



Stabilization of chromium: An alternative to make safe leathers

Ying Gong, Xiaoling Liu, Li Huang, Wuyong Chen*

National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, Sichuan, China

ARTICLE INFO

Article history:

Received 28 January 2010

Received in revised form 6 March 2010

Accepted 8 March 2010

Available online 12 March 2010

Keywords:

Leather

Chromium

Hexavalent chromium

Stabilization

ABSTRACT

In this study, the original causes for hexavalent chromium presence in the leather were first evaluated by ageing of chromium(III) solutions and chrome tanned hide powder (50 °C, UV lightening at 340 nm, 0–36 h). The results showed that the trivalent chromium at instable coordination state was easy to convert into hexavalent chromium in high pH environment, and the probability of the oxidation increased in this order: multi-coordinate chromium, mono-coordinate chromium, and free chromium. For this reason, the process for stabilizing chromium in the leather was designed with the specific material, which was mostly consisted of the reducers and the chelating agents. After treated with the developed process, these leathers were aged (50 °C, UV irradiance as 0.68 W/m² at 340 nm, 0–72 h) to estimate chromium(VI) presence. Hexavalent chromium was not found in these treated leathers even if the leathers were aged for 72 h. Moreover, the physical and mechanical properties for the leathers varied little after treating. In a word, an inherent safe and effective process was proved to avoid the formation of hexavalent chromium in the leather.

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1. Introduction

Among all the mineral and organic tannages used today, the chrome tannage carried out with basic chromium salts has numerous technical advantages. Thus, it accounts for more than 80% of the tannages in the past 20 years [1,2]. However, trivalent chromium in the leather may convert into hexavalent chromium, resulting in skin allergy [3], cancer [4] and kidney necrosis [5]. Furthermore, the unfriendly hexavalent chromium has been an increasingly sensitive issue with the development of the society.

Since hexavalent chromium traces were found in the leather products for the first time in 1994, numerous attempts have been made to understand the formation of hexavalent chromium. The researchers found that hexavalent chromium presence was tightly related to the processing and disposing conditions for the leather, such as the leather chemicals (the retanning agents [6], the fatliquoring agents [7,8]), the acidity of the leather [9], the ironing temperature [10], the relative humidity of the storing environment [11,12] and the incineration temperature [13–15]. Although carcinogenic hexavalent chromium can be temporarily converted into nontoxic trivalent chromium with the reducing agents [16], some additional hexavalent chromium is usually found in the leather during the following usage period. That is, none of the publica-

tions gives an absolutely safe “recipe” to avoid the formation of hexavalent chromium in the leather.

Conversion of trivalent chromium to hexavalent chromium is a redox reaction, so both the states of the reactants and the acidity of the reaction environment are important factors. Trivalent chromium in the leather exists as free, mono-coordinate or multi-coordinate state and its stability increases gradually as prescribed order [17]. Therefore, a hypothesis was proposed, viz., the conversion of trivalent chromium may be primarily associated to its chemical instability in the leather. This hypothesis was confirmed with the ageing study of the chromium(III) solutions, the chrome tanned hide powder and the chrome tanned leathers. Then, the difference in the hexavalent chromium presence between the belly and the butt was explained with the verified hypothesis. Finally, the specific process for stabilizing chromium was proposed and proved to avoid the formation of hexavalent chromium in the leather.

2. Experimental procedures

2.1. Materials

Chromium(III) chloride hexahydrate, formic acid, oxalic acid, L-glutamic acid and hide powder (Cr₂O₃ content as 0.3–0.5% on dry weight basis) were of analytical reagent grade. The specific material (with pH about 7) was prepared with the reducers and the metal chelating agents in the laboratory. Chrome tanned pigskin shoe lining leathers (Cr₂O₃ content as 3.5–3.8% on dry weight basis; thickness as about 0.80 mm) were from Yuanxin Tannery (China) and processed with a common chrome tanning and post-tanning

* Corresponding author at: Leather Building, 24, South Section 1, Yihuan Road, Sichuan University, Chengdu, China. Tel.: +86 028 85404462; fax: +86 028 85405237.

E-mail addresses: gongying_85@126.com (Y. Gong), wychen1952@hotmail.com (W. Chen).

procedure. The fatliquoring agent contained in the leather was a mixture of unsaturated esters.

2.2. Methods

2.2.1. Study of chromium(III) solutions

2.2.1.1. Preparation of chromium(III) solutions. A 0.1 mmol/L chromium(III) chloride solution (1000 mL) was prepared as *solution a*. Then *solution a* was divided into three equal parts and their pH values were adjusted to 4.0, 5.0 and 6.0 with 0.1 mol/L NaOH solution respectively.

A 0.1 mmol/L chromium(III) chloride solution (500 mL) was prepared as *solution b*. Then an acid was added into *solution b* to get a mole ratio of the acid to trivalent chromium as 1:1 or 3:1. The acid was formic acid, oxalic acid or L-glutamic acid. Next, the reactant mixture was heated to reflux for 1 h at 70 °C under stirring to get chromium-acid complexes [18]. At the end of the reaction, the acidity of the product mixture was adjusted to a pH 5.0 with 0.1 mol/L NaOH solution.

2.2.1.2. Ageing of chromium(III) solutions. After the chromium(III) solutions were exposed to UV lightening (10.5 W/m²) at 340 nm for 0 h, 4 h, 8 h, 12 h, 24 h and 36 h at 20 °C, the hexavalent chromium contents in these solutions were determined as IUC-18 method [19]. Here, the Cr(III) solutions without acids were the controls.

2.2.2. Study of chrome tanned hide powder (CTHP)

2.2.2.1. Preparation of CTHP. Hide powder was first soaked in a conical beaker with an 800% float (based on the weight of the hide powder) at 20 °C overnight. The soaked hide powder was squeezed lightly to remove the excess water and the moist weight was noted. The chemicals used in the following procedure were based on the weight of the soaked hide powder. The weighted hide powder was pickled with a 100% float containing 10% sodium chloride and 0.8% H₂SO₄ (98%) for 1 h. Next, the pickling mixture was shaken for 1 h after the addition of 3% chromium(III) chloride hexahydrate. After heated up to 40 °C, the tanning solution was basified with 1% sodium bicarbonate diluted 10 times with water and shaken for another 1 h with a final pH about 4.0. After washed in a 200% float, the chrome tanned hide powder (CTHP) was squeezed lightly to remove the excess water and then dried in the air.

2.2.2.2. Treatment of CTHP with acids. Chrome tanned hide powder (CTHP) was first rewetted in a conical beaker with a 600% float (based on the weight of the CTHP) at 20 °C overnight. Then the rewetted CTHP was squeezed lightly to remove the excess water and the moist weight was noted. The chemicals used in the following procedure were based on the weight of the rewetted CTHP. The weighted CTHP was treated in a 100% float containing an acid (0.61% formic acid, 1.42% oxalic acid or 1.66% L-glutamic acid) at 40 °C for 1 h. Next, the mixture was adjusted to pH about 4.0 with sodium bicarbonate diluted 10 times with water and shaken for another 1 h. After washed in a 200% float, the treated CTHP was squeezed lightly to remove the excess water and then dried in the air. The CTHP treated with formic acid, oxalic acid or L-glutamic acid was denoted as CTHP-FA, CTHP-OA and CTHP-L-Glu respectively. Here, the CTHP without treatment was the control.

The CTHP was analyzed for moisture, Cr₂O₃ and Cr(VI) content as IUC-5 method [20], IUC-8 method [21] and IUC-18 method [19] before ageing. The moisture content for all the CTHP was 20–21%. The chromium content as Cr₂O₃ was 1.14%, 1.30%, 1.26% and 1.28% (on dry weight basis) for control, CTHP-FA, CTHP-OA or CTHP-L-Glu respectively. Moreover, hexavalent chromium was not found in all the CTHP before ageing.

2.2.2.3. Ageing of CTHP. After the CTHP was aged with a QUV/se Accelerated Weathering Tester (Gotech Testing Machines Co. Ltd., China) for 0 h, 4 h, 8 h, 12 h, 16 h and 20 h, its hexavalent chromium content was determined using IUC-18 procedure [19]. The accelerated ageing conditions were as following: temperature as 50 °C, UV irradiance as 0.68 W/m² at 340 nm (equal to the solar irradiance at noon on Midyear's Day).

2.2.3. Study of chrome tanned leathers

2.2.3.1. Treatment of the leathers. Since the colorants in the extracts of the dark leathers could bring the false positive results to hexavalent chromium content determined as IUC-18 method [22,23], five pieces of light color leathers in the same production batch were selected for the experiment. One leather with Cr(VI) content about 16 mg/kg was as *leather a*, the others were with hexavalent chromium content below the spectrophotometric detection limits, as *leather b*, *leather c*, *leather d* and *leather e* respectively. Their pH values were as 4.1, 4.3, 4.1, 5.0 and 6.0 in turn.

Leather a and *leather b* were treated with the following procedure and the chemicals used were based on the weight of the leather. The two leathers were first rewetted in a drum with a 300% float at 30 °C for 30 min. The rewetted leathers were squeezed lightly to remove the excess water and the moist weight was noted. Next, the weighted leathers were treated in a drum with a 100% float containing 3.0% specific material (prepared in the laboratory) at 30 °C for 1 h. The final pH of the float was adjusted to 3.5 with 2.0% formic acid diluted 10 times with water and run for 30 min. In the end, the treated leathers were processed as the common finishing procedure.

As for *leather a* and *leather b*, their mechanical properties and color properties were analyzed before and after the treatment. After air conditioned [24], the tensile strength and the tear strength were measured with an automated tensile machine (AI 7000S, China) as per IUP 6 method [25] and IUP 8 method [26] respectively. The color of the leather was quantified with a color photometer (Premier 8200, USA) according to the Commission International de l'Eclairage (CIE) system of color measurement with 10⁰ standard observer data [27].

2.2.3.2. Ageing of the leathers. Matched samples (10.0 cm × 7.5 cm) were cut from the butt and belly areas of the five leathers. After these samples were aged with the QUV/se Accelerated Weathering Tester for 0 h, 12 h, 24 h, 36 h, 48 h, 60 h and 72 h, hexavalent chromium contents in the leather samples were measured as IUC-18 method [19].

The weathering conditions for the leather samples were the same as the CTHP. The moisture content and the pH value of the leather sample were analyzed as IUC-5 method [20] and IUC-11 method [28] during the ageing period.

3. Results and discussions

3.1. Formation of Cr(VI)

3.1.1. Effect of the acidity of the reaction environment

As shown in Fig. 1, as for the chromium(III) solutions after UV lightening, the less hexavalent chromium presence was found in the solution of high acidity.

In this work, the moisture contents for the leathers were 17–18% before ageing and maintained at 9–10% after 24-h ageing; moreover, their pH values only increased about 0.2 during the ageing period. Therefore, the difference of Cr(VI) presence would depend on the initial pH value of the leather, if the effect of the moisture content of the leather [11,12] was neglected. As indicated in Fig. 2, after ageing, the less hexavalent chromium presence was found in

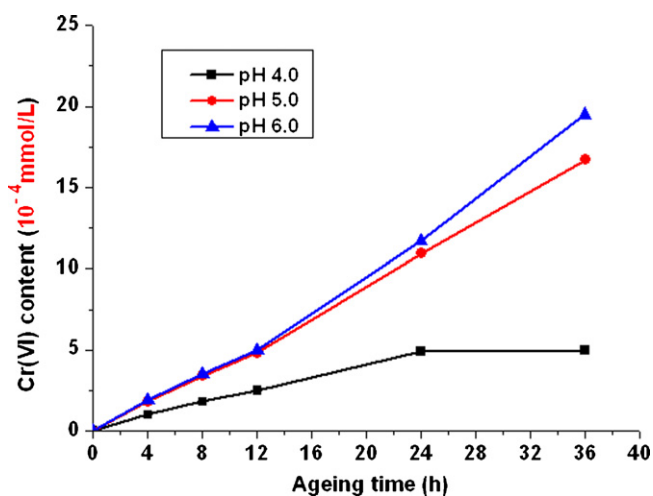


Fig. 1. Cr(VI) presence in the chromium(III) solutions of various pH values after UV lightening.

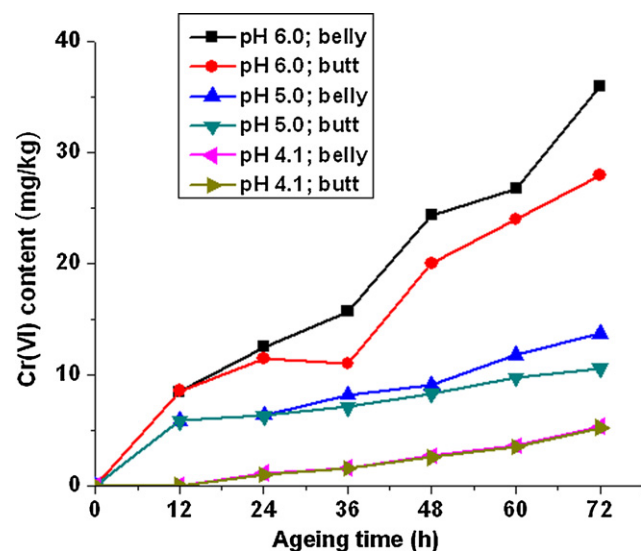


Fig. 2. Cr(VI) presence in the leathers of various pH values after ageing.

the leather of low initial pH value. The findings were similar to the ageing study of the chromium(III) solutions (Fig. 1).

According to the Gibbs free energy changes for the oxidation reaction, trivalent chromium is apt to convert into hexavalent chromium in the environment with pH value higher than 5 [29]. Thus, the acidity of the leather may be lowered to prevent the oxidation of Cr(III). This view has been confirmed by the ageing study

Table 2

Cr(VI) presence in the CTHP after ageing.

Cr(VI) content (mg/kg)	Accelerated ageing time (h)					
	0	4	8	12	16	20
Control ^a	– ^b	0.51	0.58	0.68	0.82	0.99
CTHP–L–Glu	– ^b	– ^b	0.45	0.50	0.56	0.67
CTHP–FA	– ^b	– ^b	– ^b	0.11	0.18	0.21
CTHP–OA	– ^b	– ^b	– ^b	– ^b	– ^b	0.09

^a Chrome tanned hide powder (CTHP) without treatment.

^b “–” meant “hexavalent chromium was not found”.

of both the chromium(III) solutions and the leathers of various pH values.

3.1.2. Effect of Cr(III) coordination states

As displayed in Table 1, as for the chromium(III) solutions after UV lightening, Cr(VI) concentration in the solution with an acid was lower than the control; hexavalent chromium presence was also less in the solution of CrCl₃ and an acid with mole ratio as 1:3, compared to that with equal mole. Furthermore, hexavalent chromium presence was the least in the solution with oxalic acid. Particularly, hexavalent chromium was not found in the solution of CrCl₃ and oxalic acid with the mole ratio as 1:3, even if the solution was UV irradiated for 36 h in the experiment.

As shown in Table 2, as for the CTHP after ageing, the hexavalent chromium content increased in this order: control, CTHP–L–Glu, CTHP–FA, CTHP–OA. This order was similar to that found for the chromium(III) solution with an acid after ageing (Table 1).

As we know, with the mole ratio of trivalent chromium to a mono-dentated acid as 1:1, trivalent chromium is at incomplete coordination state with instability; while with the mole ratio as 1:3, trivalent chromium may be sufficiently coordinated to be at a stable state with relative chemical inertia [18]. That is, trivalent chromium may be steadier in the solution with high content of the coordinated acid. As for L-glutamic acid, formic acid and oxalic acid, their coordination abilities to trivalent chromium increase gradually [30,31]. So the stability of the trivalent chromium complex may also increase as the order of the prescribed coordinated acid. As for both the chromium(III) solutions and the CTHP treated with acids, the least hexavalent chromium presence was just corresponding to the most stable trivalent chromium (Tables 1 and 2). In a word, the more stable the trivalent chromium, the less Cr(III) converts into Cr(VI).

Collagen, as the main part in the leather, is composed of the peptide chains. It contains a number of side chain carboxyl groups, so collagen may bind to trivalent chromium in a condition. Inorganic salts (such as sulfate and carbonate) and organic acids (such as formic acid, acetic acid and oxalic acid) used in the leather manufacture can also combine to trivalent chromium. However, there are some trivalent chromium compounds depositing in the gaps among the collagen fiber bundles, and they do not link to the car-

Table 1

Cr(VI) presence in the chromium(III) solutions after UV lightening (pH = 5.0).

Cr(VI) in the solutions ^a (mmol/L)	UV radiation time (h)					
	0	4	8	12	24	36
Cr(III):L–Glu = 1:1	– ^c	6.5×10^{-5}	1.2×10^{-4}	1.9×10^{-4}	2.9×10^{-4}	1.1×10^{-3}
Cr(III):FA = 1:1	– ^c	4.0×10^{-5}	7.5×10^{-5}	1.1×10^{-4}	1.8×10^{-4}	6.5×10^{-4}
Cr(III):OA = 1:1	– ^c	– ^c	– ^c	– ^c	9.0×10^{-5}	5.4×10^{-4}
Cr(III):L–Glu = 1:3	– ^c	– ^c	– ^c	– ^c	3.1×10^{-5}	1.6×10^{-4}
Cr(III):FA = 1:3	– ^c	– ^c	– ^c	– ^c	1.9×10^{-5}	9.8×10^{-5}
Cr(III):OA = 1:3	– ^c	– ^c	– ^c	– ^c	– ^c	– ^c
Control ^b	– ^c	1.8×10^{-4}	3.5×10^{-4}	4.8×10^{-4}	1.1×10^{-3}	1.7×10^{-3}

^a CrCl₃ and the acid were mixed with the mole ratio. L–Glu, FA and OA were the abbreviations of L–glutamic acid, formic acid and oxalic acid respectively.

^b Only CrCl₃ solution.

^c “–” meant “hexavalent chromium was not found”.

boxyl or the other chelating agents in the leather. Thus, three types of chromium are differentiated: free chromium, mono-coordinated chromium and multi-coordinated chromium, and their stability increases in turn. Moreover, the probability of the oxidation of trivalent chromium decreases in this order as proved by the ageing study of the chromium(III) solutions and the CTHP. In conclusion, the instable chromium in the leather should be stabilized in a way to avoid the formation of hexavalent chromium.

3.2. Variations of hexavalent chromium presence in different leather parts

Hexavalent chromium contents in both the butt and the belly increased with the prolonged ageing. However, Cr(VI) content in the belly was higher (Fig. 2). In a common tanning procedure, leathers or hides continually strike on the inside wall of the drum, leading to the uniform mechanical action provided by the running drum. Supposing the penetration of the chrome tanning agents into the leather is even in the tanning process, then trivalent chromium in per area or volume of the belly will be comparable to that in the butt. Since the collagen fiber weave in the belly is looser and the collagen is the main chelating component to trivalent chromium in the leather, the percentage of trivalent chromium at incomplete coordination state might be higher in the belly, including trivalent chromium at free state or at mono-coordinate state. Thus, the oxidation of Cr(III) caused by the unsaturated esters [7,8] (such as the fatliquoring agent in the leather) would be easier in the belly if the leather was subjected to UV lightening and high temperature. This may be the main reason to higher Cr(VI) presence in the belly.

3.3. Stabilization of chromium with the specific process

In the whole 72-h ageing period, hexavalent chromium was not found in the belly or in the butt of the two treated leathers (*leather a* and *leather b*), but the hexavalent chromium was constantly formed in the other three leathers without treatment (Fig. 2). Thus, the persistent elimination of Cr(VI) may be related to the stabilization of chromium with the specific treatment.

The tensile strength and the tear strength for *leather a* and *leather b* varied little after the treatment. Also, their color properties changed little after treating, including the hue, the color depth and the color uniformity. To sum up, the treatment process did not affect the physical and mechanical properties of the leather markedly.

The specific material may easily penetrate into the belly because of the loose collagen fiber weave. Consequently, not only all the hexavalent chromium in the belly can be effectively reduced to trivalent chromium, but also trivalent chromium at deficient coordination state can be sufficiently stabilized with the chelating components in the specific material. That is, the hexavalent chromium of higher content in the belly may be totally reduced and then stabilized with the specific material just like the butt in the same process.

As we know, the wet leathers with the common post-tanning procedure have similar properties to the rewetted leathers in the developed treatment process. Thus, the wet leathers may be also treated with this developed process and the treated leathers are still prepared to the following common finishing procedure. That is, there is no additional connection between the common leather-making procedure and the treatment. Furthermore, the treatment would not affect the properties of the leathers evidently, and it will only cost additional USD 10 to process 100 m² of leather with the specific material. The used specific material comprises the reducers and the metal chelating agents. The reducers are preferred to the sulfocompounds with the valence of sulfur as 4 or lower; the metal chelating agents are preferred to the compounds containing two or

more carboxyl groups. The detailed formula for the specific material is being patented in China.

This specific process for stabilizing chromium has been exploited in Yuanxin Tannery (China), which produces pigskin shoe lining leathers. Hexavalent chromium is not found in the leathers with this particular treatment, not only in the accelerated ageing period (50 °C, UV irradiance as 0.68 W/m² at 340 nm, 72 h), but also in the following 18-month storing period (room temperature as 20 °C, relative humidity as about 70%). Moreover, the physical and mechanical properties of the treated leathers still meet the demand of the Yuanxin Tannery.

In a word, the process for stabilizing chromium proposed here is an inherent safe alternative to avoid the formation of hexavalent chromium in the leather.

4. Conclusions

In this research, a conception of hexavalent chromium presence in the leather was verified by experiments, i.e. the trivalent chromium at instable coordination state was easy to convert into hexavalent chromium in the high pH environment, and the probability of the oxidation increased in this order: multi-coordinate chromium, mono-coordinate chromium, free chromium. In comparison with the butt, the higher percentage of the deficiently coordinated trivalent chromium in the belly led to higher hexavalent chromium presence after ageing.

For this reason, a new method to avoid the formation of hexavalent chromium was designed with the specific material, which mainly comprises the sulfocompounds with the valence of sulfur as 4 or lower and the metal chelating agents containing two or more carboxyl groups. Hexavalent chromium was not found in the belly or in the butt of the treated leathers, even if the leathers were aged with the intense UV lightening and high temperature for 72 h. These results in turn validated the conception of stabilizing chromium to eliminate hexavalent chromium presence.

Acknowledgements

The authors wish to thank the Ministry of Science and Technology of China for the financial support (No. 2006DFA41010). The authors also express their thanks to Yuanxin Tannery for supplying the chrome tanned pigskin shoe lining leathers.

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