

# Synthesis and Application of Cationic Color-Fixing Agent for leathers with Excellent Organoleptic Feeling<sup>1#</sup>

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**Abstract:** In practice, the application of color-fixing agents usually impairs the organoleptic feeling of leather products. The present work investigated a method to get cationic color-fixing agent that does not decrease its excellent organoleptic feeling. An *N*-alkyl reaction intermediate was prepared by the elimination reaction of divinyl *tri*-ammonium and chlorinated paraffin. Quaternary ammonium color-fixing agent with soft chains was obtained by the polymerization of the intermediate with dicyandiamide. The ratio between diethylenetriamine and chlorinated paraffin, the dosage of sodium hydroxide and dicyandiamide that may affect the color fixing efficiency and the organoleptic feeling of leathers was discussed. The dye absorbance was studied with spectrophotometer. The organoleptic feeling and water vapor permeability of leathers was investigated. It was found that the quaternary ammonium color-fixing agent can obviously increase the dye absorbance to leather in dyeing process. The optimum ratio of divinyl *tri*-ammonium to chlorinated paraffin and dicyandiamide in weight was found to be 27:10:17. The optimized dosage of color-fixing agent is 2.0% in weight of wet blues.

**Key words:** leather; color-fixing agent; organoleptic feeling; quaternary ammonium

## 1 Introduction

Leathers are widely used in our daily life. In order to fit different uses, dyeing is needed. Most dyestuffs used in leather are acidic dyestuffs [1]. The reactions between leather and dyestuff are intermolecular forces and chemical combinations (hydrogen bond, ionic bond, covalent bond and coordination bond). Color-fixing agents are usually used to improve the color fastness as it is not strong enough. Quaternary ammoniums are often used as color-fixing agents to increase the rub resistance by decreasing the water-solubility of dyestuffs. Membranes may also be formed to cover dyes on leather surface [2]. It is particularly important in sued-leather due to the shortage of finishing. The rubbing resistance affects the style and usage of leathers. Cationic color-fixing agent can not only react with anionic dyestuff to increase the rub resistance of leather, but also neutralize the negative charge of dyed leather surface [3]. Besides, it has sterilizing function [4], dustproof, static resistance and has been widely used in textile, paper and polymer material.

Traditional quaternary ammonium color-fixing agent increases dye-fastness, but decreases the organoleptic feeling of leather product. In this article, the quaternary ammonium was synthesized and applied as color-fixing agent to leather. In order to improve the organoleptic feeling, chlorinated paraffin was introduced. The soft chains of chlorinated paraffin significantly improved the impaired hand feeling of leather. The more the chlorinated paraffin was used, the better the organoleptic feeling was.

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## 2 Experiment

### 2.1 Materials

Leather Black GB dye, commercial grade, was obtained from Tijin Shengda Ruitai Chemical Co., Ltd., China. The dicyandiamide, diethylenetriamine(Guangzhou Tayer Trading Co., Ltd.) and chlorinated paraffin (Jinan Chenxu Chemical Co., Ltd.) were chemically pure.

### 2.2 Preparation of color-fixing agent

The color-fixing agents were synthesized in two steps. First, 27 g diethylenetriamine was added to a 100 ml flask equipped with a stirrer, a thermometer and condensing apparatus. After being heated to 110°C, pH was adjusted to 10. Chlorinated paraffin was added in 0.5 h by a drip funnel. The temperature was kept for 2.5 h with stirring and the pH was kept by dropping sodium hydroxide solution. Then the temperature was increased to 150° C. 17 g dicyandiamide was added by three times with an interval of 15 mins. Stirring was kept for 3 h in total. With the changes in the amount of chlorinated paraffin, different samples were obtained. The samples with various amount of chlorinated paraffin were obtained.

### 2.3 Characterization of color-fixing agent<sup>[5]</sup>

The color-fixing agent was diluted to 50% water solution and two drops was dripped onto filter paper and one drop bromophenol blue was added. Three minutes later, the paper was washed thoroughly and investigated. If the blue spot was not washed off, it indicated that the preparation contained quaternary ammonium group. Cationic indicator bromophenol blue and quaternary ammonium could react into the complex compound with blue color which was not washed away<sup>[6]</sup>.

### 2.4 Measurement of dye uptake<sup>[7]</sup>

#### 2.4.1 The optimum wavelength.

Leather Black dye was diluted to series of concentrations of solutions. 0.05 g/L solutions was used to measure the absorbencies under different wavelengths through 722-spectrophotometer. The diagram of absorbencies versus wavelengths was got. The maximum absorption wavelength was determined according to the diagram.

#### 2.4.2 The ratio of dye absorption

At the maximum absorption wavelength, the absorbency of Leather Black dye was calculated using by the formula  $A = K \times b \times C$ . A is the absorbency, K (L/g·cm), is the factor, b (cm) is the inside width of solution trough, and C (g/L) is the concentration of the solution. The b is 1cm here. So the equation transformed into  $A = K' \times C$ .

Residual dye of dye liquor was calculated by the equation:  $W_1 = V \times K_1 \times \frac{A}{K'} \times 10^{-3}$   $W_1$  (g) is residual dye, V (mL) is the volume of spent dye liquor and diluted to  $K'$  multiples in volume, A is the absorbency at maximum absorption wavelength and  $K_1$  is affecting factor. The percent of dye absorbed was calculated

using the formulation: 
$$X\% = \left(1 - \frac{V \times K_1 \times A}{C_0 \times V_0 \times K}\right) \times 100\%$$

$C_0$  (g/L) is the concentration of dye-solution, and  $V_0$  (mL) is volume of dye-solution.

### 2.5 Color-fixing agent application in leather dyeing process

The percentage of materials given in Table1 was based on the weight of wet blues. The experimental specimens were applied in leather dying according to the processes in Table1. The spent liquor was collected for determining of dye absorption ratio.

**Tab.1 Processes of neutralizing, dying and fixing**

Processes	Temperature( °C)	wt%	Products	Duration(min)
Neutralizing	40	200	Water	60
		0.8	Sodium bicarbonate	
		0.6	Sodium acetate	
Washing	35	300	Water	2x20
Dying and fatliquoring	55	250	Water	90
		1.5	Dye	
		15	Fatliquor	
Dye fixing	55	0.8	Formic acid	2x15
		2	Dye -fixing preparation	20

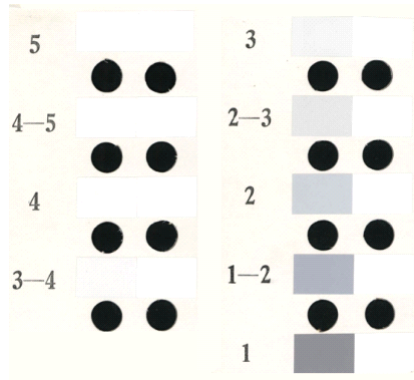
## 2.6 Color-fixing effects

### 2.6.1 Organoleptic determining

Organoleptic feelings of color-fixed leathers were determined by experienced technician and the fixing capacities were determined through the color intensity. The softness, smoothness and color intensity of color-fixed leather might change with different chloride paraffin dosages used in synthesis.

### 2.6.2 Rub resistance test

The rub resistance included dry and wet rub resistance. In the dry rub resistance test, a sample was clamped onto instrument with load and ran 25 times on lining cloth to-and-fro. Color intensity of the lining material compared with that of grey sample card. The wet rub resistance test was done by the same way as dry resistance. But the sample ran only 20 times and the relative humidity of the lining material was 70-75%. After being rubbed, wet lining cloth was dried at room temperature and poor light. The grey sample cards and their grades were as Fig.1.

**Fig.1 Grey sample cards**

### 2.6.3 Vapor permeability

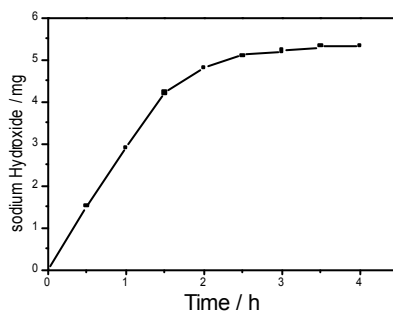
After 50 ml water was poured in a vapor permeable cup, the cup mouth was covered with leather for test, and the total weight was got, noted as  $W_1$  (g). Then they were kept in desiccators with concentrated sulfuric acid for 24 h and their weight turned  $W_2$ . The water vapor permeability (P) was calculated as follows:

$$P = \frac{W_1 - W_2}{A} \times 10 (mg / (10cm^2 \cdot 24h))$$

A was the leather area which water vapor passed through (here it was 7.065 cm<sup>2</sup>), P was the water vapor permeability of the sample.

### 3 Results and discussion

#### 3.1 Reaction time

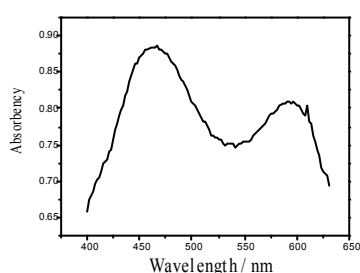


**Fig.2 Sodium hydroxide needed vs. reaction time**

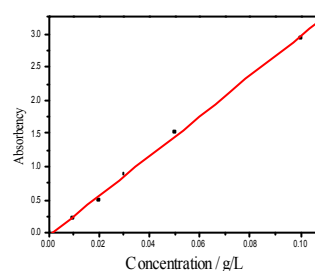
Sodium hydroxide was dissolved with distilled water and diluted to the concentration of 15 wt%. In the beginning of elimination reaction of diethylenetriamine and chlorinated paraffin, the pH was adjusted to 10 and kept by adding sodium hydroxide solution every 10 min interval. Fig.2 suggests that the amount of sodium hydroxide increased quickly at first and turned slower gradually. When the reaction time was more than 2.5 hours, the amount of sodium hydroxide did not increase any more. It may be because chlorine hydride generated in the elimination reaction neutralized sodium hydroxide. More and more sodium hydroxide was needed to keep the pH at 10. When it would not change or change very slowly, the reaction was close to balance and there was little sodium hydroxide to be neutralized. The experiment was finished. According to Fig.2, 2.5 h is needed to complete the reaction.

#### 3.2 Maximum absorption wavelength, relation between absorbencies and concentrations

The absorbencies of Leather Black dye solutions with wavelength were in Fig.3. The maximum wavelength was 460 nm (Fig.3).



**Fig.3 Light absorption spectra of Leather-Black**



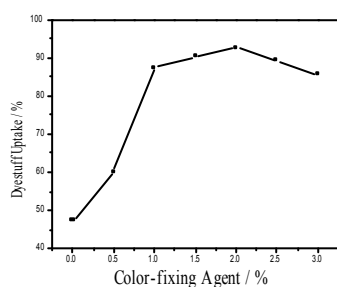
**Fig.4 absorbencies vs. concentration**

The absorbencies of different concentration dye liquors were obtained by spectrophotometer. The relationship of absorbencies and dye concentrations was shown in Fig.4, which was used as standard in next procedure.

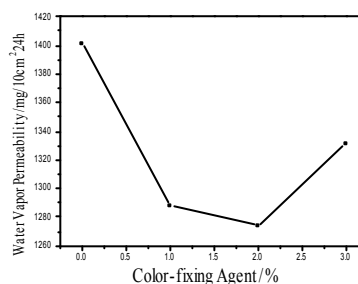
#### 3.3 Dye-uptake determining

Fig. 5 demonstrated the relationship of dye-uptake and color-fixing agent amount. With the same dye amount, the tendency of the dye absorption rate increased in the beginning, and decreased afterward. When the amount of the color-fixing agent was 2% based of the wet-blue in weight, the dye absorption rate reached its maximum value. The reason was possibly that the color-fixing agent included both

quaternary ammonium hydrophilic groups and carbon-chain lipophilic groups, and had ability to form micelle in water solution. When the color-fixing agent dosage was less, pigment deposition with dye anion and precipitated might be formed on the leather surface to improve the dye absorption rate. When excessive color-fixing agent was used, the precipitated pigment was wrapped in the micelle of color-fixing agent and dissolved in the used liquor. The dye concentration in the wastewater was increased and dye absorption rate decreased.



**Fig. 5 Dyestuff uptake vs. amount of dye-fixing agent**



**Fig. 6 Water vapor permeability vs. dye-fixing agent**

### ***3.4 Influence of color-fixing agent on water vapor permeability of leather***

Fig. 6 showed that the water vapor permeability of leathers decreased sharply with increasing the color-fixing agent at the color-fixing agent amount less than 1 wt % of wet blue. The reduction turns slower between 1% and 2%. When the dosage was more than 2.0 wt%, the water vapor permeability was increased with increasing the color-fixing agent used. The water vapor permeability reached the lowest value at the color-fixing agent dosage of 2.0 wt%. It is indicated that, as the color-fixing agent increased, more dyestuff precipitated on leathers to fill capillary of leathers and impaired the water vapor permeability. When an excessive amount of color-fixing agent (more than 2 wt%) was used, the micelles of color-fixing agent might dissolve dyestuff to release more capillaries. So the water vapor permeability of the leather is improved.

### ***3.5 Softness, rub resistance, and organoleptic Feeling***

It is essential to study the influence of color-fixing agent on the properties of leather. The softness, grain smoothness and color intensity were carried out for various experimental pig garment leather and the data were given in Tab. 2. In color-fixing agent synthesis, the dosage of chlorinated paraffin was calculated in volume (ml) of diethylenetriamine in weight (g).

Leathers were assessed for softness, grain smoothness by organoleptic feeling and color intensity. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property, where higher values indicated better property of leathers.

**Tab. 2 Influence of chloride paraffin on softness and visual assessment of leather**

parameter \ Dosage of paraffin (ml)	0.00	0.05	0.10	0.15	0.20	0.25	0.30
Softness	4.0	6.0	6.8	7.5	8.0	8.5	9.0
Smoothness	3.0	5.5	6.3	7.2	7.8	8.0	8.1
color intensity	8.5	8.4	8.4	8.2	8.0	6.5	5.5

Tab. 2 showed us that the softness of the color-fixed leather was increased with increasing the amount of chlorinated paraffin. It may be due to lubrication of carbon-chain of chlorinated paraffin, which made it easy for collagen fibers to move. At the same time, as a result of carbon-chain covered color deposit, the leather grain was smoother. Much more chloride paraffin resulted in greasy leather. The color-fixing agent was a cationic surfactant. If the chloride paraffin was over-dose, the surfactant would emulsify the excess chloride paraffin to decrease the dyestuff precipitation and to decrease the color intensity. The amount of chloride paraffin of 20wt% of diethylenetriamine was chosen in the synthesis of color-fixing agent.

### **3.6 Rub resistance**

2 wt% of color-fixing agent (based on wet blue) was applied with the results indicated in Tab. 3. The use of color-fixing agent significantly increased the dyestuff absorption and improved the rub resistance of leather by one grade.

**Tab.3 Performance of color-fixing agent**

Items	Dyestuff concentration of waste liquor (g/L)	Dyestuff concentration of original dyeing liquor (g/L)	Dyestuff uptake rate %	Rub resistance	
				Dry	Wet
With color-fixing agent	0.612	8.18	92.5	4-5	4
Without color- fixing agent	5.246	10.0	47.5	3-4	3

## **4 Conclusions**

The elimination reaction of chlorinated paraffin and diethylenetriamine should be in alkaline conditions to remove small molecules hydrochloric acid generated in the reaction. The reaction time should be 2.5 hours. The dyestuff uptake was increased first and then decreased with increasing the color-fixing agent amount. The dyestuff absorption rate reached the highest level when the amount of color-fixing agent was 2wt% of wet blues. The color-fixing agent will decrease the water vapor permeability of leathers. At the maximum dyestuff absorption, the rub resistance of leather was improved by one grade, while the water vapor permeability was the worst. The introduction of chlorinated paraffin improved the softness and grain smoothness of leathers.

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