

**COMPOSITION, PROPERTY AND STRUCTURE OF CHROME COMPLEXES
IN NEUTRALIZING EFFLUENT**

YANPING GAO^{1,2}, JUN HU¹, JIN WEI ZHANG¹, WUYONG CHEN^{1,2*}

¹*Sichuan University, Key Laboratory of Leather Chemistry and Engineering of the Ministry of Education, 610065, P. R. China, wuyong.chen@163.com*

²*Sichuan University, National Engineering Laboratory for Clean Technology of Leather Manufacture, Chengdu 610065, P. R. China*

In order to interpret the reason of chromium complexes release from the chrome tanned leather during the neutralizing process, the hide powder was tanned by chromium sulfate liquor with 33% basicity (BCS), and then the tanned collagen was treated by general neutralizing process to obtain neutralizing effluent. Ion exchange chromatography (IEC) and gel filtration chromatography (GFC) were used to separate neutralizing effluent; Ultraviolet-visible absorption spectroscopy (UV-Vis) and Fourier Transform Infrared Spectroscopy (FT-IR) were combined to analyze the structure of chrome complexes in the neutralizing effluent. The results indicated that the neutralizing effluent mainly consisted of anionic-zero valent, monovalent and bivalent chrome complexes; the molecular weight of chrome complexes in neutralizing effluent was far less than BCS; releasing chromium complexes were mainly combined with ligands through single point coordination and Cr³⁺ was mainly combined with SO₄²⁻ and HCOO⁻ by single point coordinate bond. Combined all of the results above, it could deduce that the main constituents of anionic-zero valent and low electro-positive, smaller molecular, mainly combined with single point coordination are the properties and structural characteristics of the chromium complexes released from chrome tanned leather in neutralizing process.

Keywords: hide powder; neutralizing effluent; chrome complex

INTRODUCTION

Chrome-tanned leather has excellent performance, so chrome tanning is still dominant in the leather industry. But the chromium pollution problem is increasingly brought to the attention, chrome tanning method is facing severe challenges, therefore minimize chromium pollution has significant environmental benefits. After chrome tanning, the chrome release in post-tanning process in the post-tanning process like rewetting, neutralizing, retanning, dyeing and fatliquoring effluents, leading Cr₂O₃ content of post-tanning effluents reached 10~450mg/L that is significantly more than the limit standard (Zhou *et al.*, 2012) are still needed to face. In order to solve chrome pollution problems, chrome release in post-tanning process must be highly valued and adopt corresponding measures.

Organic retanning agents, dyestuffs and fatliquoring agents are mainly anionic materials used in subsequent process of wet blue. The neutralizing process is usually used to raise the pH and adjust the charge to promote penetration of anionic materials. Therefore, there is a certain amount of chrome released in neutralizing process. This article studied the composition, structure and properties of chrome complexes released from the chrome tanned skin collagen in neutralizing effluent.

The hide powder was tanned by chromium sulfate liquor with 33% basicity (BCS), and then the tanned collagen was treated by general neutralizing process to obtain neutralizing effluent. Ion exchange chromatography (IEC) and gel filtration chromatography (GFC) were used to separate neutralizing effluent; Ultraviolet-visible absorption spectroscopy (UV-Vis) and Fourier Transform Infrared Spectroscopy (FT-IR) were used to analyze the structure of chrome complexes.

EXPERIMENTAL

Preparation of Neutralizing Effluent

Hide powder was tanned by 0.2mol/L BCS for 2h at constant temperature bath oscillator (25°C, 200r/min). 1.2% NaHCO₃ was added four times to basify, the final pH of tanning liquor was 3.8. The tanned hide powder was dried at 40°C after tanning.

0.2% formic acid and 150% water were added in dried hide powder, and then put in constant temperature bath oscillator for 2h (38°C, 200r/min). Then, the hide powder was washed by running water for 10min. 2% sodium formate and 150% water were added and put in constant temperature bath oscillator for 90min (35°C, 200r/min). After filtered with nylon filter cloth, neutralizing effluent was prepared.

Ion Exchange Chromatography Separation

5ml neutralizing effluent was filtered by 450nm microporous membranes, and then added into SP Sephadex C-25 column (inner diameter 2.0cm, packed 20.0cm). Elution conditions were as following: eluent velocity for 2.5 mL/min, followed by using H₂O, NaClO₄ (0.5, 1.0, 2.0 mol/L), HCl (2.0, 3.0 mol/L) to elute. UV-Vis spectrophotometer (Shanghai Jinghua Technology Corporation) was used to detect absorbance at 420nm and compare with BCS separated compositions (Li *et al.*, 1992).

Gel Filtration Chromatography Separation

5ml neutralizing effluent was filtered by 450nm microporous membranes, and then added into SP Sephadex G-25 column (inner diameter 2.0cm, packed 80.0cm). Elution conditions were as following: eluent velocity for 2.5 mL/min and H₂O was used to elute. UV-Vis spectrophotometer was used to detect absorbance at 420nm and compare with BCS separated compositions (Davis and Scroggie, 1973).

UV-Vis Analysis

After IEC separation, collected components were freeze-dried and then dissolved by distilled water. UV-Vis spectrophotometer was used to scan obtained liquor at 300-800 nm. R was calculated by molar absorption coefficient of chrome in 420nm and 580 nm.

FT-IR Analysis

FT-IR spectrum in the 4000–400 cm⁻¹ was recorded with a Nicolet 10 FT-IR spectrophotometer (American Thermo Scientific Corporation). Samples were prepared by grinding about 1 mg freeze-dried components with 100 mg KBr, and the mixture was pressed into very thin disks and scanned for 32 times.

RESULTS AND DISCUSSIONS

Charge Characteristics of Chrome Complexes in Neutralizing Effluent

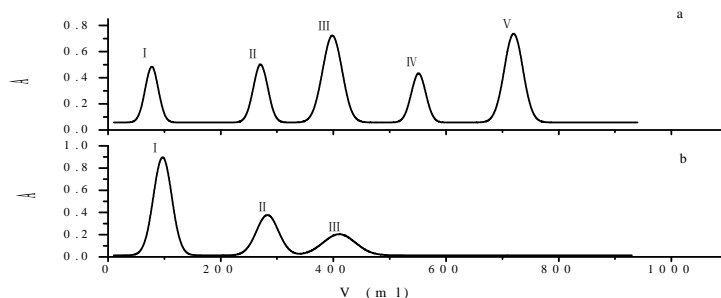


Figure 1. Ion exchange chromatography of BCS (a) and neutralizing effluent (b)

IEC of BCS and neutralizing effluent are shown in Fig.1. As can be seen from Fig.1, at the same elution conditions, BCS is separated into five components (anionic-zero valent, monovalent, bivalent, trivalent and tetravalent chrome complexes), and neutralizing effluent is divided into three components (anionic-zero valent, monovalent and bivalent chrome complexes). Based on IEC peak area, the composition of chrome complexes in BCS and neutralizing effluent can be calculated and listed in Table 1.

Molecular Weight of Chrome Complexes in Neutralizing Effluent

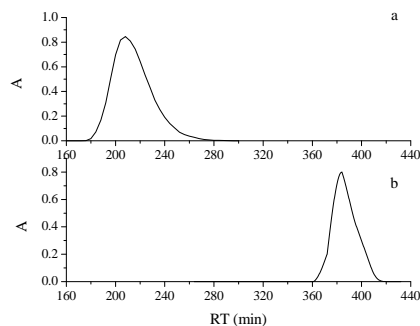


Figure 2. Gel filtration chromatography of BCS (a) and neutralizing effluent (b)

GFC is often used to analyze the molecular weight distribution to study the structure of coordination compounds. The retention time of the large molecular weight complexes is shorter while the small molecular weight is longer during the GFC separation process. GFC results of BCS and neutralizing effluent are shown in Fig.2. As shown in Fig.2, during 172min and 280min, chrome complexes in BCS are washed off completely (Fig.2 a); between 368min and 408min, chrome complexes in neutralizing effluent are washed off completely (Fig.2 b). Accordingly, the molecular weight of chrome complexes in neutralizing effluent is far less than BCS. The small molecular weight

Composition, Property and Structure of Chrome Complexes in Neutralizing Effluent

chrome complexes cannot combine with skin collagen by stable combination, therefore small chrome complexes are easier to release.

UV-Vis Results

Table 2. R values of each constituent in neutralizing effluent

R values	I	II	III	IV	V
BCS	1.08	1.10	1.09	1.15	1.36
neutralizing effluent	0.95	0.80	0.83	-	-

The combination way between ligands and Cr^{3+} can be determined by R values, R values of each constituent in neutralizing effluent are listed in Table 2. The results in Table 2 showed that, the R value of chrome complex components I, II, III, IV and V in BCS are 1.08, 1.10, 1.09, 1.15 and 1.36 respectively, however, the R value of chrome complex components I, II and III in neutralizing effluent are 0.95, 0.80 and 0.83. The R values of I, II and III are all less than 1.19 indicating that Cr^{3+} mainly combined with ligands through single point coordination and there are less bridge linkages between Cr^{3+} and ligands.

FT-IR Results of Chrome Complex in Neutralizing Effluent

Characteristic absorption peak and coordination mode of I to III components of chrome complex in neutralizing effluent are shown in Table 3. It is seen that 4 absorption peaks are found in $900\text{-}1300\text{cm}^{-1}$ for chromium complex in component I, which indicate that interconnection mode for SO_4^{2-} and central ion Cr^{3+} is two-point coordination. In the same way, 2 and 3 absorption peaks in component II and III respectively demonstrate that SO_4^{2-} is free state and coordinate with Cr^{3+} by single point coordination.

One asymmetric and one symmetric stretching vibration absorption peak are respectively found in $1550\text{-}1680\text{cm}^{-1}$ and $1370\text{-}1465\text{cm}^{-1}$ of chrome complex in component I, II and III, moreover, the interval of these two absorption peaks are small. Therefore single point coordination is speculated between Cr^{3+} and HCOO^- (Chen and Li, 2011).

Table 3. FT-IR absorption peak and coordination mode of chromium complex in neutralizing effluent

Component	Scope (cm ⁻¹)	Peak (cm ⁻¹)	Num.	Ligand	Coordination mode
I	900-1300	995,1048,1148,1114	4	SO ₄ ²⁻	two-point
	1680-1550	1633	2	HCOO ⁻	single point
	1465-1370	1405			
	3400	3439	1	OH	----
II	900-1300	941,1088	2	SO ₄ ²⁻	free
	1680-1550	1630	1	HCOO ⁻	single point
	1465-1370	1430			
	3400	3423	1	OH	----
III	900-1300	941,1087,1141	3	SO ₄ ²⁻	single point
	1680-1550	1631	1	HCOO ⁻	single point
	1465-1370	1422			
	3400	3441	1	OH	----

Chromium complex Structure in neutralizing effluent is speculated by valence state of IEC (Tab.1) and R values (Tab.2). Its possible structures are shown in Fig.3.

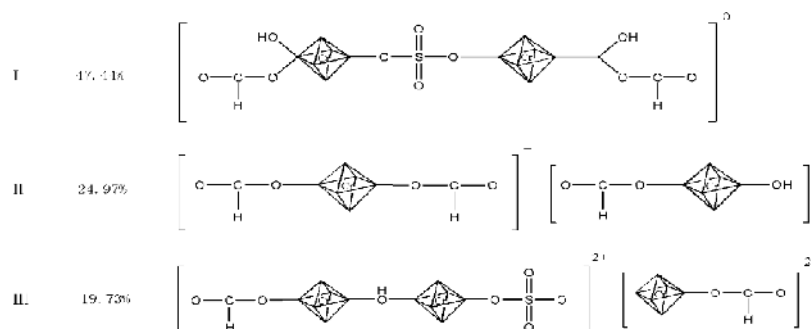


Figure 3. Possible structures of chrome complexes in neutralizing effluent

CONCLUSIONS

The results of IEC and GFC indicate that the neutralizing effluent mainly consisted of anionic-zero valent and low-positive electricity (+1 and +2) chromium complexes; the molecular weight of chrome complexes in neutralizing effluent is far less than the chromium sulfate liquor with 33% basicity. The results of UV-Vis and FT-IR show that releasing chromium complexes is mainly combined with SO₄²⁻ and HCOO⁻ by single point coordinate bond. Combined all of the results above, the main characteristics of the chromium complexes released from neutralizing process of chrome tanned leather are anionic-zero valent and low electro-positive component, smaller molecular, mainly combined with ligands through single point coordination.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (No. 21576171).

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