4	4	3
	Wool	3	2–3	2–3
Sn	Acetate	4–5	4	3–4
	Cotton	3–4	1–2	1–2
	Nylon	4–5	4–5	3
	Polyester	4	5	4–5
	Acryl	3	4–5	4
	Wool	2–3	3	3
Cu	Acetate	4–5	4	4–5
	Cotton	3	1–2	1
	Nylon	4–5	4	4–5
	Polyester	5	4–5	4–5
	Acryl	4–5	4–5	3–4
	Wool	3–4	3	3

Ⅳ. Conclusions

Environmental problems induced during the natural dyeing procedures have become the most important issues that should be overcome in the near future. The dyeing effluent during the natural dyeing processes have been regarded as discharge of edible organic matters. But it is revealed that the possibility of environmental pollution is very high by the seemingly harmless discharge. Since the mordant discharge may induce heavy metal pollution, the issue should be examined thoroughly.

The elution of mordants attached to the dyed fabrics have not been systematically dealt with so far. It was revealed that the elution concentration was high by the action of perspiration solution.[5)]

It is definitely required in terms of the improvement in the natural dyeing processes in order to develop the methods of measuring fastness of dyed fabrics accurately and the methods of improving fastness. In this study, in order to improve fastness, chitosan pretreatment methods were introduced. In dyeing of fabric using cochineal, by the inspection of light fastness and perspiration fastness of the fabrics mordanted using Al, Sn, and Cu, the following conclusions were obtained.

1. Contrary to our expectations, the light fastness did not improve by the chitosan treatment. It was interpreted that the light fastness was not determined by the bond strength of fiber–dyestuff or chitosan–dyestuff.

2. The grades of perspiration fastness to the simulated acid perspiration solution were in the range of 2∼5 for the cotton fabrics, 3∼5 for the PET fabrics, and 2∼5 for the nylon fabrics. Alkaline perspiration fastness grades were a little lower than the acid perspiration fastness grades. The fastness grades were maintained in the range of 1∼5 for cotton fabrics, 3∼5 for PET fabrics, 2∼5 for the nylon fabrics.

3. The perspiration fastness grades for the chitosan untreated fabrics and the chitosan treated fabrics by the Method 1 and Method 2 showed all similar results. Based on a simple numerical comparison, it was postulated that the effect of the method changes such as chitosan treatment, chitosan non–treatment, or the chitosan treatment method varieties was not very substantive. However, considering the fact that the dye uptake was not established on the chitosan untreated fabric specimens while the dye uptake level was high for the chitosan treated fabrics, it was concluded that the perspiration fastness is maintained high for the chitosan treated dyed fabric specimens.

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