New Chrome Tanning Method Assisted by Wringing and Ultrasound

by

Jinwei Zhang,[1] Yu Wang,[1] Bo Teng[1] and Wuyong Chen[1,2]*

[1]*Key Laboratory of Leather Chemistry and Engineering of Ministry of Education*
Sichuan University, Chengdu 610065, China

[2]*National Engineering Laboratory for Clean Technology of Leather Manufacture*
Sichuan University, Chengdu 610065, China

Abstract

A new chrome tanning method was designed using wringing (10 kg/cm^2) and ultrasound (28 kHz, 300W). The grain down pickled skin was put into the penetration tank to let the chrome tanning agent penetrate for 3min. After penetration, the skin was transferred into the fixation tank to basify for 3min. Then the skin was again penetrated and fixated to finish the tanning process as is described above. During the penetration and fixation stage, an ultrasound field was used and the skin was transported with belts one by one. Before each stage skins were wrung to recover the penetration solution or fixation solution and lower the water content of the leathers to about 55%. The results showed that tanning time was obviously shorted compared with a conventional method because of the mechanical extrusion formation of the micro vacuum and ultrasonic cavitations' effect. The wet blue obtained by the new method remained the same properties compared with conventional wet blue, such as shrinkage temperature, chrome content in leather, and physical properties after retanning, fatliquoring and finishing in a normal shoe upper leather process. Furthermore, collagen structure and cross section of the leathers maintained integrity during the tanning process proved by SEM. In short, this new chrome tanning method assisted by wringing and ultrasound could be used in future tanning industry.

Introduction

Cavitation effect was the main dynamic power in ultrasonic chemistry, which could promote chemical reactions that were difficult to occur naturally.[1,2] Because of the properties of ultrasound, tanners used it in leather-making process, such as soaking, degreasing, and dyeing. [3-5] The results of the chrome tanning process in drum assisted by ultrasound showed that no considerable changes of components could be observed after the chrome solutions were treated with ultrasound.[6] Besides, ultrasonic of 20kHz could remarkably improve the penetration of titanium in pelt and increase Ts of the leather.[7] Ultrasound could also accelerate the speed of penetration rate in vegetable tanning process.[8] In addition, the research conducted by Gong Ying showed that a new dyeing method by means of wringing, ultrasound and microwave could finish dyeing process in several minutes. [9]

With mechanical extrusion, some of the moisture could be removed from the fiber bundle, so the leather fiber is in a microenvironment of the vacuum state, because leather is a matrix of pore-size ranging from 3×10^{-10} to15×10^{-5} m.[10] When the leather restored the state from the extrusion to prior, the liquid could penetrate rapidly into it due to the capillary action. If the wrung leather is put into the tanning liquid with ultrasound source, the synergy of cavitation effect combination with capillary action may accelerate the penetration of tanning agent.

*Corresponding author, e-mail address: wuyong.chen@163.com
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Chrome tanning process could be divided into two stages, penetration and fixation. In stage one, chrome tanning agent penetrates from float to the skin, which determines the chrome content and chrome distribution of wet blue. In fixation stage, chrome complexes binds with skin to improve hydrothermal stability of leather.[11]

In this experiment, a new chrome tanning method was design based on the synergy of cavitation effect combination with capillary action, which could short the tanning time to about 12min. Although the penetration and fixation of chrome tanning agent were separated, the leather was transported with belts one by one. Meanwhile, the chrome tanning solution could be reused by adding extra chrome powder based on the analysis results.

EXPERIMENTAL

Materials

Pickled goat skins were prepared as a common process(pH 2.5, thickness was about 1.0mm), chrome powder (B=33% Cr_2O_3 content 25%, Anjian Leather Chemical Corporation, China). Chemicals used for leather processing were commercial grade, and reagents used for analysis were research grade.

Experimental Set-up and Chrome Tanning

The schematic diagram of the new chrome tanning method assisted by wringing and ultrasound (CAWU) set-up was shown in Fig. 1. The ultrasonic cleaner (JK-300DVB, Anhui China Jinnike Ultrasonic Equipment Co.) was used as an ultrasound source with the ultrasound power intensity at 28 kHz, 300W. An extruding machine (Ø55×180mm) was used for wringing with a pressure of 10 kg/cm^2. Pickled skins (10cm×15cm) were taken from the back area and weighted as a base for the following process. The float length of penetration and fixation was 2000%.

CAWU was carried out in the equipment showed in Figure 1. During the penetration and fixation, ultrasound field (28 kHz, 300W) was used to accelerate the speed of each reaction. Firstly, skin was wrung before and at the end of each reaction to recycle the penetration solution or fixation solution and lower the water content of skin to 55%. Secondly, the skin was put into the penetration tank for 3min (Step 2). After penetration, the skin was transferred into the fixation tank to basify for 3min (Step 3). Then the skin was penetrated and fixed again to finish the tanning process as described above. In this process, the skin was put the grain down and transported with belts one by one. In Step 2 and Step 5 the penetration solution was chrome liquid (sodium chloride 60g/L,pH 2.5, mass fraction of chrome powder was 20%,) and in Step 3 and Step 6 the fixation solution was sodium bicarbonate (1.5%) and sodium formate (1%). During the process, the temperature maintained about 25°C. The control wet blues were tanned in a drum as a conventional method.

Shrinkage Temperature (Ts) Test

The shrinkage temperature was tested using the Shrinkage Temperature Tester (MSW-YD4, China) with a bath of glycerin (75%). Each value was an average of two, which were along and across the backbone.

Chrome Content Test

The leather samples were cut into about 1×1mm pieces, and then dried in 102±2°C for 6h to constant weight. Each sample (about 0.1500g) was digested in a flask with 10ml HNO_3 and 5ml H_2O_2 heated for 30min. After cooling down, the digested solution was dissolved in a volumetric flask (100ml). The total chromium content in digestion solution was determined by ICP (Optima 2100DV America) following the manufacturer's direction. And the content of Cr_2O_3 in leather was calculated.

Chrome distribution test

The samples were split into 3 uniform layers (about 0.3mm) and the chrome content was determined by the ICP method mentioned above. The uniformity of chrome distribution was calculated as follow formula:

$$\text{Uniformity (\%)} = \frac{2 \times Cr_2O_3 \text{ in Middle layer}}{Cr_2O_3 \text{ in Grain layer} + Cr_2O_3 \text{ in Flesh layer}} \times 100\%$$

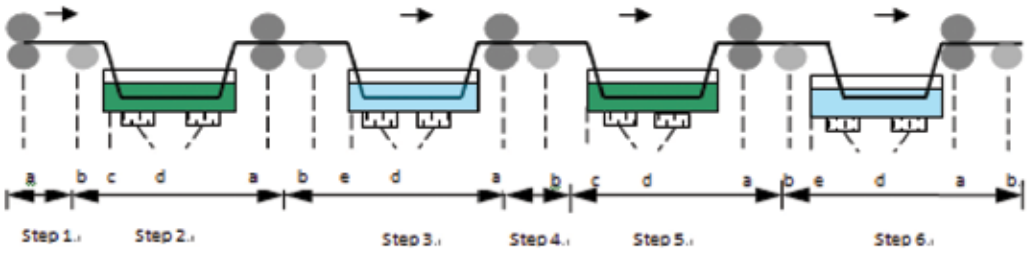

Figure 1: Schematic diagram of chromium tanning assisted by wringing and ultrasound a–wringing rolls; b–tray rolls; c–penetration tank; d–ultrasound source; e–fixation tank; '→' represents transfer of leathers with belts.

Scanning Electron Microscopic test (SEM)
A JSM-5900LV scanning electron microscope (Japan) was used for the analysis. The micrographs for the cross section were obtained by operating the SEM at low vacuum with an accelerating voltage of 20kV in different magnification levels.

Physical Properties Test
Both CAWU wet blue and control were finished in a normal shoe upper leather process. The final leathers were sampled and conditioned as the standard method.[12, 13] The physical properties of the leather were tested by tensile machine (AI-7000S) and the rub fastness was tested by measuring apparatus for color rub fastness (GJ9E1) following a standard method.[14, 15]

Analysis of Chromium in Spent Liquors
At the end of each tanning process, the penetration solution was analyzed for chrome content as the standard procedure.[16]

Results and Discussion

The Properties of Wet Blues by CAWU
The Cr_2O_3 content and Ts of wet blues by CAWU were showed in Figure 2 and Figure 3.

As shown in Figure 2, Cr_2O_3 content of all leathers were higher than 30mg/g. The Cr_2O_3 content of the first 10 times was higher than 33mg/g, but after ten times tanning, the Cr_2O_3 content in leathers trended going down. As shown in Figure 3, in the first 10 times, the Ts of leathers were higher than 100°C, and after 24h standing, the Ts of leathers were higher than 110°C, showing the leathers tanned with this method have no negative effects for at least 10 times tanning.

As shown in Table I, the Cr_2O_3 content decreased during the tanning process and the pH of fixation solution was dropped, too. With the increasing of tanning times, the synergy of decreased Cr_2O_3 content combination with dropped pH of fixation solution may be the reason of the Cr_2O_3 content decreasing and Ts of leathers dropping. At this time, the extra chrome powder should be added in the penetration float and the fixation float should also be replenished with sodium bicarbonate and sodium formate for recycling according to analysis data.

The Contrast of CAWU Wet Blues and Control
Cr_2O_3 Distribution
The results in Table II showed that the uniformity of control was better than CAWU. But the Cr_2O_3 content of every layer of the CAWU wet blue was higher than control's, especially the Cr_2O_3 content in middle layer of CAWU was higher than any layers of traditional wet blue. Also, the whole tanning time of CAWU was only 12min, indicating the synergy of cavitation effect combination with capillary action could obviously accelerate the speed of tanning.

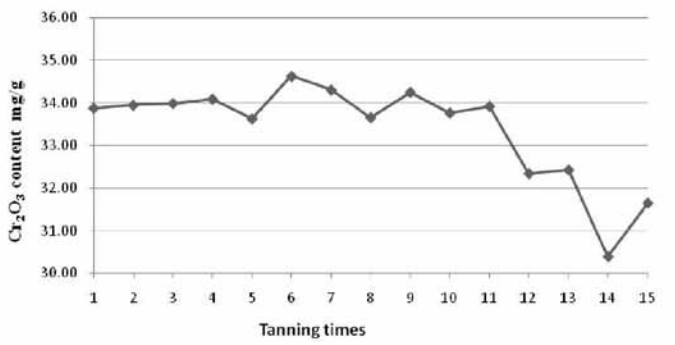

Figure 2 Cr_2O_3 content of each sample.

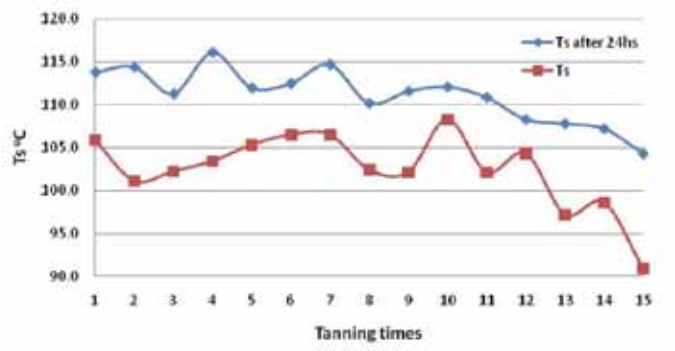

Figure 3 Shrinkage temperature of each sample.

TABLE I
Cr_2O_3 content of penetration solution and pH of fixation solution.

Tanning times	0	5	10	15
Cr_2O_3 content: mg/L	45.60	44.31	42.15	41.52
pH of fixation	8.02	7.91	7.74	7.18

TABLE II
Chrome content distribution in leather.

Sample	Grain: mg/g	Middle: mg/g	Flesh: mg/g	Uniformity: %
CAWU	34.57	27.64	32.62	82.27
control	27.08	25.75	26.09	96.86

TABLE III
Properties contrast of two wet blues.

Sample	Ts (°C)	Tensile strength (Mpa)	Elongation at break (10N%)	Tear strength (N/mm)	Rub fastness
CAWU	105.2	13.77	40.10	56.17	5
control	103.5	10.67	47.20	56.98	5

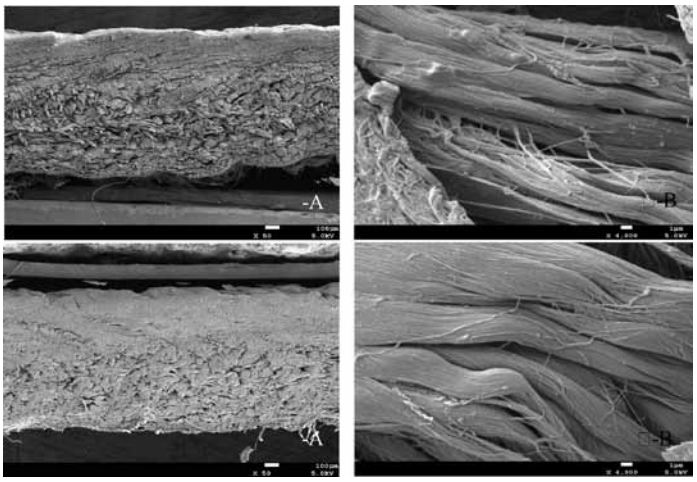

Figure 4 SEM images of the cross section of the wet blues ① represented CAWU wet blue, (A) -50Å~ and (B)-4000Å~; ② represented the control, (A) -50Å~and (B)-4000Å~.

SEM Analysis

There was no evident difference for the structures of fiber between the two wet blues (Figure 4), which indicated that wringing and ultrasound in the new method could not make the structure of collagen fiber damaged. Also, since the cavitation effect of ultrasound, the porosity of CAWU wet blue was more than the control which could speed the penetration of tanning liquored.

Contrast of Physical Properties

As shown in Table III, there was no evident difference between CAWU wet blue and control, which indicated that wringing and ultrasound could not influence the physical properties of the CAWU wet blue.

Conclusions

A new chrome tanning method was designed with wringing and ultrasound, which could shorten the tanning time to 12min. The Ts of wet blue obtained by the method was higher than 100°C and Cr_2O_3 content was more than 30mg/g. Also, the fiber structure integrity was maintained and the leather had competitive properties compared with a conventional wet blue; showing this method will be applicable as a choice to future tanning industry.

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