

DYEING PROCESS FOR IMPROVING PROPERTIES OF BLACK COLOR USING NATURAL DYES AND MORDANT

by

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ABSTRACT

An environmentally friendly nontoxic leather product was produced using two kinds of natural dyes (gallnut and sappan wood) to create a black colorant that can be universally used in leather manufacturing. A chrome free aldehyde and aluminum tanning system was used to prepare the leather for the dye experiments. For the dye preparation experiments gallnut and sappan wood, which are representative polygenetic natural dyes, were extracted by alcohol extraction; then decompressed and refined under concentrating conditions to produce dye in powder form. To produce natural dyed leather with a black color, 5% gallnut and sappan wood were used and the mordant agent, iron mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) at 1% of the leather weight, was applied in three different sequences. Applying the mordant simultaneously produced a superior result compared to its application before or after the application of the natural dye. To evaluate the softness and color change of leather, an anionic fatliquor agent was used at 12% of the leather weight. An excellent dark black color and chroma was obtained on the leather surface as a mordant agent and complex compound. The excellent results obtained during the evaluation of rubbing fastness, K/S (coloring matter concentration of surface), and color difference enabled the conclusion that leather with a deep black color could be manufactured with this method.

RESUMEN

Un producto para teñir cuero amigable al medio-ambiente y sin toxicidad se produjo en base a dos colorantes naturales (agalla de roble y madera de sappan [sibucáo en las Filipinas]) para crear un colorante negro que puede usarse ampliamente en la fabricación del cuero. Un curtido basado en aluminio y alhído exento de cromo se empleó para preparar el cuero para los experimentos de tintura. Para las preparaciones de las tinturas experimentales en base a agallas de roble y madera de sappan, los cuales son representativos poli-genéricos de colorantes naturales, se recuperaron por extracción alcohólica; para luego descomprimir y refinar los extractos bajo condiciones de concentración para obtener el colorante en polvo. Para producirse cuero naturalmente en color negro, 5% de agallas de roble así como de madera de sappan se utilizaron y el agente mordiente, de hierro ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) al 1% por peso del cuero, se aplicó en tres secuencias diferentes. Aplicación del mordiente simultáneamente produjo resultados superiores que la aplicación del mordiente antes o después del ofrecimiento del colorante natural. Para evaluar la blandura y el cambio en color en el cuero, un agente engrasante aniónico fue empleado al 12% sobre el peso del cuero. Un excelente color negro oscuro saturado resultó en la superficie complejamente amordantada por el resultante compuesto. Los excelentes resultados obtenidos durante la evaluación de resistencia al frote, K/S (concentración de materia tintórea superficial), color diferencial, ocasionó la conclusión que cuero de color negro intenso se puede producir con este producto.

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INTRODUCTION

Gallnut and sappan wood are representative polygenetic dyes that are found in nature. Both have unique original colors: gallnut is gray, and its main element is pyrogallol tannin; sappan wood is red, and its main element is a dihydropyran derivative. There have been many studies on the use of sappan wood with different mordants; they include investigations on antibacterial and deodorizing action,¹ addition of color to leather using natural dye,² and the natural dyeing of textile fabrics.³⁻⁶ Currently, there are ongoing studies on dye extraction^{7,8} mainly concerned with food coloring. As there has lately been increasing consumer demand for environmentally friendly and nontoxic materials, more attention is being paid to eco-leather in leather production. Natural dyes of various colors are already being commercially produced in the textile industry. However, owing to uneven dyeing, degraded physical properties, and low economic efficiency, the natural dyeing of leather products is still at the craftwork stage.

To study their effect on the color of leather, polygenetic natural dyes such as gallnut and sappan wood were applied to wet white leather⁹ produced by a non-chrome tanning process. To improve the thermal resistance and softness of leather. Natural dyes are divided into two types: monochromatic natural dyes, for which the color does not change by mordant application, and polygenetic natural dyes, for which color does change by mordant application. We tried basic and applied studies to produce leather with a black color by using natural dyes; in particular, we focused on upper leather, which has the most demand among leather products. In this study, we tried to realize a black color for upper leather material through color variation according to mordant application; we used different types and content of the fatliquor agent and binder and different tanning and dyeing methods to establish a natural dyeing process for nontoxic eco-leather production that overcomes the limits of natural dyes.

EXPERIMENTAL

Materials

In this study, steer hide (1.2–1.4 mm limed pelt) imported from Texas, USA, was used. For a dyed crust, wet white leather without chrome was used as the raw material in this experiment. The representative natural dyes gallnut (*Aphis chinensis*. J. Bell, Gray color) and sappan wood (*Caesalpinia sappan*. L., Red color) used in this experiment were manufactured in water-soluble powder form by the alcohol extraction method shown in Fig. 1. For the mordant, reagent-grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (iron mordant, Junsei Chemical) and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (aluminum mordant, Samchun Chemical) were used, and other leather production chemicals were

applied to each process according to the general leather production process recipe.

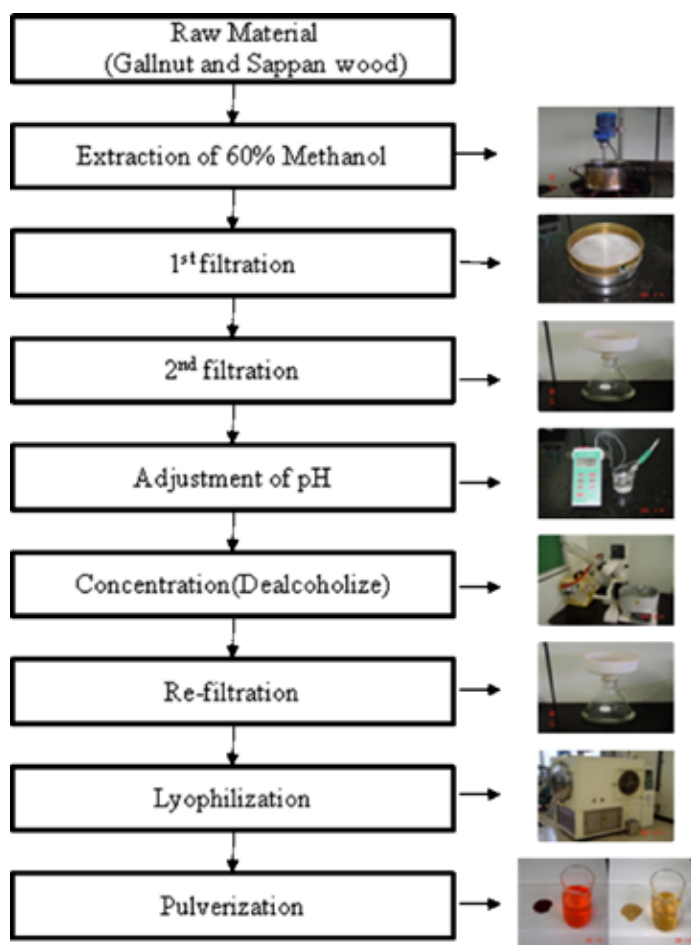


Figure 1. Manufacturing process for extraction method of natural dyes

Apparatus

In this experiment, a rotation drum made by DOSE, Germany (VGI 50531) with dimensions of 950 mm (D) × 500 mm (W) and rotation speed of 7–36 rpm was used together with other leather equipment for the general processing method.

Process of eco-leather manufacture

To establish an environmentally friendly leather production process, the tanning process presented in Table I was performed instead of the existing tanning process, which uses chrome, to produce wet white leather by using aluminum and aldehyde. Mordant was applied before, simultaneously with, and after the dyeing process, as listed in Table I, to produce leather with a black color.

Extraction of natural dyes

The gallnut and sappan wood used in this experiment are representative polygenetic natural dyes and were produced in the order described in Fig. 1 by the alcohol extraction method. Gallnut or sappan wood and 60% methanol were mixed in a 1:5 ratio. The mixture was slowly agitated for 24 h at room

TABLE I
Formulation of chrome-free tanning and Natural dyeing process

Process	%	Chemicals	min	pH	
Pretanning	2.0	Aldehyde tanning agent	60		
	3.0	Aluminum tanning agent			
	1.0	Synthetic fatliquor(Stable in acid or Salt)	60		
	3.0	Aluminum tanning agent	60		
	0.5	NaHCO ₃ (Temp. 35°C)	480	4.2	
	Drain and rinse → Hors up → Sammying → Shaving (1.2–1.4 mm)				
Tanning	150	Water (35°C)			
	6.0	Aluminum tanning agent	60		
	1.0	Sodium formate	20		
		Drain and rinse			
Neutralizing	150	Water (40°C)			
	2.0	Neutral tanning agent	30		
	6.0	Phenol synthetic tanning agent	100		
	1.0	Sodium bicarbonate	60	5.5	
		Drain and rinse			
Dyeing	No-mordant	100	Water (45°C)		
		5.0	Natural dyes(Gallnut or sappan wood)	60	
		Y	Anionic synthetic fatliquor agent	60	
		1.0	Formic acid	30	
			Drain and rinse		
	Pre-mordant	100	Water (45°C)		
		X	Mordant (Fe or Al)	30	
		5.0	Natural dyes(Gallnut or sappan wood)	60	
		Y	Anionic synthetic fatliquor agent	60	
		1.0	Formic acid	30	
		Drain and rinse			
	Simultaneous-mordant	100	Water (45°C)		
		X	Mordant (Fe or Al)		
		5.0	Natural dyes(Gallnut or sappan wood)	60	
		Y	Anionic synthetic fatliquor agent	60	
		1.0	Formic acid	30	
		Drain and rinse			
	After-mordant	100	Water (45°C)		
		5.0	Natural dyes(Gallnut or sappan wood)	60	
		X	Mordant (Fe or Al)	30	
Y		Anionic synthetic fatliquor agent	60		
1.0		Formic acid	30		
	Drain and rinse				

※ X : Mordant content of 0.5-2.0%

Y : Anionic fatliquor content of 1-12%

temperature and extracted at pH 5.3. After a sieve with #100 mesh separated the extract and raw material, the material was washed separately with water. Diatomite filtration was then performed with the filtrate from the second filtration to obtain a transparent filtrate. To increase the solubility of the filtrate, the pH was adjusted to 7.0, and vacuum concentration was performed to dealcoholize the filtrate. After refiltering of the filtrate by diatomite, it was powdered in a pulverizer, and the dried pigment was ground with a grinder to produce the natural dye.

Measure of K/S

A computer color matching system (Spectrophotometer CM-3500d, Minolta Co., Japan) was used to measure the K/S value of each dyed sample, which was calculated using the Kubelka-Munk equation.

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

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

K: Absorption coefficient

S: Scattering coefficient

R: Reflectance coefficient

Measure of color difference

The computer color matching system (Spectrophotometer CM-3500d, Minolta Co., Japan) was used to measure the color by the brightness L^* and color coordinate indices a^* and b^* according to the CIELAB color system (CIE system of color specification); measurements were repeated three times for random dyed areas to calculate the average value.

Fastness measuring of natural dyed leather

The light fastness was tested by using a sun lamp tester (Dongwon Scientific System) according to ASTM D 1148, and the rubbing fastness was analyzed by using a motor-type crock meter (GOTECH) according to ASTM D 1175.

RESULTS AND DISCUSSION

pH change by natural dye and mordant content

The pH change shown in Fig. 2 was the result of 0–10% iron mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) added to the gallnut and sappan wood when extracted in 100 ml of distilled water.

For gallnut, the pH gradually moved toward acidity as the content increased, and when more than 3% dye was used, pH reached equilibrium status with little further change.

For sappan wood, pH gradually moved toward alkalinity as the content increased; pH reached equilibrium when more than 3% dye was used, similar to gallnut, and there was no

rapid pH change in the drum. For the iron mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), when 0.1% mordant was used, the pH rapidly changed to acidic, up to pH 5.53. When 1% mordant was used, pH showed little change even when more mordant was used once the pH reached 3.17. The pH change according to concentration had no effect on the leather properties after the final dyeing was completed; the pH ranged from 3.2 to 3.8 in the final dyeing process.

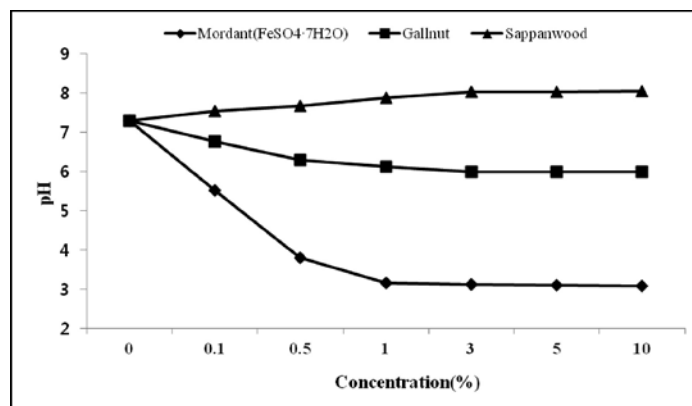


Figure 2. pH according to mordant and natural dye concentration

Effect of mordant content and dyeing process on color

The color formation when metal ion used as the mordant is combined with leather and dye can be explained by the crystal field theory (CFT).¹⁰ As shown in Fig. 3 (Gallnut dyes), an increase in the mordant content used moved the L^* value toward the (-) direction to a dark color and gradually changed it to black. Changes in the L^* value according to the mordant content when applied before, simultaneously with, and after the natural dye gallnut were observed. As shown in Fig. 3 (Sappan wood dyes), changes in the L^* value according to the mordant content when applied before, simultaneously with, and after the natural dye sappan wood were observed. In this case, L^* rapidly decreased when 1% mordant was applied, and the amount of the decrease was less when even more mordant was used.

As listed in Table II, when 1% mordant was used, a deep black color was produced when applied before, simultaneously with, and after the dye. For rubbing fastness, when less than 1% mordant was used, a grade of 2–3 was maintained with dry conditions. As more mordant was used, the dry condition of the rubbing fastness was slightly reduced as more dye was absorbed by the leather surface. Since almost no changes in the color and physical properties were observed according to the mordant method (applied before, simultaneously with, and after the dye), the simultaneous mordant application, which gives a smooth workability in leather production, was considered to be most beneficial. To produce the black color, using gallnut, which is gray without mordant, is considered to be better than using sappan wood, which is red without mordant. As shown in Fig. 4, when mordant was applied to

gallnut and sappan wood, the K/S value change was maintained at a constant level with mordant content of 1.0% and up, regardless of when the mordant was applied during the

dyeing process. Therefore, the appropriate content of iron mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) to obtain a deep black color was determined to be 1.0%.

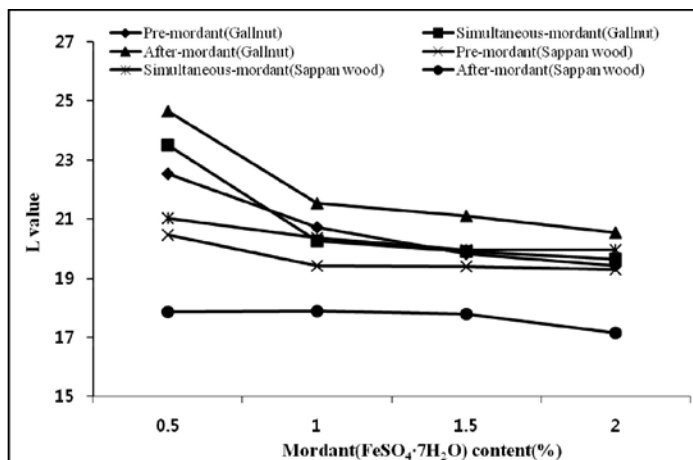


Figure 3. Change in L* (lightness) according to Fe-mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and mordant method (gallnut and sappan wood dyes)

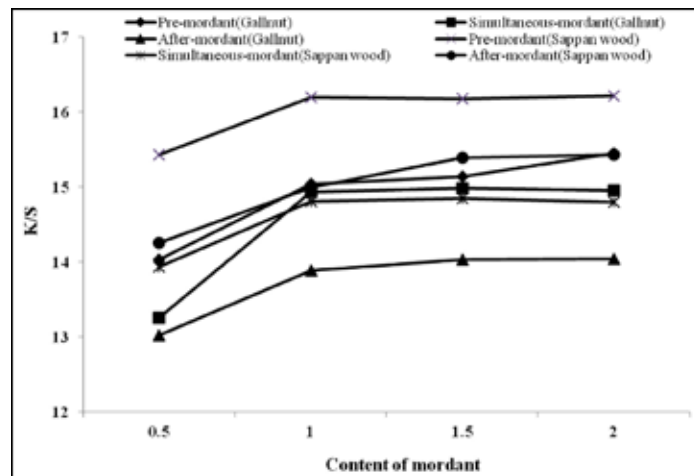


Figure 4. Change in K/S according to Fe-mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) content and dyeing process (gallnut and sappan wood dyes)

TABLE II
Properties according to method of mordant and content of mordant agent during dyeing process (Gallnut and Sappan wood dyes)

Mordant process and mordant content	Dyeing color		Rubbing fastness		UV test	
	Gallnut	Sappan wood	Gallnut	Sappan wood	Gallnut	Sappan wood
No-mordant			Dry: 4 Wet: 4-5	Dry: 4 Wet: 4-5	4	4
Pre-mordant: 0.5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$			Dry: 2-3 Wet: 3-4	Dry: 2-3 Wet: 3-4	4	4
Pre-mordant: 1.0% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$			Dry: 2-3 Wet: 3-4	Dry: 2-3 Wet: 3-4	4	4
Pre-mordant: 1.5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$			Dry: 1-2 Wet: 4	Dry: 1-2 Wet: 4	4	4
Pre-mordant: 2.0% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$			Dry: 1-2 Wet: 4	Dry: 1-2 Wet: 4	4	4
Simultaneous-mordant: 0.5% $\text{SO}_4 \cdot 7\text{H}_2\text{O}$			Dry: 2-3 Wet: 4-5	Dry: 2-3 Wet: 4-5	4	4
Simultaneous-mordant: 1.0% $\text{SO}_4 \cdot 7\text{H}_2\text{O}$			Dry: 2-3 Wet: 4-5	Dry: 2-3 Wet: 4-5	4	4
Simultaneous-mordant: 1.5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$			Dry: 1-2 Wet: 3-4	Dry: 1-2 Wet: 3-4	4	4
Simultaneous-mordant: 2.0% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$			Dry: 1-2 Wet: 3-4	Dry: 1-2 Wet: 3-4	4	4
After-mordant: 0.5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$			Dry: 2-3 Wet: 3	Dry: 2-3 Wet: 3	4	4
After-mordant: 1.0% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$			Dry: 2-3 Wet: 3	Dry: 2-3 Wet: 3	4	4
After-mordant: 1.5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$			Dry: 2 Wet: 3	Dry: 2 Wet: 3	4	4
After-mordant: 2.0% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$			Dry: 2 Wet: 4	Dry: 2 Wet: 4	4	4

Effect of mordant type on color

The gallnut and sappan wood were extracted by the alcohol extraction method and were used at 5% of the leather weight; after treating, 12 wt% fatliquor agent and 2 wt% iron mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and aluminum mordant ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) were used to apply mordant simultaneously with the dye. In the results, leather treated with aluminum mordant ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) showed almost the same color trends as leather treated without mordant, with no color change; non-chrome leather treated with iron mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) showed a color change to a deep black color with both of the natural dyes (gallnut and sappan wood). As listed in Table III, since the L^* , a^* , and b^* values of aluminum mordant ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) are similar to leather treated without mordant, iron mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) provides a superior performance compared to aluminum mordant ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) for producing the black leather generally used in leather manufacturing.

Effect of anionic fatliquor agent content on color

To study the effect on chemicals used in the leather dyeing process and realize a deep black color, experiments were performed while varying the mordant type and content. In the results, 1.0% iron mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) showed the best properties for realizing a black color. For gallnut and sappan wood, they each required similar mordant content to produce a deep black color; however, gallnut was found to be superior since it is gray in the non-mordant process, while sappan wood is red. When the effect of the anionic fatliquor agent content

on the black color was studied, the black color was found to become deeper as the fatliquor content increases. The color change according to the fatliquor content by the dyeing process in Table I (Simultaneous-mordant process, X (Iron mordant) : 1.0%, Y (Anionic synthetic fatliquor agent): 1,3,6,12%) is listed in Table IV. When the fatliquor content was increased gradually from 1% to 12%, a change in the leather surface color from purple to black was observed. This result confirms that the anionic fatliquor agent, mordant, and natural dye have complex relationships with the color during the leather manufacturing process. As shown in Fig. 2, owing to the property that pH decreases when mordant and gallnut are used, gallnut and mordant seem to show cationic properties. In contrast, when the anionic fatliquor agent was gradually increased, the leather in the drum gradually changed from mildly acidic to neutral; it combined with fatliquor on the leather surface to produce leather with a deep black color. As shown in Table IV, the K/S value also constantly increased as the fatliquor content increased; an ionic combination was found to form on the leather surface, which increased the absorption rate to change the color of the leather from purple to deep black.

CONCLUSION

In natural dyes such as gallnut and sappan wood, which realized black color with the addition of iron mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), the black color become darker as the iron

TABLE III
Color according to method and kind of mordant

Natural dyes	Kinds of mordant	L^*	a^*	b^*
Gallnut	No-mordant	63.35	5.45	20.79
	Simultaneous-mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	19.65	0.66	-1.88
	Simultaneous-mordant ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$)	51.37	6.09	18.9
Sappan wood	No-mordant	33.39	38.86	18.14
	Simultaneous-mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	19.96	0.82	-0.03
	Simultaneous-mordant ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$)	33.09	37.74	17.63

TABLE IV
Change in color according to content of fatliquor agent

Content of anionic fatliquor agent (%)	Color	L^*	a^*	b^*	K/S
1	Purple	26.91	25.23	-4.71	9.24
3	Purple	25.23	2.43	-4.86	10.59
6	Purple	22.75	2.19	-3.76	12.86
12	Black	21.18	1.85	-2.97	14.64

mordant content was increased, and the L^* value moves toward the (-) direction. When more than 1.0% of this iron mordant was used, the K/S value stayed constant but the rubbing fastness was generally reduced. Owing to this problem, 1.0% iron mordant content was determined to be appropriate for realizing a deep black color when using gallnut and sappan wood. Applying the mordant simultaneously with the dyeing process was considered the most appropriate when considering workability for leather production. When this iron mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and aluminum mordant ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) were applied to obtain a black color using gallnut and sappan wood, the natural dyes treated with iron mordant were better for achieving a deep black color. For the aluminum mordant little color difference was found compared to treatment without this mordant. Therefore, this aluminum mordant was determined to not form complex compounds with natural dyes; while the iron mordant produced a superior result in enhancing the black color. For color realization of the natural dyes, gallnut was found to be superior to sappan wood for uniform deep black color. In the experiment with different fatliquor contents, the pH changed to mildly acidic when iron mordant ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was used and the bath has cationic properties. When more anionic fatliquor agent was added, which is commonly in leathermaking, the reacting iron mordant and complex compound of the dye combine on the leather surface, resulting in an increase in the absorption rate on the surface. In this study, an excellent deep black color was realized when 12% fatliquor was used. Therefore, the most commonly used color in leather manufacturing tanneries was produced with a natural dye while enabling good productivity, even dyeing and improved fastness. The manufacture of a variety of eco-leathers can be expected by using this natural dyeing technique.

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