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A Study of the Fashion Accessory Product Development by Use of Korean Traditional Hanji (Part III)
-Dyeing of Hanji with Direct Dye-

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전통한지를 활용한 패션 악세서리 상품개발 (제3보)
-직접염료를 이용한 한지의 염색-

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Abstract

To utilize hanji for fashion accessory efficiently, dyeability of Hanji should be improved. Though Hanji mostly consists of cellulose such as cotton and ramie, also has various impurities, and has the different internal and surface structure from textile materials. Because of them, Hanji might show different dyeing behavior. As physical properties of Hanji are reduced in wet condition, dyeing process would damage the physical properties of Hanji Therefore, in this study, dyeing properties of Hanji using direct dye were examined in comparison with cotton and ramie. Effect of dyeing on tensile strength, and bleeding of direct dye by water from Hanji, colorfastness to light were also estimated. While Hanji showed the maximun dye exhaustion at 25°C, cotton and ramie showed those at 60°C. Tensile strength of Hanji reduced after Hanji was dyed. When Hanji was dyed at 25°C, the more bleeding occurred than at higher dyeing temperature. Hanji which had higher K/S values were bled more than those had lower K/S value. Colorfastness to light of Hanji dyed with direct dye was not inferior to those of cotton and ramie.

Key words: Hanji, Direct dye, Dyeability, Bleeding; 한지, 직접염료, 염색성, 블리딩

I. Introduction

In general, to produce the colored Hanji(Korean traditional paper), the colorants are added to the dispersion of dissociated pulps before sheet making process. But to utilize the traditional Hanji for fashion accessory, the color of Hanji should be diverse, and the demand can not be satisfied with the commercial colored Hanji.

Previous studies about the dyeing of Hanji focused on dyeing with natural dyestuffs. But, natural dyestuffs have the limited color range, and dyeing methods for

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natural dyestuffs are more complicated. Kim studied about dyeing of Hanji by using the loess(2000) and Gardenia(2001). Jeon also investigated to apply on Hanji with yellow type natural dyestuffs(2000) and onion peeling(2003). And the available color ranges are only yellow, orange and brown types.

Natural dyestuffs are applied beautifully on silk fiber, but do not show the good effect on cellulose fiber. Because Hanji is mostly composed with cellulose such as cotton, it might be difficult that various and beautiful colors on Hanji are obtained by natural dyestuffs. Therefore, it seems that there are needs to attempt to dye Hanji with synthetic dyes.

Dyeing of Hanji with synthetic dyes was investigated scarcely. Though major component of Hanji is cellulose, Hanji contains many impurities such as pectin, lignin, and hemicellulose(Jeon, 2003), and has different internal and surface structures from cellulose fiber for textiles. Hanji would show different dyeing behaviors with direct dye.

Physical properties of Hanji reduced drastically in wet condition and can be damaged after drying. It seems that it is necessary to observe the changes of physical properties before and after dyeing.

In part I(Kim et al., 2006), water repellent finish was applied on Hanji in order to improve the physical properties of Hanji in wet condition. And in part II(Shim & Kim, 2006), we reviewed the previous researches about Hanji and tried to form the basis for development of fashion products using Hanji.

In this study, we investigated the dyeing properties of Hanji with direct dye in comparison with cotton and ramie as a cellulose fiber. Effect of dyeing on the tensile strength, and bleeding of direct dye by water from Hanji, colorfastness to light were also analyzed.

II. Experimental

1. Materials

As the substrates, commercial Hanji produced from Chonju, commercial ramie fabric, and standard adjacent cotton fabric for color fastness were used without pretreatment. The characteristics of substrates were summarized in <Table 1>. C.I.Direct Red 81 (Direct Fast Red 5B 150%, from Taiheung Corp.) in the form of commercial was used without other purification, and the structure showed in <Fig. 1>. Sodium Chloride(guaranteed grade reagent) was also used.

Table 1. Characteristics of the substrates

	weight (g/m^2)	thickness (mm)	Fabric count (warp x filling/cm)
Hanji	53.7 ± 3	0.15	-
Ramie	109 ± 5	0.24	26/22
cotton	115 ± 5	0.23	35/32

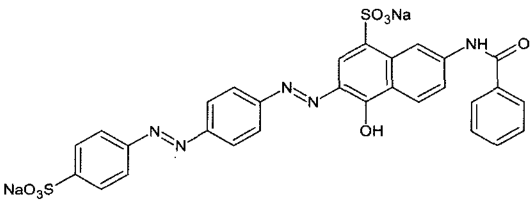


Fig. 1. Chemical constitution structure of C.I.Direct 81.

2. Methods

1) Dyeing

Dyeing was carried out in the dyebath containing dye and salt. Substrates were immersed in dyebath and agitated keeping temperature constantly. After dyeing, the excess amount of dye solution was removed through a laboratory wringer and dried without rinsing, because tensile strength of dyed Hanji is reduced by rinsing process largely. Dye concentration, salt concentration, dyeing temperature, and dyeing time were varied. Dyeability was determined by exhaustion from dyebath or K/S value of Hanji.

2) Tensile Strength

Before the tests, the samples were stored at standard condition(20±2°C, 65±2%) more than 24 hours according to KS K 0901. Tensile strength before and after dyeing was measured in machine and cross direction by constant rate of the elongation method by instron(model WL2100, Withlab.Co.Ltd) according to KS M 7015.

3) Bleeding

Dyed Hanji was immersed in distilled water with a liquor ratio of 500:1 and agitated at room temperature. After drying, K/S values were evaluated. Degree of bleeding was calculated by the followed equation, from the K/S value before and after bleeding.

$$\text{Bleeding}(\%) = \frac{(K/S)_D - (K/S)_B}{(K/S)_D - (K/S)_O}$$

$(K/S)_D$: K/S of dyed Hanji
$(K/S)_B$: K/S of dyed Hanji after bleeding
$(K/S)_O$: K/S of undyed Hanji

4) Colorfastness to light

Color fastness to light of cotton ramie, and Hanji dyed with C.I.Direct Red 81 in various conditions were measured according to KS K 0218 and compared one another.

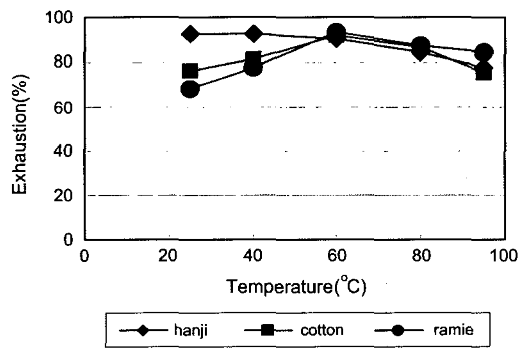
III. Results and Discussion

1. Dyeing Properties

<Fig. 2> showed Exhaustion of C.I.Direct Red 81 into Hanji, cotton and ramie dyed at various temperatures. Cotton and Ramie had the optimum dyeing temperature, but in case of Hanji, Exhaustion decreased with increasing dyeing temperature.

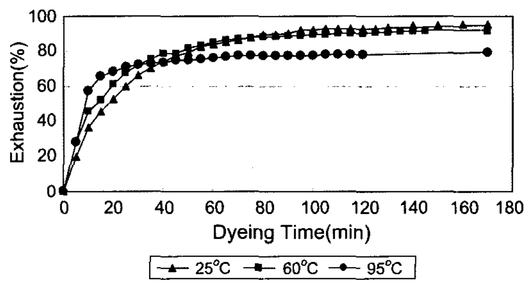
Dyeability of Direct dye depends on the dyeing temperature and from <Fig. 2>, the optimum dyeing temperature is 60°C. In case of Hanji, the highest exhaustion showed at 25°C and after that, exhaustion decreased with the increasing dyeing temperature. It seems that because Hanji pulp has more amorphous region and surface structure of Hanji is looser than cotton and ramie fiber, exhaustion at 25°C was larger than those of cotton and ramie. Cotton and ramie fiber have the compact internal structure and less amorphous regions. To penetrate into cotton and ramie, dye molecules needs larger energy than into Hanji. Therefore, dyeing of cotton and ramie are more difficult at 25°C. It was assumed that 60°C was suitable for cotton and ramie, because affinity between dye and cellulose fiber decreased at high temperature(Kim, 1992).

<Fig. 3> showed dyebath exhaustion for C.I.Direct Red 81 on Hanji according to dyeing time at various Temperature. Equilibrium exhaustions were 95.5% at 25°C, 91.7% at 60°C, and 74.8% at 95°C, respectively, and the lower the value was, the higher the dyeing temperature was. When dyeing temperature increased, while the affinity between fiber and dye decreased, kinetic energy of dye molecules increased(Kim, 1992). It made the rate of dyeing faster. <Table 2> showed the effect of dyeing temperature on rate of dyeing. Time of half dyeing of Hanji decreased when



dyeing time: 170min liquor ratio: 50:1
dye concentration: 0.25% owf. salt concentration: 10g/L

Fig. 2. Effect of dyeing temperature on Hanji, cotton and ramie.

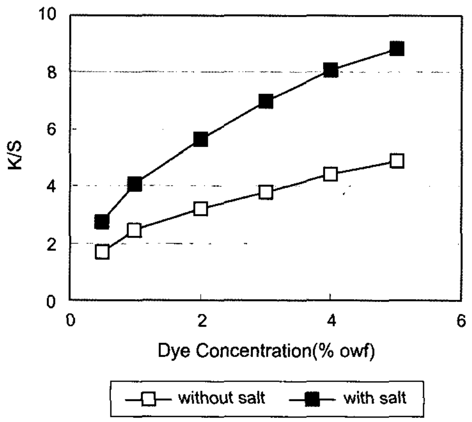


dye concentration: 0.25% owf., liquor ratio: 50:1 salt concentration: 10g/L

Fig. 3. Dyebath exhaustion profile for C.I.Direct Red 81 on Hanji at various temperature.

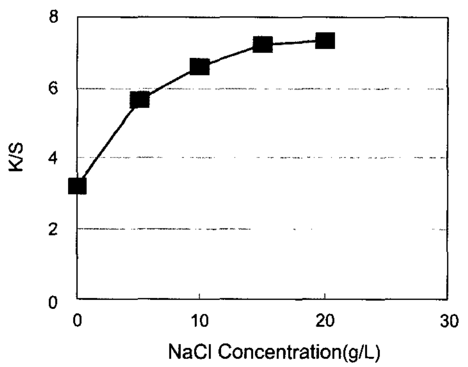
Table 2. Times of half-dyeing of Hanji at various dyeing temperature

	25°C	60°C	95°C
$t_{1/2}$(min)	15	10	7



dyeing temperature; 95°C dyeing time; 120min

Fig. 4. Effect of dye concentration on K/S value of Hanji dyed with C.I.Direct Red 81.



dyeing temperature; 95°C dyeing time; 120min

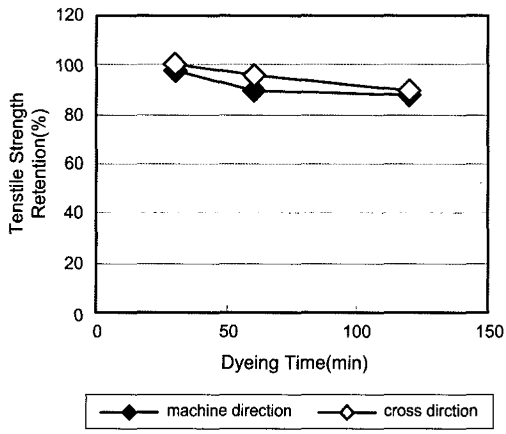
Fig. 5. Effect of NaCl concentration on K/S value of Hanji dyed with C.I.Direct Red 81.

dyeing temperature increased.

Effect of dye concentration on K/S value of Hanji dyed with C.I.Direct Red 81 was shown in <Fig. 4>.

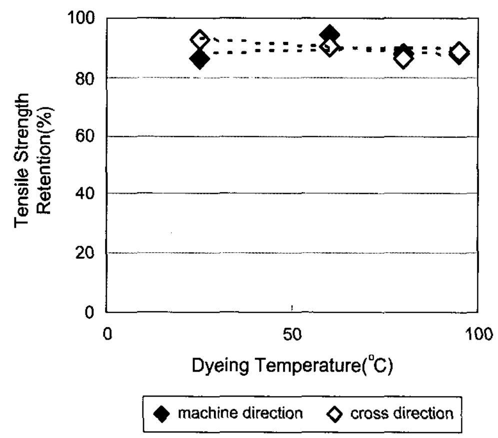
K/S value of Hanji increased with the increasing dye concentration. It is because adsorption of direct dye on cellulose is due to the existence of hydrogen bond and van der waals forces between dye and substrates(Kim, 1992).

Addition of salt to dyebath cause K/S value of Hanji higher. Cellulose fibers and direct dye are charged to negative in water, repulsive forces between fibers and dye hinder the adsorption of dye. In the presence of electrolyte in dyebath, attracted positive ions around cellulose fiber reduced the repulsion forces between dye and substrates(Vickerstaff, 1954).



dye concentration; 3% owf dyeing temperature; 95°C

Fig. 6. Effect of dyeing time on tensile strength retention of Hanji after dyeing.



dye concentration; 3% owf dyeing time; 120min

Fig. 7. Effect of dyeing temperature on tensile strength retention of Hanji after dyeing.

<Fig. 5> showed the effect of salt concentration on K/S value of Hanji dyed with C.I.Direct Red 81. K/S value of dyed Hanji increased and levelled off with the increasing salt concentration. It seemed because the positive ion was saturated around negative charged substrates.

2. Tensile strength

Tensile strengths of Hanji were measured before and after dyeing with various dyeing temperature and time because wetting paper by water made tensile strength decrease drastically.

Effect of dyeing time and dyeing temperature on tensile strength retention of Hanji after dyeing appeared in <Fig. 6 and 7>. Hanji was dyed at 3% owf dye concentration without salt, at 95°C for <Fig. 6>, and during 2 hours for <Fig. 7>.

Tensile strength of Hanji decreased with the increasing dyeing time. But, though tensile strength of Hanji decreased after dyeing, dye temperature did affect little.

Adhesion forces between Hanji pulps are destroyed and Hanji pulps are dissociated in the water. Agitation during dyeing process encourages the effects and made the arrangement of pulps scattered. It was considered that because the orientation of Hanji pulps remained scattered after dyeing and drying, tensile strength decreased.

Water absorbed by pulps penetrate into the internal structure of Hanji and cause the swelling. Because the configuration of pulps is distorted through the drying process, physical properties are damaged. The longer the pulps are immersed in water, the more the swelling occurs and the larger the damage of physical properties is. But moisture absorption is not endothermic reaction and to increase temperature does not accelerate the reaction. Therefore, the effect of dyeing temperature was slight.

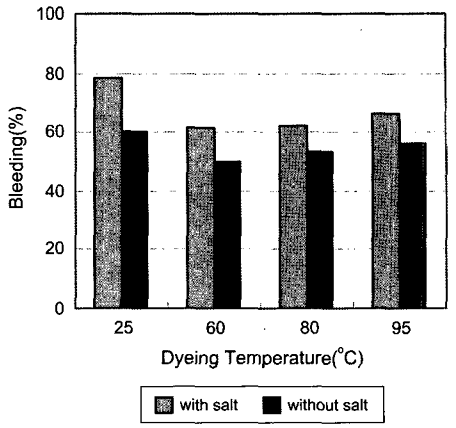
3. Bleeding

<Fig. 8> showed the effect of Temperature on Bleeding of Hanji dyed with C.I.Direct Red 81.

Bleeding of dyed Hanji at 25°C was largest and dropped at 60°C, changed scarcely after that. At lower temperature, because the formation of dye aggregates are too large to penetrate into Hanji deeply(Vickerstaff, 1954), more amount of dye molecules exist on surface of Hanji than at higher temperature than 60°C. It was assumed that dyes existed on surface were bled rather than the one inside of Hanji.

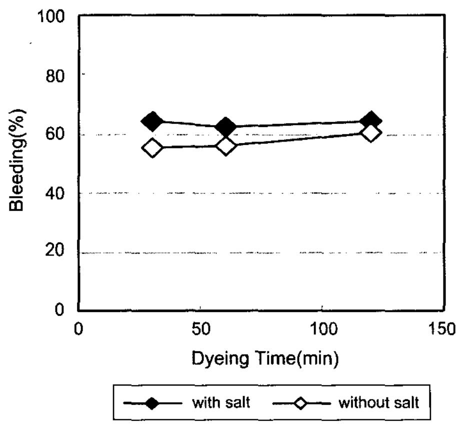
In case of Hanji dyed with salt, more bleeding occurred, because amount of dye molecules existed on Hanji was larger than without salt.

The effect of dyeing time on bleeding was shown in <Fig. 9>.



dye concentration; 3% owf dyeing time; 120min

Fig. 8. Effect of dyeing temperature on bleeding of Hanji dyed with C.I.Direct Red 81.



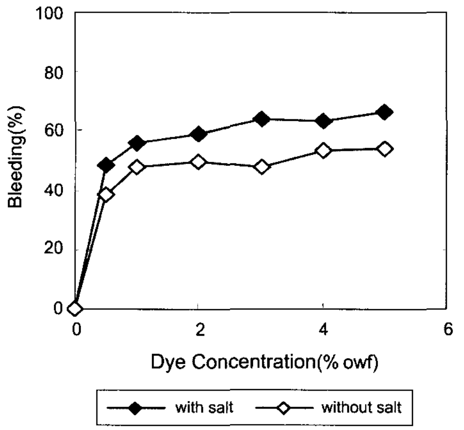
dye concentration; 3% owf dyeing temperature; 90°C

Fig. 9. Effect of dyeing time on bleeding of Hanji dyed with C.I.Direct Red 81.

Dyeing time did not affect on bleeding from Hanji. It seemed that 30mins are long enough for dye molecules to penetrate into Hanji deeply.

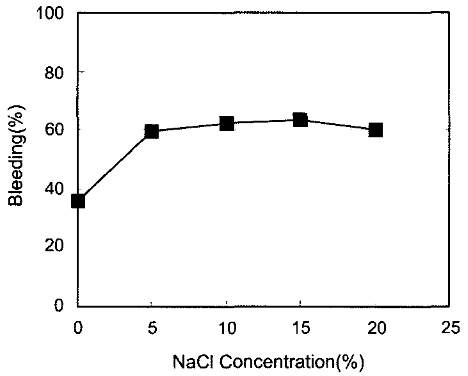
After Hanji were dyed with various dye and salt concentration at 95°C for 2 hours, bleedings were measured. The results was shown in <Fig. 10 and 11>.

Bleeding showed the tendency to increase with the increasing dye concentration. It was assumed because when dye concentration increased, amount of dye existed on and inside Hanji increased, and bleeding also increased. But there is not a large difference



dyeing temperature; 90°C salt concentraion; 10g/L
dyeing time; 120min

Fig. 10. Effect of dye concentration on bleeding of Hanji dyed with C.I.Direct Red 81.



dye concentraion; 3% owf dyeing time; 120min
dyeing temperature; 90°C

Fig. 11. Effect of NaCl concentration on bleeding from Hanji dyed with C.I.Direct Red 81.

between degrees of increase according dye concentration.

When salt was added in dyebath, bleeding from Hanji increased. The reason seemed that the addition of salt in dyebath, caused dye adsorption into Hanji larger and amount of dye exist in Hanji larger, too. When salt concentration contained in dyebath increased, bleeding was levelled off.

4. Colorfastness to light

After Hanji were dyed with direct dye in various condition, colorfastness to light of Hanji were compared with cotton and ramie in <Table 3>.

Table 3. Colorfastness to light

Substrates	grade	
cottonB	3-4	Dyeing Condition
RamieB	4	A : 25°C, 60min, with salt
Hanji A	3-4	B : 60°C, 60min, with salt
Hanji B	4	C : 80°C, 60min, with salt
Hanji C	4	D : 95°C, 60min, with salt
Hanji D	4	E : 25°C, 60min, without salt
Hanji E	3	

Colorfastness to light of dyed Hanji was not inferior to those of cotton and ramie dyed in the same condition. Colorfastness to light of direct dye depend on the type of dyes and substrates, but a little difference showed when the dyeing conditions were changed. As previously stated, it was assumed that though dye adsorption was high at 25°C, a part of dye molecules did not absorbed inside Hanji deeply and remained on surface of Hanji than at 60, 95°C. It seemed those molecules were detached easily by the external factors.

IV. Conclusions

From the above results, we can have the conclusions as followed,

1. In case of Hanji, Exhaustion of dyebath decreased with the increasing dyeing temperature while cotton and ramie had the highest exhaustion at 60°C.
2. The higher the dyeing temperature was, the faster the Hanji had the rate of dyeing and the lower equilibrium exhaustion.
3. Salt in dyebath accelerated dye adsorption into Hanji. Dye adsorption increased and levelled off with the increasing salt concentration.
4. Tensile strength of Hanji decreased after dyeing.
5. Dyed Hanji at 25°C showed highest bleeding. Bleeding increased with the dye concentration, but degree of increasing was not large in comparison with K/S value according to dye concentration.
6. Colorfastness to light of dyed Hanji was not inferior to those of cotton and ramie.

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요 약

의복재료로서 한지를 더 효율적으로 사용하기 위해, 직접염료를 이용하여 한지를 염색하였다. 한지의 주성분은 면, 마와 같은 셀룰로오스이지만, 많은 불순물을 포함하고 있고, 섬유제품과 내부구조와 표면구조가 다르므로, 다른 염색거동을 보일 수 있다. 또, 물을 흡수하면 한지의 물성은 크게 저하하므로, 염색과정에 의해 강도가 변화될 가능성이 있다. 따라서, 본 연구에서는 직접염료를 이용한 한지의 염색특성을 셀룰로오스 섬유인 면, 마와 비교하여 고찰하고, 염색에 따른 인장강도 변화를 살펴보았으며, 염료의 물에 의한 블리딩 및 일광 견뢰도를 평가하였다. 직접염료로 한지를 염색할 때, 한지는 25°C에서 최대흡진율을 보인 반면, 면과 저마는 60°C에서 최대흡진율을 보였으며, 염색 후, 한지의 인장강도는 감소하였다. 낮은 온도에서 염색하였을 때 블리딩이 컸고, 염색한 한지의 K/S 값이 크면 블리딩이 커지는 경향을 보였다. 직접염료로 염색한 한지의 일광견뢰도는 면, 마에 비해 떨어지지 않았다.