

# Application of the Deepening Agent in the Low-temperature Dyeing of Pigskin Leather

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**Abstract:** Theilgaard SN, Theilgaard WLD, and Serbisen were applied to the dyeing of wet blue pigskin leather, in expectation to improve the color yield percentage and the fixation rate, save dye, reduce dyeing wastewater and the temperature of dyeing, to improve the problem of low yield ratio of leather in dyeing by the traditional way of medium temperature, so enhance the quality of the leather surface and the effects of dyeing, giving the leather a good color fastness. The effect of dye uptake was discussed by the treatment method of deepening agent, the temperature, time, pH value, deepening agent concentration and the dyeing temperature. The results showed that the optimum amount of the three deepening agents were Theilgaard SN 10g/L, Theilgaard WLD 5g/L, and deepening agent Serbisen 7.5g/L. The optimal technical process of Theilgaard WLD was temperature 50°C, time 15min, pH value 4. Under the conditions of this process, the K/S value of pigskin grain leather was 7.831, meat side K/S value was 13.854, and the rubbing fastness and water fastness was improved.

**Key words:** Deepening agent; pigskin leather; low-temperature; dye uptake

## 1 Introduction

The deepening agent is a production which can make the reflectance spectroscopy of the dyestuff moving to the long-wave, and can raise the absorption intensity of the dyestuff to arise hyperchromic effect<sup>[1-3]</sup>. In addition, the majority of deepening agent also can fix the dyestuff during the dyeing. With the wide range application of the anionic vinyl polymer retanning (filled) agent and anionic aromatic synthetic tanning agents in the light leather, their “lost color” effect had caused widespread concern<sup>[4-6]</sup>. And the research of deepening agent was attended more and more to resolve the phenomena of “lost color”. The main dyestuff used in dyeing of leather were anionic dyes, which be deepened and fixed effect by the materials, such as multivalent metal salts, nitrogen compounds and derivatives of these materials. Some dyestuffs can complex with multivalent metal ions, so that it can not only make the hyperchromic effect, but also generate slightly soluble water-soluble complex in the surface of fiber to reduce the water-soluble of dyestuff and improve their fastness of wet and color fastness to sunlight. Traditionally, leather dyeing always has been at middle-temperature, but temperature can impact on handle and elasticity of leather, and dyeing in low-temperature can improve the yield ratio of leather. Thus, the low-temperature dyeing of leather not only adapt the trend of energy-saving, but also conducive to improving the quality of leather products, which is a dream of the engineer and worker of leather. The deepening agent was applied to treat leather. Through analyzing the effect of treatment methods, temperature, time, pH value, dosage of deepening agent, and dyeing temperature to the dye uptake, the application of deepening agent in the dyeing of leather was discussed.

## 2 Experimental

### 2.1 Materials

Wet blue of pigskin leather was purchased from Wuji of Shijiazhuang. Xili Fur Wine Red G-NB, Xili Fur Orange FGS, Xili Fur Red O-3Y and Xili Fur Green DM was purchased from Beijing PanBo Science and Technology Co., Ltd, Reactive Scarlet K2G and Reactive Red BES was provided by Taixing

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Jinji Dyestuff Co., Ltd, Colozol Brill Orange 3R was purchased from Taiwan Colortech Chemical Co., Ltd.

deepening agent: Theilgaard SN, Theilgaard WLD were purchased from WuXi Colotex Chemicals Co., Ltd, Serbisen was purchased from Shanghai Dawnsun Chemical Co., Ltd.

## **2.2 Equipments**

721-spectrophotometry (Shanghai Third Analytical Instruments Factory, China), Datacolor SF600 Color Measuring and Matching instrument (Data Color Co, American), FA2004 Electronic Balance (Shanghai Precision and Scientific Instrument Co., Ltd)

## **2.3 Methods of measurement**

### **2.3.1 Dye exhaustion**

The dye exhaustion percentage (%E) was calculated according to the following equation:

$$\%E = [1 - A_n / A_0] \times 100\%$$

Where  $A_0$  and  $A_n$  is, respectively, the absorbance of the dye bath before and after dyeing at  $\lambda_{\max}$  of the dye used. The absorbance was measured on a 721-spectrophotometer at  $\lambda_{\max}$  of the dye used<sup>[7]</sup>.

### **2.3.2 Color strength**

The reflectance of printed samples was measured with the Reflectance Spectrophotometry (Datacolor SF600 Color Measuring and Matching instrument, Data Color Co, American), under the illuminant D<sub>65</sub> using 10° standard observer. The color strength of printed samples was expressed with K/S value calculated by the Kubelka-Munk equation<sup>[8]</sup>.

### **2.3.3 Dyeing fastness**

The rubbing fastness and washing fastness were tested according to QB/T 1327-1991 and QB/T 1808-1993 respectively.

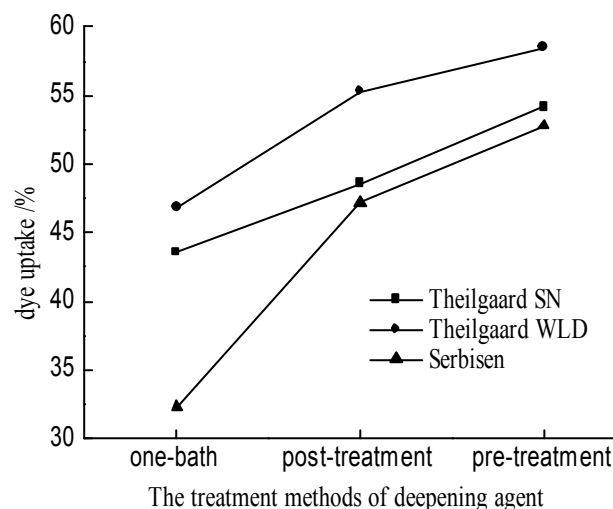
### **2.3.4 Technical process**

The treatment methods of deepening agent were pre-treatment, with bath and post treatment. The treatment process of deepening agent was deepening agent 0-X g/L, T 0-60 °C, t 0-25min, pH value of 2-10 and the bath ratio 1:10. Dyeing processing of acid dyes was dyestuff 2g/L, bath ratio 1:10, T 0-70 °C, dyeing pH value of 5 and the fixing pH value of 3-4. Dyeing processing of reactive dyes was dyestuff 2g/L, liquor ratio 1:10, T 0-70 °C, dyeing pH value of 5-5.5 and fixing pH value of 7-8.

## **3 Results and discussion**

### **3.1 Effect of deepening agent treatment methods on the dye uptake**

The wet blue pigskin leather was treated by deepening agent with pre-treatment, one-bath and post-processing respectively. Then the treated sample with Theilgaard SN, Theilgaard WLD and Serbisen was dyed with Xili Fur Red O-3Y, Xili Fur Orange FGS and Xili Fur Red O-3Y respectively at 60 °C. And the dye uptake was shown in Fig 1.

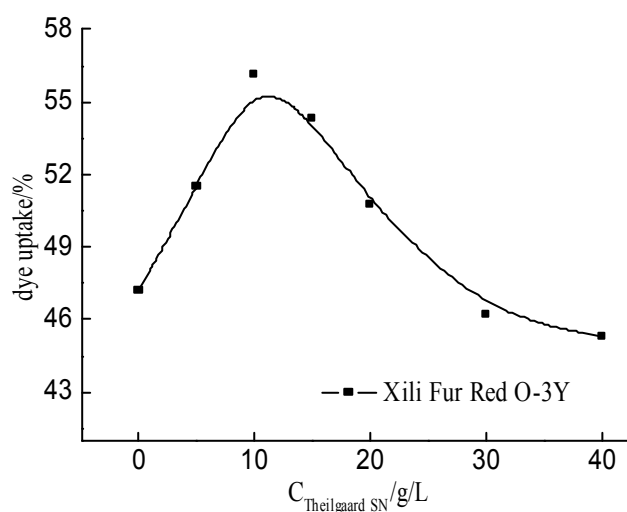


**Fig.1 Effect of deepening agent treatment methods on the dye uptake**

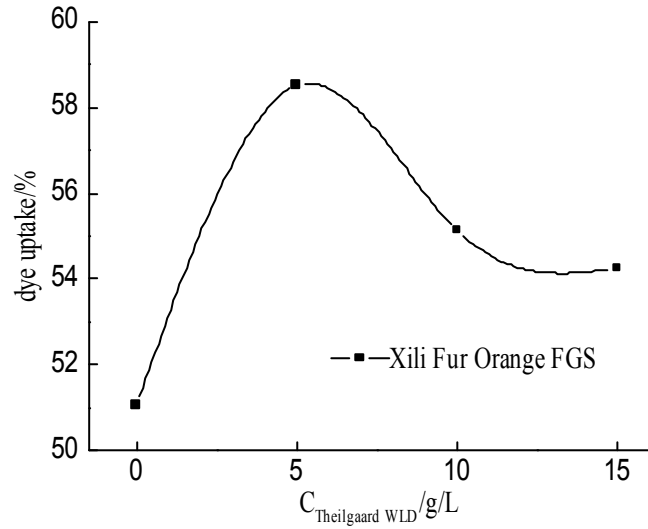
As shown in the curves in Fig 1, the dye uptake of pre-treatment was significantly higher than the dye uptake of post-treatment and one-bath. Deepening agent, with weak positive electricity, is a production which was compounded of cationic and non-ionic compounds. During the pre-treatment process, the deepening agent can combine with collagen fibers of leather, making more positive electricity in leather. During the dyeing, the acid dyestuff with negative electrical or reactive dyestuff can be more accessible to the surface of leather and penetrate into the internal leather, so as to enhance the dye uptake percentage to deepen the color. During the one-bath process, deepening agent combined with dyestuff to hinder the adsorption and penetration of dyestuff in the surface of leather, and lead to lower dye uptake percentage. During the after-treatment process, the dyestuff into the leather was striped, resulting in lower dye uptake percentage. At the same time, one-bath and after-treatment might also cause the leather surface shading and lower fastness.

### 3.2 Effect of deepening agent concentration on dye uptake percentage

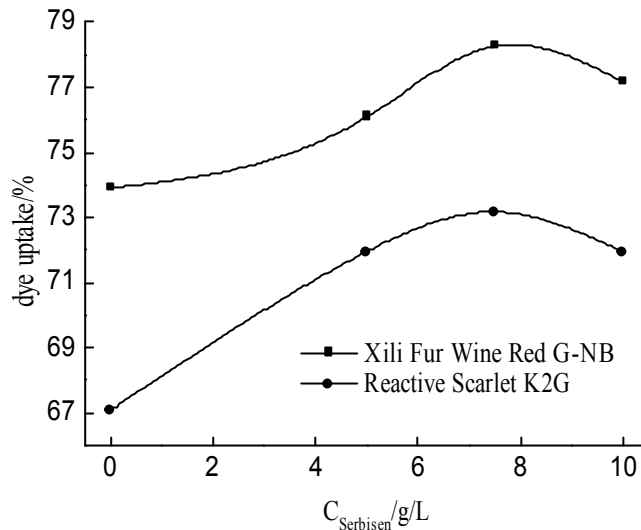
The wet blue pigskin in leather was pre-treated by deepening agent with the condition T 50°C, t 15min, pH value 4. Then the treated sample with Theilgaard SN, Theilgaard WLD and Serbisen was dyed with Xili Fur Red O-3Y, Xili Fur Orange FGS and Xili Fur Wine Red G-NB, Reactive Scarlet K2G respectively at 50°C. The effect of dosage of hyperchomic agent on dye uptake percentage was shown in Fig 2-4.



**Fig.2 Effect of Theilgaard SN concentration on dye uptake percentage**



**Fig.3 Effect of Theilgaard WLD concentration on dye uptake percentage**

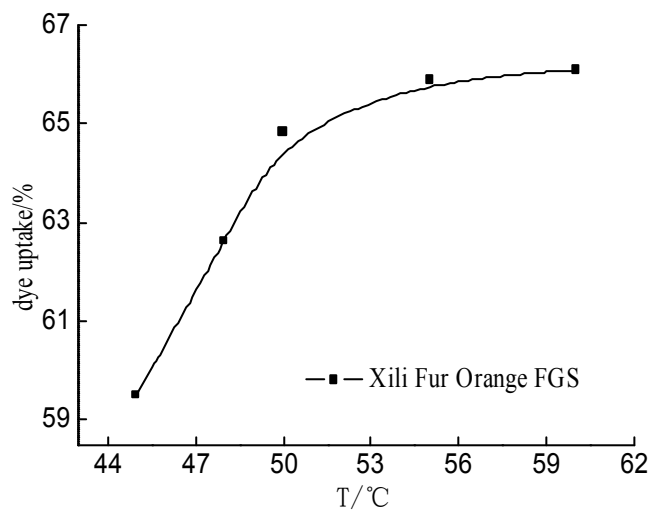


**Fig.4 Effect of Serbisen concentration on dye uptake percentage**

As shown in Fig 2-4, the dye uptake percentage was increased with the concentration of deepening agent increasing, and then reduced with the concentration of deepening agent increasing. When the concentration of deepening agent was increasing, more deepening agent combined with collagen fiber. So the dye uptake percentage was increasing<sup>[9]</sup>. But, when the concentration of deepening agent was increasing continually, deepening agent might combine with dyestuff and produce precipitate to decline the dye uptake percentage. Therefore, the concentration of Theilgaard SN, Theilgaard WLD, Serbisen was 10g/L, 5 g/L, 7.5 g/L respectively.

### ***3.3 Effect of pre-treatment temperature on dye uptake percentage***

The pre-treatment condition of leather was Theilgaard WLD 5 g/L, 15min, pH value 4, and then the treated leather was dyed with Xili Fur Orange FGS at 50 °C. The effect of pre-treatment temperature on dye uptake percentage was shown in Fig 5.

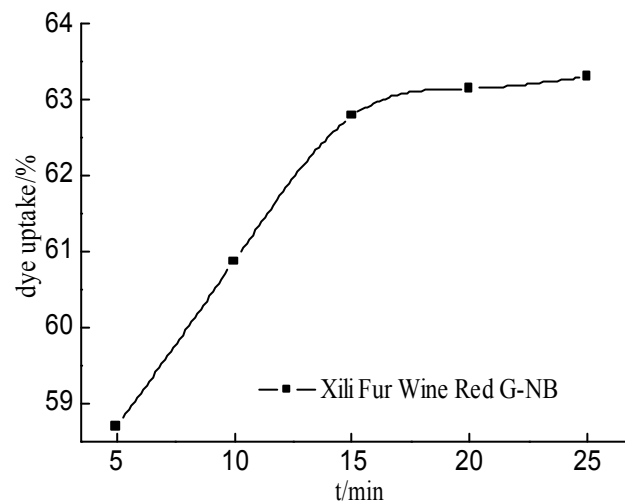


**Fig.5 Effect of pre-treatment temperature on dye uptake percentage**

As can be seen from Fig 5, the dye uptake percentage was increased with the pre-treatment temperature increasing. When the temperature was higher than 50°C, the trend growth of dye uptake got slowly. It suggested that molecular get activity with the increasing of temperature and deepening agent moved to the surface of leather and penetrated into the leather more easily. Therefore, the concentration of deepening agent in the leather was increasing, and the number of positive charge of leather was also increasing, which led to dyestuff easily to dyeing leather, and the dye uptake percentage increasing.

### **3.4 Effect of pre-treatment time on dye uptake percentage**

The pre-treatment condition of leather was Theilgaard WLD 5 g/L, 50°C, pH value 4, and then the treated leather was dyed with Xili Fur Wine Red G-NB at 50°C. The effect of pre-treatment time on dye uptake percentage was shown in Fig 6.

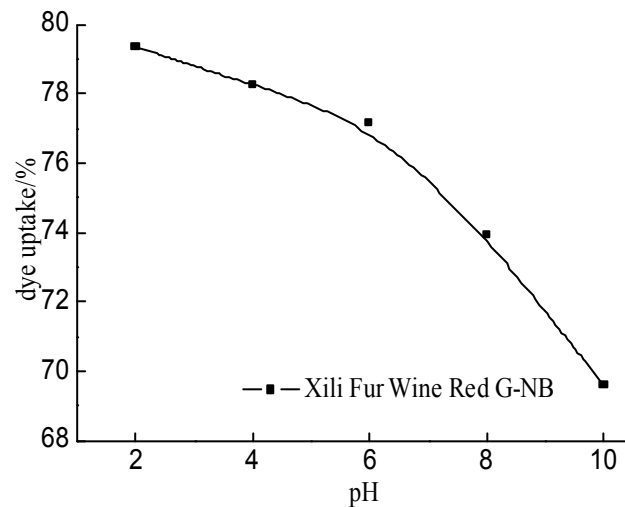


**Fig.6 Effect of pre-treatment time on dye uptake percentage**

As shown in Fig 6, the dye uptake percentage was increased with the pre-treatment time increasing. When the time is more than 15 min, the dye uptake percentage closed to a balance value. With the increase of time, more and more deepening agent combined with collagen fibers to increase the dye uptake percentage. After 15 min, the combination of deepening agent and collagen fibers reached to top, so the dye uptake percentage trended a balance value.

### **3.5 Effect of pre-treatment pH value on dye uptake percentage**

The pre-treatment condition of leather was Theilgaard WLD 5 g/L, 50°C, 15min, and then the treated leather was dyed with Xili Fur Wine Red G-NB at 50°C. The effect of pre-treatment time on dye uptake percentage was shown in Fig 7.

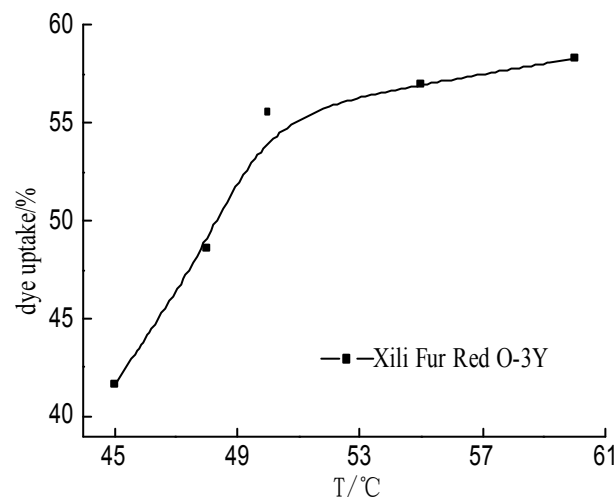


**Fig.7 Effect of pre-treatment pH value on dye uptake percentage**

When the pH value was 2-4, deepening agent might combine with collagen fibers of leather easily. It made leather own more positive charge to increase the dye uptake percentage, as shown in Fig 7. When the pH value was higher than 5, the positive charge of deepening agent was neutralized by OH<sup>-</sup>, so the dye uptake percentage significantly reduced. Low pH value might cause damage to leather, so the pre-treatment pH value was 4.

### **3.6 Effect of dyeing temperature on dye uptake percentage**

The pre-treatment condition of leather was Theilgaard WLD 5 g/L, 50°C, 15min, pH value 4, and then the treated leather was dyed with Xili Fur Red O-3Y. The effect of dyeing temperature on dye uptake percentage was shown in Fig 8.



**Fig.8 Effect of dyeing temperature on dye uptake percentage**

The dye uptake percentage was increased with the dyeing temperature increasing, as shown in Fig 8. Collagen fibers of leather were swelling with dyeing temperature increasing, so that the dyestuff molecules more easily penetrated into the leather. In addition, the solubility and activation energy of dyestuff molecules was enhanced with the dyeing temperature increasing. Therefore, the dye uptake percentage was increased with the dyeing temperature increasing,

### 3.7 Low-temperature dyeing process

Through above experiments, we can see that Theilgaard WLD is the best one. Leather was pre-treated by Theilgaard WLD and dyed with Reactive Red BES. The rubbing fastness and washing fastness was shown in Table 1 and the K/S value of leather was shown in Table 2.

**Tab.1 Effect of dyeing temperature on the fastness of leather**

T/°C	Rubbing				Washing	
	Flesh side		Grain side		Grain side	Flesh side
	Dry	Wet	Dry	Wet		
40	3-4	2-3	5	3-4	4	3-4
50	4	3	5	3-4	4	3-4
55	3-4	2-3	4-5	3	4-5	4-5
60	3-4	2-3	4-5	3-4	4-5	4
70	3	2	4-5	3	4-5	4-5

**Tab.2 Effect of deepening agent on the K/S values of leather**

Num	deepening agent concentration/ g·L <sup>-1</sup>	K/S
Grain side leather	5	7.8312
	0	7.3911
Flesh side leather	5	13.8537
	0	13.2222

Data in Tab I indicated that when the dyeing temperature was 50 °C, the dry and wet rubbing fastness of flesh and grain side were the highest, and the washing fastness of grain and flesh side were also satisfactory. Data in Tab. 2 indicated that the K/S value of flesh side was significantly higher than the K/S value of the grain side. It mainly due to the flesh side of leather is looser than the grain side, and the surface of flesh side was roughness. The K/S value of treated was higher than the K/S value of untreated, which indicated that the deepening agent deepen the leather in the dyeing.

### 4 Conclusions

The impact of factors, which effected the result of leather dyeing, were treatment methods, concentration of deepening agent, pre-treatment time, temperature and so on. The results showed that the optimum amount of the three deepening agents were Theilgaard SN 10g/L, Theilgaard WLD 5g/L, and deepening agent Serbisen 7.5g/L. The optimal technical process of Theilgaard WLD was temperature 50 °C, time 15min, pH value 4. Under the conditions of this process, the K/S value of pigskin in grain leather was 7.831, meat side K/S value was 13.854, and the rubbing fastness and water fastness was improved.

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