〔보 문〕

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Dyeing of Cotton Fabrics with Loess Using Soybean Milk
- The Compositions of Loess Deposited on the Cotton Fabrics -

콩즙을 이용한 면직물의 황토염색
-면직물에 부착된 황토의 성분분석을 중심으로-

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Abstract

황토는 대표적인 천연 무기염재의 일종으로서 바람에 의해 운반되어 퇴적된 담황색 내지는 황회색을 띠는 실트질의 퇴적물을 일컫는다. 황토의 구성물질은 주로 석영, 장석, 산화철광물, 깁사이트 등의 여러 가지 점토광물을 포함하는데, 주로 적색을 띠는 것은 소량의 산화철 광물에 기인되는 경우가 많으며 황토를 구성하는 점토광물로는 버미큘라이트, 카오린 광물인 캐올리나이트와 할로이사이트, 일라이트 등이 있다.

본 연구에서는 면직물에 천연 무기염재인 황토를 사용한 염색시에 황토 단독염색과 콩즙 전처리 후 황토염색으로 나누어 염색을 실시하고, 원료 황토와 황토염색 후 면직물에 부착된 성분 간에 차이가 있는지를 확인하기 위해 X선 형광분석(X-ray fluorescence analysis, XRF)을 이용하여 염색 전·후 황토의 성분을 분석하였고, X선 회절분석(X-ray diffraction analysis, XRD)을 이용하여 황토 및 염색 전·후 면직물에 부착된 광물질의 주성분을 분석하였으며, energy dispersive spectrometer (EDS)가 장착된 주사전자현미경을 이용하여 면직물에 부착된 광물의 성분을 조사하였다.

그 결과, 황토로 면직물을 염색하는 경우 면직물에 부착되는 황토의 양과 K/S 값은 거의 비례하여 증가하는 것으로 나타났다. 황토 염색 후 면직물에 부착되는 주성분은 주로 SiO_2, Al_2O_3, Fe_2O_3 등인 것으로 나타났으며, X선 회절분석과 EDS 분석에 의해 캐올리나이트, 일라이트 등의 점토광물의 형태로 존재하는 것인 확인되었다.

Key words: loess, X-ray fluorescence analysis, X-ray diffraction analysis, Energy Dispersive Spectroscopy ; 황토, X선 형광분석, X선 회절분석, Energy Dispersive Spectroscopy

I. Introduction

Natural dyes generally fall into two categories; organic dyes coming from animals and plants and inorganic dyes obtained from various minerals such as malachite [$Cu_2CO_3(OH)_2$)], azurite [$Cu_3(CO_3)_2(OH)_2$], carbon and gypsum powder [$CaSO_4 \cdot 2H_2O$][1-4] and etc. The chief components of mineral dyes are loess, iron oxide, manganese oxide, cinnabar (HgS), azurite, copper, zinc, lead, chrome.

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Loess is a pale yellow or grayish yellow silt deposit[5] carried by wind and mainly found in northern parts of China, Europe, North America, and New Zealand[6, 7]. Loess found in Korea is mainly composed of soil from weathered rock. The components of loess are quartz, feldspar, clay mineral, iron oxide mineral, gibbsite [$Al(OH)_3$] etc. Different clay minerals are classified according to the deposited place, kind of mother rock and composition rate. And the reddish color mainly comes from iron oxide.

The main component of loess is clay mineral, hydrated aluminum silicates usually obtaining a sheet-like structure that occur as particles usually less than 2 microns in size. Clay minerals composing loess are vermiculite [(Mg0.7) (Mg, Fe, Al)$_6$ (Si, Al)$_8$ O_{22} $(OH)_2 \cdot 8H_2O$], kaolinite [$Al_2Si_2O_5(OH)_4$], halloysite [Al_2Si_2O $5(OH)_4 \cdot 2H_2O$], illite [(K, H_3O) (Al, Mg, Fe)$_2$ (Si, Al)$_4$ O_{10}[$(OH)_2$, (H_2O)]] etc.[8] These clay minerals have great adsorption, ion exchange and far-infrared emmision properties.

Recent days, various inner wears, sheets and interior goods are manufactured using materials dyed with loess emphasizing its improved blood circulation, metabolism, anti-bacterial and deodorizing properties.[9, 10]

The traditional dyeing method of cotton fabric with loess immersing the fabrics in the loess suspension bath[11~14] is very simple. But fabrics dyed in this method have inferior color fastness to washing.

In these days, in order to improve the fastness to washing, cotton fabrics are pre-treated with cationizing agent[15~17]. But most of the cationizing agents have functional groups such as chlorohydrine, epoxy, chloro triamine and chloro pyrimidine. But these chemicals are usually irritating the skin and mucous membrane or contain the possibilities to be toxic.

Besides using chemicals, one of the traditional pre-treating method of cotton fabrics to improve affinity to dyes is immersing the fabrics in various animal or vegetable protein solution such as soybean milk, cow milk, animal dung solution or nut gall extract. These materials are more ecological than cationizing chemicals mentioned above.

In this paper, two different classes of dyeing process were tested; dyeing with loess only and soybean milk pre-treatment followed by dyeing with loess. K/S values were determined to examine the dyeing properties. And the components of minerals deposited on the cotton fabrics before and after dyeing were studied by XRD, XRF and EDS-SEM.

II. Experimental

1. Materials

1) Cotton fabric

Cotton fabrics used in this experiment were white cotton fabric scoured with 10%(o.w.f.) sodium carbonate solution (liquid ratio 1:50), for 2 hours, followed by washing with distilled water and dried at room temperature. The characteristics of the fabrics are shown at Table 1.

Table 1. Characteristics of fabrics

Material	Cotton 100%
Yarn number (Ne)	36×36
Weave	Plain
Fabric count (ends×picks/5cm^2)	161×157
Thickness (mm)	0.26
Weight (g/m^2)	110

2) Loess

Loess was taken from Ha-Dong province (Daedong Green Industries Co. Inc). The mean particle size was 19.94μm and the weight distribution of loess sample (CILAS, France, - Daedong Green Industries Co. Inc) is shown in Figure 1.

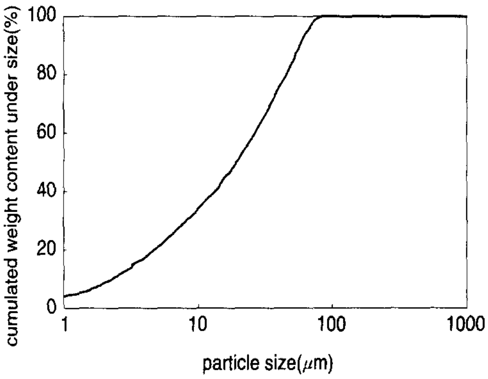


Fig. 1. Weight distribution of loess sample (M=19.94㎛).

3) Soybean

Soybean used in this experiment were harvested in 1999 in Dan-Yang province (Chungcheongbuk-Do, Korea).

2. Dyeing

1) Soybean milk treatment

The soybeans were soaked in distilled water for 4 hours at 30℃. The swollen beans were then ground for 1 minute using a blender and filtered through de-fatted nylon sheet. The filtrate was designated as soybean milk.

The cotton fabrics were treated with soybean milk using the IR dyeing machine (Model : DL 6000, Daelim Starlet Co., Ltd.). The soybean milk treatment conditions were fixed as follows : soybean milk concentration; 25g/l, soybean milk treating temperature; 40℃, soybean milk treating time; 30min.

Soybean milk treated cotton fabrics were wringed (100% of wt. pick up) and air dried.

2) Dyeing the cotton fabrics

Two different classes of dyeing process were tested; those are dyeing with loess only and soybean milk pre-treatment followed by dyeing with loess. The cotton fabrics were dyed with loess using the IR dyeing machine (Model: DL 6000, Daelim Starlet Co., Ltd.).

And dyeing conditions were fixed as follows : concentration of loess; 30%(o.w.b.), dyeing time; 60min, dyeing temperature; 100℃.

After the dyeing process, cotton fabrics were washed with distilled water and air dried.

3. Measurements

1) K/S value

The surface reflectance of dyed cotton fabrics were measured at the maximum absorption wavelength using a spectrophotometer (spectrophotometer CM 3500D, Minolta, Japan). K/S values were calculated by the Kubelka-Munk equation.

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

where, R: Reflectance coefficient (λmax = 400)
K: Absorption coefficient
S: Scattering coefficient

2) The amount of loess deposited on the cotton fabrics

The amount of loess deposited on the cotton fabrics after dyeing was investigated with a furnace (Electric muffle furnace, Samik scientific Co.) The cotton fabrics burnt out at 850℃ during 3 hours, and remained weight was identified as the weight of loess.

3) X-ray fluorescence analysis (XRF)[18]

The compositions of loess powder and loess deposited on the cotton fabrics after dyeing were investigated by X-ray fluorescence analysis(XRF) using a X-ray fluorescence photometer (Shimadzu XRF-1700 Sequential X-Ray Fluorescence Spectrometer) with Rh target at 40KV, 30mA.

The glass bead was made with 0.7g of dryed loess sample at 100℃ and 7g of lithium tetraborate ($Li_2B_5O_7$).

4) X-ray diffraction analysis (XRD)[19]

The mineral identification and crystal lattice of the cotton fabrics dyed with loess were investigated by X-ray diffraction analysis (XRD) using a Rigaku Geigerflux diffractometer (Rigaku Geigerflux 2100, Japan) with CuKα radiation (Kα= 1.5412Å) at 40KV/30mA in a continuous scanning mode of scanning speed of 1°/min (2θ/min).

5) Energy Dispersive Spectroscopy (EDS-SEM)

Scanning electron microscope (SEM, Model: LEOS-1455VP) equipped with energy dispersive spectrometer (EDS, Model: Pioneer EDS LEOS-1455VP SEM 138eV) were used for the identifications of loess deposited on the cotton fabrics by the morphology and chemistry.

SEM images and EDS patterns were obtained from the surfaces of the cotton fabrics after gold coating under vacuum.

Ⅲ. Results and Discussion

1. The amount of loess deposited on cotton fabrics

After burning out the fabrics, the weight of loess deposited on the cotton fabrics was measured. (Figure 2)

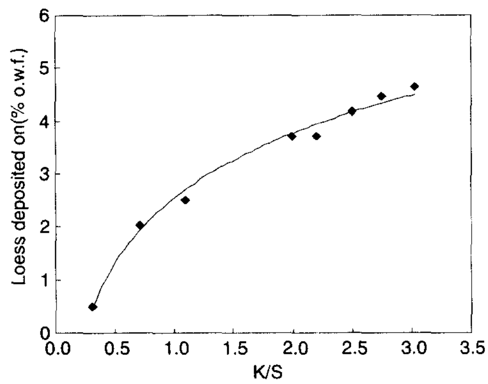


Fig. 2. Weight of loess deposited on the fabric according to K/S.

In proportion to the amounts of loess deposited on the fabrics, K/S values increased. But the increasing tendency somewhat weakened as the amount of loess deposited on the fabrics increased.

2. X-ray fluorescence analysis

The compositions of loess powder and loess deposited on the cotton fabrics after dyeing were investigated by X-ray fluorescence analysis(Table 2).

The most abundant components of loess used in this experiment were SiO_2, Al_2O_3, Fe_2O_3, TiO_2, which accounted for 95% or more of the whole weight.

After dyeing, the components of the loess remained on the fabrics also turned out to be the major 4 components mentioned above. But among them, the compositions of SiO_2 and Al_2O_3 decreased abruptly, whereas the composition of

Table 2. Component ratios of loess

component	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO
ratio of A(%)	47.89	31.70	2.01	11.27	0.90	0.21	—	0.56	0.10
ratio of B(%)	38.92	32.15	1.06	23.48	—	—	—	—	—

* loss of ignition : 4.39% A; loess before dyeing B; loess deposited on the fabric after dyeing

Fe_2O_3 was increased to nearly 25%. Therefore, the major component of the loess which represents the reddish color would be the iron oxide. In the dyed sample, MgO, CaO, Na_2O, K_2O, MnO were not detected, these components may be solubilized in the dyebath or the amount was too little to be measured.

3. X-ray diffraction analysis

The mineral identification and crystal lattice of the cotton fabrics dyed with loess were investigated by X-ray diffraction analysis(Figure 3).

The XRD patterns of loess powder used in this experiment shows the peaks of illite (2θ= 8.26), amphibole (2θ= 10.62), kaolonite (2θ= 12.20), quartz (2θ= 26.60) and kaolinite was the major component. illite, kaolinite and quartz are clay minerals mainly composed of oxide compounds of aluminum and silicone, and have chemical formulas $[(K, H_3O)\ (Al, Mg, Fe)_2\ (Si, Al)_4O_{10}[(OH)_2, (H_2O)]$, $Al_2Si_2O_5(OH)_4$ and SiO_2 respectively.

The result of XRD analysis have good agreement with XRF analysis(Table 2) which represent high compositions of silicone oxide and aluminum oxide. These clay minerals have sheet-like structure, less than 2μm in size and have colors ranging from white to yellow or greenish white but are often reported to having changed to a reddish color. By the weathering process, the surface of the clay minerals are surrounded by the iron oxide materials.

The XRD patterns of untreated cotton fabrics showed the peaks of the crystal lattice of cellulose I. The 101 (2θ= 14.48), $10\overline{1}$ (2θ= 10.62) and 002 (2θ= 10.62) peaks of cellulose I were clearly separated.

In the case of soybean milk treated cotton fabrics, like the untreated cotton fabrics, the 101, $10\overline{1}$ and 002 peaks of cellulose I were clearly separated. The organic compounds of soybean milk had but little influence on the flattening the 101 peak of cellulose I.

The cotton fabrics dyed with loess have the peaks of amphibole (2θ= 2.58) and kaolonite (2θ= 20.62) except the peaks of cellulose I.

The XRD patterns of the cotton fabrics which were soybean milk pre-treated and followed by dyeing with loess showed the peaks of amphibole (2θ= 11.24) and kaolonite (2θ= 12.26, 20.42, 20.68)

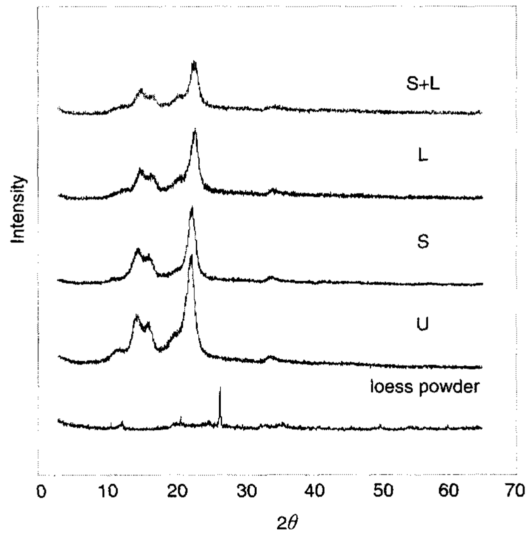


Fig. 3. X-ray diffractometer scans of
S+L; cotton fabric pre-treated with soybean milk and dyed with loess
L ; cotton fabric dyed with loess
S ; cotton fabric treated with soybean milk
U ; untreated cotton fabric
and loess powder.

4. Identification of particles on loess dyed cotton fabrics

The SEM photographs of the cotton fabrics magnified to 1000 times are showed in Figure 4. The soybean milk surrounds the surface of the fabrics.

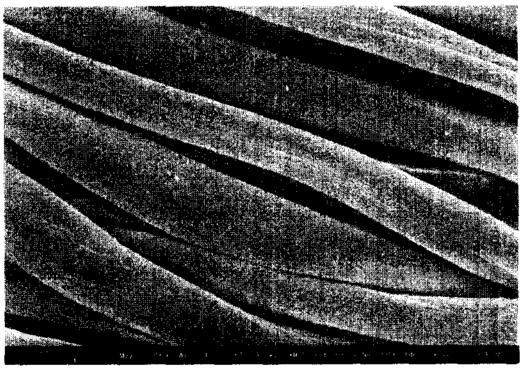
In contrast to the fabrics dyed with loess only, pre-treatment with soybean milk increasing the amount of loess deposited on the fabrics. But the deposited particles were μm in size, so the major portion of the particles would be the clay minerals.

Scanning electron microscope equipped with energy dispersive spectrometer were used for the identifications of loess deposited on the cotton fabrics by the morphology and chemistry. Typical EDS-SEM patterns are presented in Figure 5 and 6.

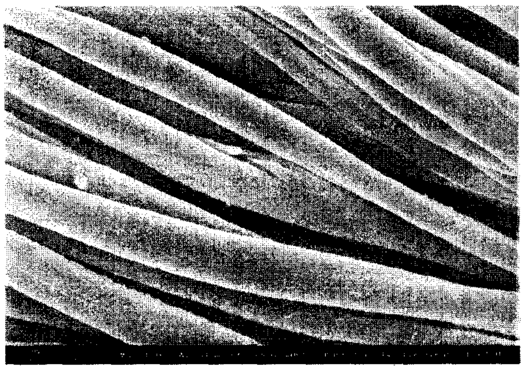
In the case of particle A, the size was somewhat large for a clay mineral, but by the analysis of EDS, the peaks of silicone, aluminum and oxygen clearly showed up whereas the peaks of other elements were not detected. And the ratio of silicone to aluminum was 1:1. Therefore particle A may be seen as a pure kaolin mineral.

In the case of particle B, the peaks of aluminum were not detected but only the peaks of silicone and oxygen showed up. Particle B therefore could be declared quartz, a pure silicone oxide.

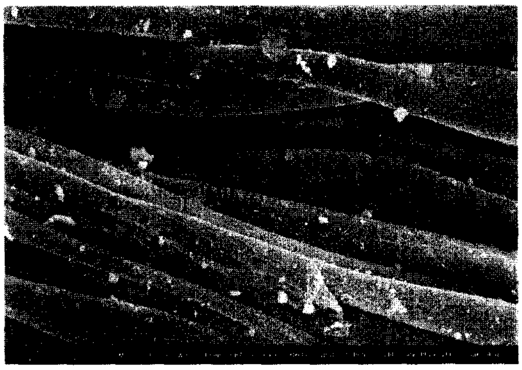
In the case of particle C, the ratio of silicone to aluminum was nearly 2:1, and small peaks of iron



U



S



L

S+L

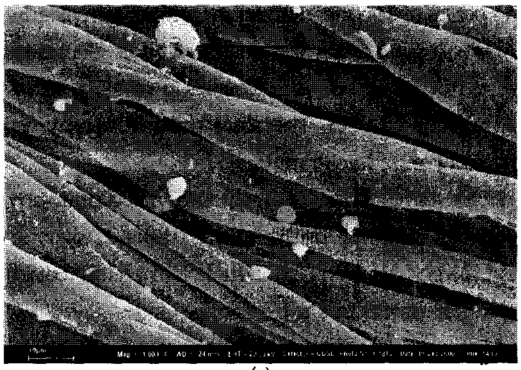
Fig. 4. SEM of the surface of cotton fabrics.

U : untreated

S : soybean milk treated

L : dyed with loess

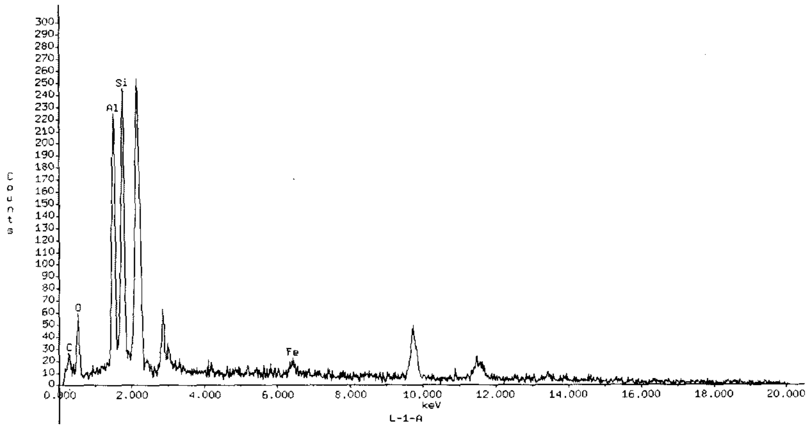
S+L : soybean milk pre-treated followed by dyeing with loess



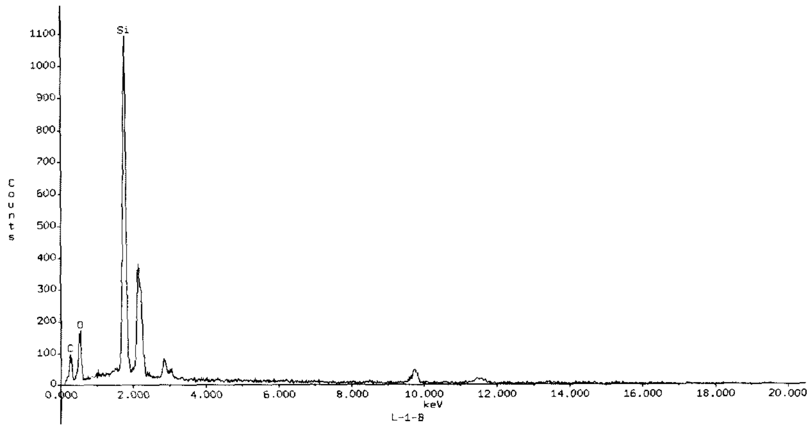
(a)

showed up. Therefore the particle could be either illite or vermiculite which has 2:1 type of lateral silicate mineral. But the peak of potassium was not clear, therefore it can be presumed to be pyrophillite [$AlSi_2O_5(OH)$].

As mentioned above, it was identified that various clay minerals composing loess deposited on the cotton fabrics through the dyeing process.



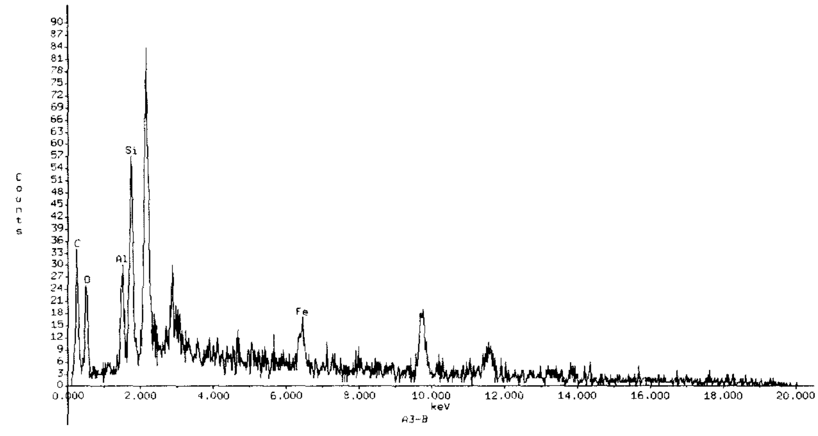
(b)



(C)

Fig. 5. EDS-SEM of cotton fabric dyed with loess

(a) SEM image **(b) EDS pattern of point A** **(c) EDS pattern of point B**



(a)

(b)

Fig. 6. EDS-SEM of cotton fabric dyed with loess
(a) EDS pattern of point C
(b) SEM image

IV. Conclusion

In this paper, the cotton fabrics were dyed with loess and the compositions of the loess deposited on the fabric have been studied in various ways. Soybean milk was used to pre-treat the cotton fabrics in the dyeing process.

The more loess deposited on the fabrics, the higher K/S value was obtained. However the increasing tendency weakened as the amount of loess deposited on the fabrics increased.

The major chemical components of loess deposited on the cotton fabrics turned out to be iron oxide, silicon oxide and aluminum oxide and etc. According to the analysis by XRD and EDS-SEM, kaolinite, illite and quartz were also identified.

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