CHARACTERISTICS OF CHROME COMPLEXES IN NEUTRALIZING EFFLUENT

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ABSTRACT. In order to explain the reason of chromium released from chrome tanned leather to effluent in neutralizing, the chromium complex composition, structure and property in neutralizing effluent were characterized. Hide powder was tanned by chromium sulfate liquor with 33% basicity (BCS), and then the tanned hide powder was treated by conventional neutralizing to prepare neutralizing effluent (NE). Ion exchange chromatography (IEC) and gel filtration chromatography (GFC) were used to separate NE to study its chromium composition firstly; then ultraviolet-visible absorption spectroscopy (UV) and Fourier Transform Infrared Spectroscopy (FT-IR) were combined to analyze the structure of chrome complexes in NE; at last, chromium from NE was used for tanning and the thermal properties of the tanned hide powder were measured by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The results indicated that NE mainly consisted of anionic-zero valent, monovalent and bivalent chrome complexes and the molecular volume was small also. The Cr(III) complexes in NE were mainly combined with ligands like SO_4^{2-} and $HCOO^-$ through single point coordination. Compared with the control, higher weightlessness rate but lower maximum thermal decomposition temperature (T_{max}), thermal denaturation temperature (T_d) and enthalpy (ΔH) of NE chrome tanned hide powder demonstrated poor tanning ability of the chromium. In short, the characteristics of chromium complexes released from neutralizing process were: anionic-zero valent and low positive charge composition, small molecular volume, mainly combined with ligands through single point coordination and poor tanning ability. The study would provide foundation and reference for developing chromium solidifying methods in neutralizing.
KEY WORDS: neutralizing effluent, chromium complex, composition, structure, tanning property

CARACTERISTICILE COMPLECȘILOR DE CROM DIN EFLUENTUL DE LA NEUTRALIZARE

REZUMAT. Pentru a explica eliberarea cromului din pielea tăbăcită în crom în efluentul de la neutralizare, au fost caracterizate compoziția, structura și proprietățile complecșilor de crom din efluentul de la neutralizare. S-a tăbăcit pulbere de piele cu soluție de sulfat de crom cu bazicitate de 33% (BCS), apoi pulberea de piele tăbăcită a fost supusă unui proces convențional de neutralizare pentru a prepara efluentul rezultat în urma acestei operațiuni (NE). Mai întâi s-au utilizat cromatografia prin schimb ionic (IEC) și cromatografia prin filtrare cu gel (GFC) pentru a separa NE în vederea studierii compoziției sale în crom, apoi s-au combinat spectroscopia de absorbție în ultraviolet-vizibil (UV) și spectroscopia în infraroșu cu transformată Fourier (FT-IR) pentru a analiza structura complecșilor de crom din NE; în cele din urmă, cromul din NE a fost utilizat pentru tăbăcire, iar proprietățile termice ale pulberii de piele tăbăcită au fost măsurate prin analiza termogravimetrică (TG) și calorimetrie de scanare diferențială (DSC). Rezultatele au indicat că NE a conținut în principal complecși de crom anionici cu valență zero, monovalenți și bivalenți, iar volumul molecular a fost mic. Complecșii de Cr(III) din NE s-au combinat preponderent cu liganzi, cum ar fi SO_4^{2-} și $HCOO^-$ printr-un singur punct de coordinare. Comparativ cu martorul, rata de scădere în greutate mai mare și temperatura maximă de descompunere termică (T_{max}), temperatura de denaturare termică (T_d) și entalpia (ΔH) mai scăzute ale pulberii de piele tăbăcită cu crom din NE au demonstrat capacitatea slabă de tăbăcire a cromului. Pe scurt, caracteristicile complecșilor de crom eliberați în urma procesului de neutralizare au fost: complecși anionici cu valență zero și cu sarcină pozitivă scăzută, volum molecular mic, combinați preponderent cu liganzi printr-un singur punct de coordinare și cu o capacitate slabă de tăbăcire. Studiul de față constituie un punct de plecare și o referință pentru dezvoltarea unor metode de solidificare a cromului în procesul de neutralizare.
CUVINTE CHEIE: efluenți de la neutralizare, complex de crom, compoziție, structură, capacitate de tăbăcire

LES CARACTÉRISTIQUES DES COMPLEXES DE CHROME DES EFFLUENTS RÉSULTANTS DE LA NEUTRALISATION

RÉSUMÉ. Pour expliquer la libération de complexes de chrome dans les effluents résultants de l'opération de neutralisation des cuirs tannés au chrome, on a caractérisé la composition, la structure et les propriétés des complexes de chrome dans les effluents de neutralisation. On a tanné du cuir en poudre en utilisant une solution de sulfate de chrome à une basicité de 33% (BCS), puis le cuir en poudre est soumis à un procédé classique de neutralisation pour préparer l'effluent résultant de cette opération (NE). On a d'abord utilisé la chromatographie par échange d'ions (CEI) et la chromatographie par filtration sur gel (GFC) pour séparer le NE afin d'étudier sa composition de chrome, et puis on a combiné la spectroscopie d'absorption ultraviolet-visible (UV) et la spectroscopie infrarouge à transformée de Fourier (FT-IR) pour analyser la structure des complexes de chrome dans le NE; enfin, le chrome résultant du NE a été utilisé dans le tannage et les propriétés thermiques de la poudre de cuir tanné ont été mesurées par l'analyse thermogravimétrique (TG) et par la calorimétrie différentielle à balayage (DSC). Les résultats indiquent que le NE se composait principalement de complexes de chrome anioniques zérovalents, monovalents et divalents, et que le volume moléculaire était faible. Les complexes de Cr(III) du NE ont été combinés principalement avec des ligands, tels que SO_4^{2-} et $HCOO^-$ par un point unique de coordination. Par rapport au témoin, le taux de la perte de poids plus élevé et la température maximale de décomposition thermique (T_{max}), la température de dénaturation thermique (T_d) et l'enthalpie (ΔH) plus diminuées du cuir en poudre tanné au chrome résultant du NE démontrent la faible capacité de tannage du chrome. En bref, les caractéristiques des complexes de chrome libérés par le processus de neutralisation étaient: des complexes anioniques zérovalents, à faible charge positive et au volume moléculaire faible, combinés principalement avec les ligands par un point unique de coordination et avec une faible capacité de tannage. La présente étude est un point de départ et de référence pour l'élaboration de méthodes de solidification du chrome dans le processus de neutralisation.
MOTS CLÉS: effluent de neutralisation, complexe de chrome, composition, structure, capacité de tannage

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INTRODUCTION

Chrome tanned leather has excellent performance, so chrome tanning is still dominant in the leather industry, however the chromium pollution problem is increasingly brought to the attention. Therefore minimizing chromium pollution has significant environmental benefits and is important for sustainable chrome tanning technology. To reduce chromium discharge, cleaner chrome tanning methods like pickle free, high exhaustion, reversing process, organic solvent and adding auxiliary chrome tanning technologies and so on were studied [1-5]. In order to decrease chromium pollution further, recycle and reuse chrome tanning effluent technologies were also developed [6, 7]. However, chromium will release in post-tanning process such as rewetting, neutralizing, retanning, dyeing and fatliquoring effluents, leading to Cr_2O_3 content in post-tanning effluents reaching 10-450 mg/L which is higher than wastewater disposal limit standard [8, 9]. It is great trouble as chrome content in the effluents is too low to reuse or recycle in tanning but too high to use as float in corresponding processes at the same time. Thus, chrome releasing in post-tanning processes must be paid more attention and needs effort to minimize for clean chrome tanning process and high chromium exhaustion in whole leather making.

Organic retanning agents, dyestuffs and fatliquoring agents are mainly anionic materials used in subsequent processes for improving wet blue properties. The neutralizing process is usually used to raise the pH and diminish wet blue positive charge to facilitate anionic materials penetration. Whether alkaline, like sodium bicarbonate, or organic acid salts like sodium formate or sodium acetate, they all have strong affinity to chromium, therefore, the chrome release in neutralizing process is the highest in wet end except chrome tanning [10, 11]. Realizing why chromium is easily released in neutralizing is important and essential to reduce chrome discharge in the process and increase chrome comprehensive exhaustion in leather making. Although chromium complex structure and composition in rewetting process were studied [12], chromium characteristics in neutralizing had not been studied in detail.

In this work, the research grade hide powder was tanned by chromium sulfate liquor with 33% basicity (BCS), and then the leather was rewetted and neutralized to prepare neutralizing effluent (NE). The NE was separated by Ion exchange chromatography (IEC) and gel filtration chromatography (GFC) and to study the chrome complex composition; then both ultraviolet-visible absorption spectroscopy (UV) and Fourier Transform Infrared Spectroscopy (FT-IR) were used to analyze the structure of the chromium complexes in NE; finally, hide powder was tanned by the chrome recovered from NE and thermal stability of the hide powder was characterized by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) to present the chrome complex property. The study would help illustrate the reason why chromium is released in neutralizing as well as provide foundation and reference for developing chromium solidifying methods in the process.

EXPERIMENTAL
Materials

Hide powder was research grade product from Tanning Chemical Lab of Chinese Academy of Forestry Sciences in Nanjing. Chromium sulphate was bought from Shanghai Aladdin Reagents Company. SP Sephadex C-25 cation exchange resin and SP Sephadex G-25 glucan gel resin were obtained from GE Healthcare. Other chemicals in the study were research grade and purchased from Chengdu Kelong chemical reagent factory, China.

Preparation of Basic Chromium Sulphate

1000mL 0.2mol/L chromium sulphate solution was prepared at first, and then 0.067mol sodium bicarbonate was added after 30min under stirring to obtain chromium sulfate liquor with 33% basicity (BCS).

Preparation of Neutralizing Effluent

20.00g hide powder was soaked with 100mL water in a 500mL flask at 25°C for 30min. A 100mL BCS was put in the system and interacted with hide powder in a thermostatic water bath oscillator at 25°C for 120min. Then, sodium bicarbonate was used to adjust the tanning liquor pH to 3.8-4.0 and then ran at 38 for 60min. At last, the tanned hide powder was dried in a vacuum drying oven at 40°C to constant weight.

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 with 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 filtering with nylon filter cloth, NE was collected. All the chemicals used for rewetting and neutralizing were based on dried hide powder weight.

Chromium Composition Determination by IEC and GFC

5 mL BCS and NE were filtered by microporous membranes (pore size, 450nm), and then added into pretreated SP Sephadex C-25 cation exchange chromatographic column (inner diameter 2.0 cm, packed 20.0 cm). Elution conditions were selected as follows: flow velocity of eluent 2.5 mL/min, followed by using H_2O, $NaClO_4$ (0.5mol/L), $NaClO_4$ (1.0mol/L), $NaClO_4$ (2.0mol/L), HCl (2.0mol/L) and HCl (3.0mol/L) to elute. UV1900 UV-Vis spectrophotometer (Shanghai Jinghua technology instrument co., LTD, China) was used to detect the absorbance at 420 nm [12, 13].

5 mL BCS and NE were filtered by microporous membranes (pore size, 450nm), and then added into pretreated SP Sephadex G-25 gel filtration chromatographic column (inner diameter 2.0 cm, packed 80.0 cm). H_2O with flow velocity of 2.5 mL/min was used to elute. UV-Vis spectrophotometer was used to detect the absorbance at 420 nm [12].

Chromium Structure Determination by UV and FT-IR

After IEC separation, each composition was lyophilized and then dissolved by distilled water. UV-Vis spectrophotometer was used to scan obtained liquor at 300-800 nm. R values were calculated by formula (1) as follows:

$$R = \varepsilon_1 / \varepsilon_2 \qquad (1)$$

where ε_1 - molar absorption coefficient of chrome at about 420nm and ε_2 - molar absorption coefficient of chrome at about 580nm.

Lyophilized chromium complexes were ground with KBr and made into thin sheets, then a Nicolet 10 FT-IR (American Thermo Scientific Corporation) was used to scan in wavelength range of 500-4000 cm^{-1} for 32 times, and the data was recorded.

Chromium Property Determination

1.00g hide powder was tanned by 100mL 10g/L chrome solution prepared by dissolving lyophilized NE in a thermostatic water bath oscillator at 25°C for 120min. Then, sodium bicarbonate was used to adjust the tanning liquor pH to 3.8-4.0 and then ran at 38°C for 60min. Then, the tanned hide powder was dried in a vacuum drying oven at 40°C to constant weight. The dried hide powder was put in a dryer with saturated sodium sulphite to keep the temperature at 25°C and the air relative humidity of 65% before DSC and TG test [14]. The hide powder tanned by BCS was used as control.

The hide powder samples were put into ceramic crucibles and heated with 10°C min^{-1} heating rate in a N_2 atmosphere (flow N_2:100mL min^{-1}); the range of temperature was from 50 to 650°C. A NETZSCH TG 209 F1 thermal gravimetric analyzer (Germany) was used for the determination, and the TG and DTG curves were recorded. Then the weightlessness rate at 200-600°C and maximum thermal decomposition temperature (T_{max}) was calculated.

The hide powder samples were put into Aluminum crucibles and heated with 10°C min^{-1} heating rate a N_2 atmosphere (flow N_2: 100mL min^{-1}); the range of temperature was from 25 to 250°C. A DSC 200 PC differential scanning calorimeter (Germany) was used for the determination, and the DSC curves were recorded. Then thermal denaturation temperature (T_d) and enthalpy (ΔH) was calculated.

RESULTS AND DISCUSSIONS
Chromium Complex Composition in Neutralizing Effluent
Charge Characteristics of Chrome Complexes in Neutralizing Effluent

According to the results of Li *et al.* [13], peak I, II, III, IV and V represented anionic-zero valent, monovalent, bivalent, trivalent and tetravalent chromium complexes, respectively. Notably, NE consists of anionic-zero valent, monovalent and bivalent chrome complexes (as shown in Figure 1b) only, however, BCS is separated into five components (in Figure 1a). The chrome complexes composition in BCS and NE are calculated based on the area of IEC peak (listed in Table 1). Moreover, the content difference of each composition between NE and BCS is also calculated in Table 1.
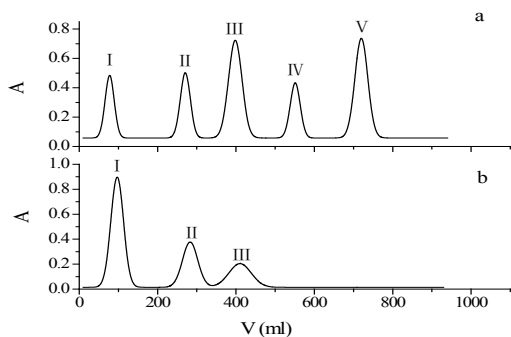
Figure 1. Ion exchange chromatography of BCS (a) and NE (b)

Table 1: R values of each constituent in neutralizing effluent

Peak	I	II	III	IV	V
Valence state	Anionic-zero valent	+1	+2	+3	+4
BCS	14.02	15.63	26.16	14.02	25.56
NE	47.44	24.97	19.73	0	0
NE-BCS	33.42	9.34	-6.43	-14.02	-25.56

As shown in Table 2, charge distribution of BCS is more uniform, and composition is abundant. However, only anionic-zero valent, monovalent and bivalent chrome complexes exist in NE, in addition, the anionic-zero valent composition is dominant (47.44%) while high positive charge compositions cannot be detected. The results indicate that low-positive electricity chrome complexes are easy to be released in neutralizing, because the binding capacity between anionic-zero valent, low positive electricity chrome complexes and collagen are weak [15].

Molecular Volume of Chrome Complexes in Neutralizing Effluent

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

molecular volume in NE is far less than BCS. Smaller molecular volume means there is rarely polynuclear complexes, thus, the chromium complexes volume are too small to combine collagen through multiple crosslink [15].
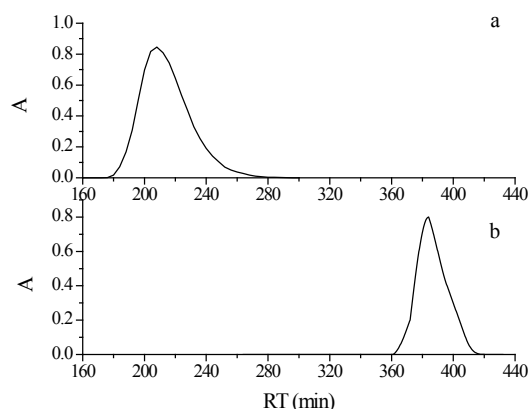

Figure 2. Gel filtration chromatography of BCS (a) and NE (b)

In short, some measures should be taken to enlarge positive charge and increase size of chromium complex for forming stable and multi-crosslink between collagen and itself, it would be the foundation of reducing chromium releasing in neutralizing.

Chromium Complex Structure in Neutralizing Effluent
UV Results of Chrome Complex in Neutralizing Effluent

The R value of chrome complex compositions of I, II, III, IV and V in BCS is 1.08, 1.10, 1.09, 1.15 and 1.36 respectively, while only anionic-zero valent, monovalent and bivalent chrome complexes with R value 0.95, 0.80 and 0.83 are in NE. Composition with 1.36 R value being in BCS means Cr(III) combines with ligands mainly through a multi-point coordination mode which has better affinity and binding stability with collagen. Nevertheless, coordination patterns of chrome complexes combined with ligands in NE are mainly single as R values are always lower than 1.19 [15]. In consequence, chromium releasing in neutralizing should ascribe to lacking sufficient combination between chrome and ligands.

Table 2: R values of each composition in NE and BCS

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

FT-IR Results of Chrome Complex in Neutralizing Effluent

Characteristic absorption peak and coordination mode of chrome complexes in NE are shown in Table 3. There are four absorption peaks in 900-1300cm^{-1} for chromium complex in composition I, which indicates that combination mode for SO_4^{2-} and central ion Cr(III) is two-point coordination. In the same way, two and three absorption peaks in composition II and III demonstrate that SO_4^{2-} is in free state and coordinates with Cr(III) by single point coordination [15].

Table 3: FT-IR absorption peak and coordination mode of chromium complex in NE

Compo-sition	Scope (cm^{-1})	Peak (cm^{-1})	Num.	Ligand	Coordina-tion mode
I	900-1300	995,1048, 1148,1114	4	SO_4^{2-}	two-point
	1680-1550 1465-1370	1633 1405	2	HCOO$^-$	single point
	3400	3439	1	OH	----
II	900-1300	941,1088	2	SO_4^{2-}	free
	1680-1550 1465-1370	1630 1430	1	HCOO$^-$	single point
	3400	3423	1	OH	----
III	900-1300	941,1087, 1141	3	SO_4^{2-}	single point
	1680-1550 1465-1370	1631 1422	1	HCOO$^-$	single point
	3400	3441	1	OH	----

One asymmetric and one symmetric stretching vibration absorption peak are respectively found in 1550-1680cm^{-1} and 1370-1465cm^{-1} of chrome complex in composition I, II and III, moreover, the interval of these two absorption peaks are small. Therefore single point coordination is speculated between Cr(III) and HCOO$^-$ [15]. Based on the UV, FT-IR and IEC results, chromium complexes structure in neutralizing effluent are speculated and shown in Figure 3.
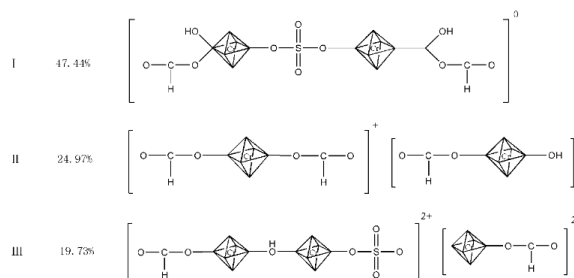

Figure 3. Possible structures of chrome complexes in NE

Table 4: Chrome tanned hide powder thermal stability

Sample	Weightlessness rate %	T_{max} °C	T_d °C	ΔH J/g
BCS	30.72	332.13	84.26	547.85
NE	46.82	309.35	70.71	386.27

The weightlessness rate, T_{max}, T_d and ΔH of BCS and chromium from NE tanned hide powder are presented in Table 4. As shown in Table 4, weightlessness rate of NE tanned hide powder is 46.82%, which is higher than BCS tanned sample; however, Tmax of NE tanned hide powder is lower than control. These results indicate that NE tanned hide powder could be decomposed easily under high temperature. In addition, T_d and ΔH of NE tanned hide powder are 70.71°C and 386.27 J/g which are lower than corresponding value of BCS tanned hide powder too; they demonstrate inferior thermal stability of NE tanned hide powder. Given the lower charge and molecular volume as well as lacking of multi-combination between chrome and ligands, tanning ability of chromium in NE is too poor to improve collagen thermal resistance representing as easier decomposed under high temperature and thermal stability showing as low energy being needed for leather denature.

CONCLUSIONS

Chromium in neutralizing effluent mainly consists of anionic-zero valent and low-positive electricity (+1 and +2) chrome complexes, and the molecular volume is far less than the chromium sulfate liquor with 33% basicity. The basic structure character of chromium in neutralizing

effluent is chromium combined with SO_4^{2-} and $HCOO^-$ by single point coordinate bond. Tanning ability of chromium in neutralizing effluent is still poor. To sum up, the characteristics of chromium complexes released from neutralizing process are anionic-zero valent and low positive charge composition, small molecular volume, mainly combined with ligands through single point coordination and poor tanning ability. The study may have important hints for improving the tanning and post-tanning process to reduce chromium discharge in wet end and promote chromium comprehension exhaustion in leather making.

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