Inverse Chrome Tanning Technology Based on Wet White Tanned by Al-Zr Complex Tanning Agent

by

Siwei Cai,[1] Yunhang Zeng,[1] Wenhua Zhang,[2] Ya-nan Wang[2] and Bi Shi[1, 2]*

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

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

Abstract

In conventional leather production, the chrome in wet blue will be inevitably released into all the floats in post-tanning processes, which brings about a big amount of chrome-containing wastewaters, which can be difficult to treat. As a solution to this problem, an inverse chrome tanning technology based on wet white tanned by Al-Zr tanning agent (AZ) was investigated in present work. The AZ was the co-complexes of Al^{3+} and Zr^{4+} (9:1, mole ratio) with polycarboxylic acids synthesized in our laboratory. The wet white tanned by AZ had a shrinkage temperature (Ts) of 95°C under optimal tanning conditions, and therefore, it met the needs of splitting and shaving operations without generation of chrome wastes. More importantly, the wet white was suitable to be followed by retanning, dyeing and fatliquoring processes because of its satisfactory thermal stability and analogous electric charge characteristic to chrome leather. After fatliquoring and fixing by acid, chrome tanning was undertaken as final step. The leather with Ts around 110°C and comparable physical and aesthetic properties to conventional chrome tanned leather was obtained when 0.5-1% Cr_2O_3 was used in this inverse chrome tanning technology. The evident advantage of this technology is that no chrome was discharged in whole leather making processes except final chrome tanning and washing processes, and as a result, the volume of chrome-containing wastewater was largely reduced and easier to collect for recovery.

Introduction

Conventional chrome tanning technology is still the most popular tannage in leather industry due to its convenient operations and the excellent properties of chrome tanned leather.[1,2] However, in recent years, the chrome discharge caused by the conventional chrome tanning has attracted more and more attention. The chrome discharge is mainly derived from following sources: (1) chrome-containing effluents discharged in chrome tanning and chrome retanning processes, whose chrome concentration and volume are usually 1000-4000 mg/L and 4-6 m^3 per ton of limed hide, respectively; (2) chrome-containing effluents discharged in post-tanning processes, whose average chrome concentration and total volume are about 100 mg/L and 25-30 m^3 per ton of shaved chrome leather, respectively;[3] (3) chrome-containing leather waste produced by shaving and trimming chrome leather.

The effluents with high chrome concentration discharged from chrome tanning and chrome retanning have received much attention from tanneries, and as a result, many techniques, such as recycling of used chrome liquor and recovery of chrome from used chrome liquor,[4] have been developed to efficiently reduce the discharge of chrome from these two processes. As for the post-tanning effluents, they have relatively lower concentration of chrome, but their total volume is quite large. Moreover, the chrome in the post-tanning effluents might form complexes with the residual post-tanning chemicals, which results in a significant increase in technical difficulty and cost in recovering the chrome from these effluents. So it is nearly impossible for tanneries to effectively recycle the chrome from all the post-tanning effluents. In fact, the post-tanning effluents are the major source of the chrome discharge at present, which make the chrome concentration in integrated wastewater of most tanneries much higher (>20 mg/L) than the industrial standard of chrome discharge. Meanwhile, the chrome-containing leather waste is always difficult to be treated. Hence, if the conventional chrome tanning technology continues to be used, excessive discharge of chrome will still baffle tanneries.

The chrome free tanning agents and tannages have been continuously developed to solve the problem of chrome discharge.[5-9] However, numerous practical applications showed that the leathers tanned by existing chrome free tannages do not possess comparable physical and aesthetic properties to chrome tanned leather at present. Although it is difficult to predict whether chrome free tanning is able to completely replace chrome tanning in the future, it is definite that the chrome

*Corresponding author, e-mail address: sibitannin@vip.163.com

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tanning will be still adopted for a long period of time. Therefore, an important issue is to effectively control the discharge of chrome while chrome is used in leather manufacture.

As mentioned above, the solution to the chrome discharge during post-tanning processes is crucial for leather industry in meeting the standard of chrome discharge. As we know, it is impossible to avoid chrome discharging from chrome leather into the post-tanning effluents. To solve this problem, an "inverse chrome tanning technology" was developed in our previous study, so as to keep the advantages of chrome tanning while eliminate the discharge of chrome.[10] Firstly, a "wet white" was obtained by tanning pelt with chrome free tanning agent that has good pre-tanning property and can endow wet white with a comparable positive charge to chrome tanned leather. Then, the wet white was shaved, trimmed and processed with post tanning processes. After dyeing and fatliquoring, chrome tanning was finally performed at the end. By using this technology, all the effluents discharged during leather making processes except the final chrome tanning didn't contain chrome and were easily treated. Although the effluent of the final chrome tanning still contained chrome, its volume was small, which can dramatically reduce management difficulty and treatment cost of wastewater. In addition, this technology prevented the generation of chrome-containing leather waste.

Our previous study indicated that the inverse chrome tanning technology based on the wet white tanned by an amphoteric organic tanning agent was successful in achieving comparable properties to conventional chrome leather, as well as avoiding generation of chrome-containing effluents during post-tanning processes.[11] However, the wet white tanned by the amphoteric organic tanning agent (TWT) cannot be directly traded like the wet blue because of its poor storage stability. Therefore, to ensure general applicability of the inverse chrome tanning technology, an Al-Zr complex tanning agent (AZ) was developed in our laboratory, which could be used for producing wet white with good storage stability and high absorption of post-tanning chemicals. In this work, the inverse chrome tanning technology based on the AZ tanned wet white was systematically studied.

EXPERIMENTAL

Materials

Common pickled sheepskins (pH 3.0) supplied by a local tannery were used for trials. Al-Zr tanning agent (AZ), the complex of Al^{3+} and Zr^{4+} (9:1, mole ratio) with polycarboxylic acids synthesized in our laboratory, was employed for preparation of wet white. The precipitation pH of AZ was 4.2. The chrome powder (Cr_2O_3 23%, 33% basicity) and chrome liquors (Cr_2O_3 8%) with 0%, 33%, 40%, 50% and 60% basicity prepared according to the methods described in the literature[12] were used for the final chrome tanning, respectively. All the chemicals used for leather processing were of commercial grade, and the chemicals employed for analyses of leathers and effluents were of analytical grade.

Preparation of Wet White

On the basis of our previous experiments, wet white was prepared by using the optimized chrome free tanning process as follows. The pickled pelt was tanned in the pickling liquor (pH 3.0) by 3% AZ (counted by metal oxide, based on weight of limed sheepskin) for 120 min. Then, the pH of liquor was basified to 3.8.

After tanning, the hydrothermal stability of the wet white (No. 1) was evaluated by measuring shrinkage temperature (Ts) using a standard shrinkage temperature recording instrument. The isoelectric point of the wet white was determined by SDBS adsorption method.[13] To investigate the storage stability, the wet white was stored and observed at 1, 2, 3 and 6 months.

Inverse Chrome Tanning Technology

The inverse chrome tanning technology is shown in Table I. The wet white obtained above (No. 1) was sammed, shaved and weighed, and then post tanning processes was performed followed by chrome tanning.

Conventional Chrome Tanning Technology

According to the conventional chrome tanning technology, pickled sheepskin was chrome tanned by using 6% chrome powder (23% Cr_2O_3, 33% basicity), rewetted, chrome retanned by using 4% chrome powder (23% Cr_2O_3, 33% basicity), neutralized, retanned and fatliquored. The rewetting, neutralizing, retanning and fatliquoring procedures were the same as those given in Table I. Moreover, the crust leather treated with the conventional technology was washed three times after fatliquoring, while that treated with the inverse chrome tanning technology wasn't washed after fatliquoring.

Absorption Capacity of Wet White to Post-tanning Chemicals

The concentrations of total organic carbon (TOC) in retanning effluent No.1 and fatliquoring effluent No.2 (named residual TOC concentration) were determined by using TOC/TN analyzer (LiquiTOC, Elementar, Germany). Meanwhile, the initial retanning and fatliquoring baths were prepared according to the formula in Table I, and their TOC concentrations were measured as initial TOC concentrations. The absorption capacity of wet white to retanning agents/fatliquors was calculated as:

$$\text{absorption capacity of wet white to post-tanning chemicals} = \frac{\text{initial TOC - residual TOC}}{\text{initial TOC}} \times 100\% \quad (1)$$

Besides, the absorption capacity of conventional chrome tanned leather to post-tanning chemicals was calculated by using the same procedures described above.

TABLE I
Inverse chrome tanning technology.

Process	Chemical	Temp./°C	Dosage/%	Time/min	Remark
Rewetting	Water	40	200		
	Formic acid		0.3	60	Drain
Washing	Water	45	200	10	Drain
Neutralizing	Water	40	200		
	$NaHCO_3$ + NaHCOO		1.5+0.5	60	Drain
Washing	Water	25	200	15×2	Drain
Retanning	Water	30-35	100		
	Acrylic resin		3	20	
	Dispersing syntan Melamine Amino resin		1 2 1.5		
	Dye		3	30	
	Mimosa		2	60	
	Formic acid		0.5-1	30	pH=4.0, effluent sampling (No. 1), drain
Washing	Water		200	15	Drain
Fatliquoring	Water	45-50	200		
	Compound fatliquors		12	60	Emulsified
	Formic acid		0.5	30	Effluent sampling (No.2), drain
Chrome tanning	Water	25	100		
	Chrome powder/chrome liquor		X [a]	120	
	$NaHCO_3$		Y [b]	30×3	pH=3.8-4.0
	Water	40	100	120	Effluent sampling (No. 3), drain
Washing	Water	25	200	15	Leather sampling (No. 2), effluent sampling (No. 4)
Horse up, drying and staking. Leather sampling (No. 3).					

[a]When chrome powder (33% basicity) was used, X represents the dosage of Cr_2O_3 and was 0.5%, 1.0%, 1.5%, and 2.0%, respectively. When chrome liquors with 0%, 33%, 40%, 50%, 60% basicity were used, X represents the dosage of Cr_2O_3 and was 1.0%.

[b]Y represents the dosage of sodium bicarbonate depended on the basicity and dosage of chrome tanning agent.

Physical Properties of Leathers

The Ts of leather No.2 was evaluated using a standard shrinkage temperature recording instrument. Leather No.3 was first conditioned at 20°C and 65% relative humidity for 48h, and then their physical properties such as tensile strength and tear strength were tested according to ASTM standard method.

Concentration of Chrome in Effluents

The final chrome tanning effluent No. 3 and the washing effluent No. 4 were taken for the determination of chrome concentration. 10 mL of the effluents were digested by 5 mL of 30% H_2O_2 and 10 mL of 65% HNO_3, and then the concentration of chrome in the digestion liquor was determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 2100DV, PerkinElmer, USA). The chrome content per unit volume of effluent was calculated, and the absorption extent of chrome was evaluated as:

$$\text{Absorption extent of chrome} = \left(1 - \frac{C_3 + C_4}{C_{initial}}\right) x100\% \qquad (2)$$

where C_3 is the chrome concentration (mg/L) in the final chrome tanning effluent No. 3. C_4 is the chrome concentration (mg/L) in the washing effluent No. 4. $C_{initial}$ is the initial chrome concentration (mg/L) of the final chrome tanning bath. 0.5, 1.0, 1.5 and 2.0 g of Cr_2O_3 were dissolved in 200 g of water, and the concentrations of chrome in these solutions were used as $C_{initial}$.

The effluents of all processes in the conventional chrome tanning technology were taken for determination of chrome concentration. Additionally, the absorption extent of chrome in chrome leather was calculated using the same procedures described above.

RESULTS AND DISCUSSION

Properties of Wet White

As mentioned previously, the purpose of this study was to develop an inverse chrome tanning technology with general applicability based on wet white that has good storage stability and sufficient absorption capacity for post-tanning chemicals. For this purpose, we first need to obtain wet white with appropriate properties. The Ts of AZ tanned wet white was found to be 95°C, which met the needs of splitting and shaving operations. The ionic charge of wet white is an important factor influencing the absorption extent of anionic post-tanning chemicals by wet white. So the isoelectric point (pI) of the AZ tanned wet white was determined. As shown in Figure 1, the pI of the wet white was about 7.1, which was slightly lower than that of common wet blue (7.7-7.9)[12]. The result suggests that the wet white possesses positive charge during post-tanning processing (usually undertaken in the pH range of 4.0-6.0) and could take up enough post-tanning chemicals. Furthermore, after storage for 6 months, the wet white wasn't moldy and almost kept the same color and sensory properties, which indicates that the AZ tanned wet white possesses better storage stability compared with the wet white tanned by using amphoteric organic tanning agent.

Absorption Capacity of Wet White to Post-tanning Chemicals

It is well known that most of the present post-tanning chemicals are developed based on the applicability for conventional chrome tanned leather. Hence, the absorption capacity of wet white to the post-tanning chemicals definitely decides whether chrome tanning would be successfully transposed to the end of the post tanning processes.

As shown in Figure 2, the absorption extent of retanning agents and fatliquors by the AZ tanned wet white were as much as 88.1% and 81.9%, respectively. These absorption levels were slightly lower than those by the chrome leather (90.5% and 86.4%), but they could meet the demand of leather production. The results were due to the fact that AZ, as a kind of metal tanning agent similar to chrome tanning agent, was prone to react with carboxyl groups of collagen, and as a result, the AZ tanned wet white had positive charges analogously to chrome leather, which favors the combination of wet white with anionic post-tanning chemicals. Compared with the chrome leather, the slightly lower absorption capacity of wet white to post-tanning chemicals may be attributed to its less positive charges (slightly lower pI value). It can be postulated that the absorption levels of post-tanning chemicals could be further improved if suitable amphoteric auxiliary or retanning agent is employed in post-tanning processes. We will investigate this assumption in the

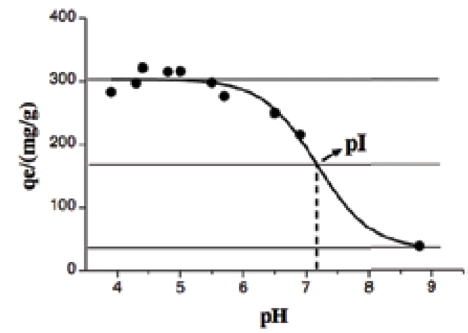

Figure 1. The isoelectric point of AZ tanned wet white (qe represents the equilibrium adsorption amounts of SDBS at different pH.)

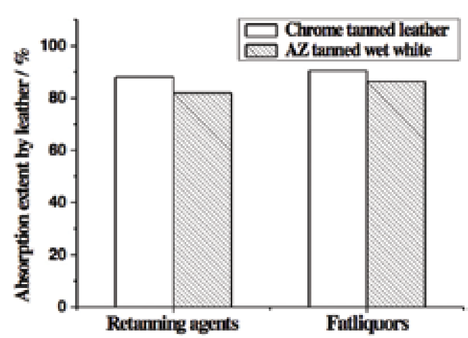

Figure 2. Absorption capacities of chrome leather and wet white to post-tanning chemicals

next work. Overall, the AZ tanned wet white had a satisfactory absorption capacity to post-tanning chemicals and could provide a good basis for the inverse chrome tanning technology.

Effects of Dosage and Basicity of Chrome Tanning Agent on Properties of Leather

The AZ tanned wet white was subsequently treated by post tanning processes and finally chrome tanned according to the procedures in Table I. The effect of dosage of chrome tanning agent (33% basicity) on properties of the leather were first investigated. As shown in Figure 3(a), the Ts of the leathers was above 100°C even when only 0.5% Cr_2O_3 was employed in the inverse chrome tanning technology, which should be due to the fact that the AZ tanned wet white itself had a high hydrothermal stability (Ts=95°C). The increase in dosage of Cr_2O_3 in the final chrome tanning exhibited positive effect on the Ts of leathers. The Ts of the leather was around 120°C when 2.0% Cr_2O_3 was used, which was comparable to that of the leather (121°C) processed by the conventional chrome tanning technology (i.e. chrome tanning with 1.5% Cr_2O_3 followed by chrome retanning with 1.0% Cr_2O_3). Obviously, the inverse chrome tanning technology can satisfy the requirement for thermal stability of leather. As can be seen in Figure 3(b) and 3(c), the tensile strength and tear strength of leathers tanned by using different dosages of Cr_2O_3 were a little changed in the inverse chrome tanning technology. However, it should be noted that, by using inverse chrome tanning technology, the tensile strength of leather was slightly higher than that of the leather processed by conventional chrome tanning technology (8.9 N/mm), while the tear strength was lower than that of the conventional leather (57.6 N/mm^2). These results might be caused by the change of the object reacting with chrome in the inverse chrome tanning technology. In conventional chrome tanning, chrome mainly reacted with skin collagen. But in the inverse chrome tanning technology, chrome was prone to react with post-tanning chemicals on the surface of collagen, besides skin collagen. As a result, the cross-linking density between collagen fibers would increase, although some of the cross-linking reactions were relatively weaker, which might be the reason for increase of tensile strength and decrease of tear strength. The mechanism of chrome reaction in this new system will be further investigated in our future work.

In consideration of the difference in the tanning circumstance between conventional chrome tanning and inverse chrome tanning, it is necessary to reconsider the influence of status of chrome species on tanning effect. As we know, the basicity of chrome tanning agent significantly affects the molecular dimension and reactivity of chrome complex. So the chrome liquors with different basicities (0%, 33%, 40%, 50% and 60%) were used in the final chrome tanning in our experiments. It is shown that the Ts of leathers tanned by using chrome liquors with different basicities were not significantly different (Figure 4(a)). But the basicity of chrome liquors obviously influenced the tensile strength and tear strength of leathers (Figure 4(b) and 4(c)). The optimal physical properties of leathers were obtained when the basicity of chrome liquors was 40%. We know that a rational basicity of chrome liquor is required for chrome tanning in order to well balance its penetration in pelt and reaction with collagen. The optimal basicity of chrome liquor is 33% in conventional chrome tanning. As for inverse chrome tanning, the wet white has been pre-tanned, retanned and fatliquored, and therefore, the collagen fibers were well scattered compared with those in pelt. So the chrome tanning agent with bigger molecular dimension and higher reactivity (at 40% basicity) were more suitably employed in inverse chrome tanning. But, when the chrome liquors with higher basicity (50% and 60%) were used, the molecular dimension of chrome complexes was too big to evenly penetrate in the wet white, which might be the reason leading to the decline of physical properties of leathers.

Discharge of Chrome

As shown in Figure 5, the absorption extents of chrome in the inverse chrome tanning technology were all above 90%. Particularly, the absorption extents of chrome were as high as 97.57% and 95.77% when 0.5% and 1.0% Cr_2O_3 were used,

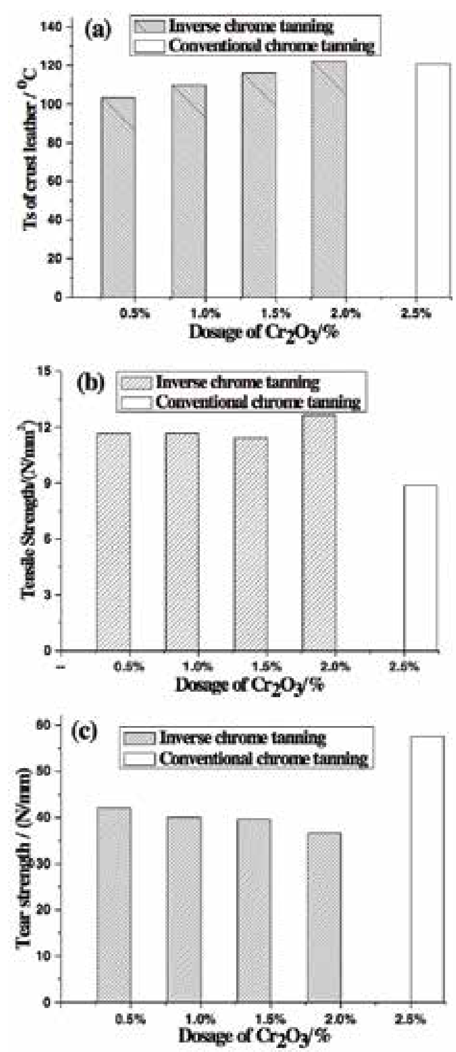

Figure 3. Effect of dosage of chrome tanning agents on leather properties: (a) shrinkage temperature, (b) tensile strength, (c) tear strength (conventional chrome tanning: tanning with 1.5% Cr_2O_3 followed by retanning with 1.0% Cr_2O_3).

where the Ts of leathers were 103.5°C and 110.0°C, respectively, as shown in Figure 3(a). The absorption extent of chrome in the inverse chrome tanning technology was obviously higher than that in conventional chrome tanning (around 80%). This may be due to the fact that chrome not only reacted with collagen, but also with post-tanning chemicals. The high absorption extent of chrome favors reduction in chrome discharge.

It is worth noting that the volume of chrome-containing effluents discharged from chrome tanning and all post-tanning processes in conventional technology was approximately 29 ton per ton of shaved chrome leather, and nearly 85% of the chrome-containing effluents were generated in the post-tanning processes (Table II). The effluents discharged from the post-tanning processes are difficult to manage and treat, because they have large total volume and low chrome concentration. As for inverse chrome tanning technology, only 4 ton of chrome-containing effluents were generated when 1 ton shaved wet white was processed (Table III). Compared with the conventional technology, the amount of the chrome-containing effluents in the inverse chrome tanning technology was reduced by about 86%, since the chrome-containing effluents were only generated in the final chrome tanning and the subsequent washing processes. As a result, it is easy to collect and recycle chrome with mature treatments.

Generally, our experiments showed that, depending on basicity and dosage of chrome tanning agents, the chrome concentration in the effluents discharged from the inverse technology was in the range of 21 - 310 mg/L, and the total chrome output was in the range of 0.1 - 1.3 kg/ton shaved wet white. As for the conventional technology, the average chrome concentration in effluents and the total chrome output were 307 mg/L and 8.9 kg/ton shaved chrome leather, respectively (Table II). These results indicated that the chrome output could be at least reduced by 85% by using the inverse technology, mainly due to the decrease in chrome dosage and the higher utilization efficiency of chrome in the inverse technology.

CONCLUSIONS

The wet white tanned by Al-Zr complex tanning agent (AZ) has satisfactory properties ensuring shaving and post-tanning processing, and therefore, provides a good basis for undertaking inverse chrome tanning technology. Moreover, compared with the wet white tanned by organic tanning agent, the AZ tanned wet white has much better storage stability, which ensures the general applicability of the inverse chrome tanning technology.

The inverse chrome tanning technology developed in this research has presented significant advantages, such as small volume of chrome-containing effluents, low chrome output and manageable chrome-containing effluents, which largely favors the reduction in chrome discharge from tannery.

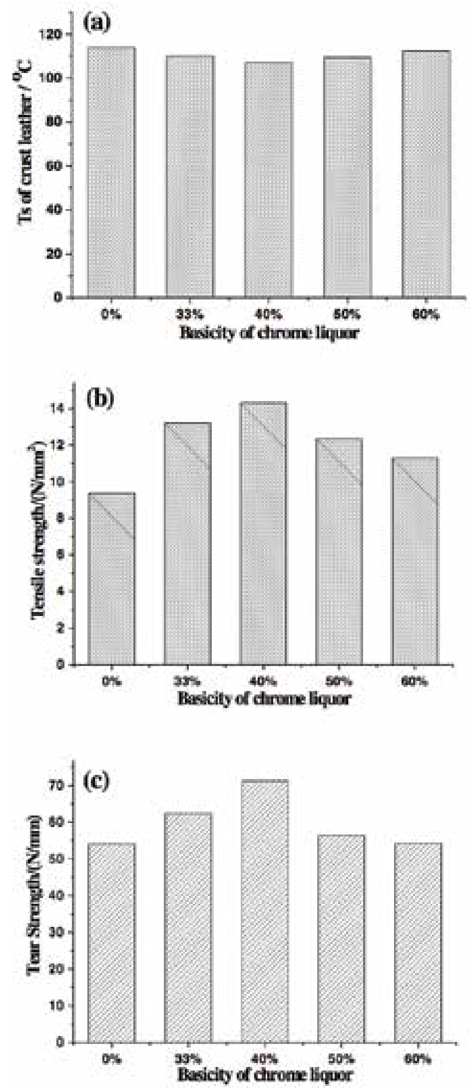

Figure 4. Effect of basicity of chrome tanning agents on leather properties: (a) shrinkage temperature, (b) tensile strength and (c) tear strength (Cr_2O_3 dosage 1.0%)

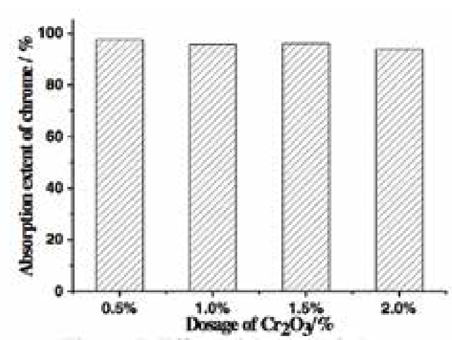

Figure 5. Effect of dosage of chrome tanning agent on absorption extent of chrome in the inverse technology

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TABLE II
Chrome discharge from conventional chrome tanning technology.

Sample of effluent	Concentration of chrome (mg/L)	Amount of effluent (ton)	Chrome output (g/ton shaved chrome leather)
Chrome tanning	950	6.0	5700
Rewetting	633	2.0	1266
Chrome retanning+ Washing	459	4.0	1836
Neutralizing+ Washing ×2	3	6.0	18
Retanning+ Washing ×1	12	3.0	36
Fatliquoring+ Washing ×3	6	8.0	48
Total		29.0	8904

TABLE III
Chrome discharge from inverse chrome tanning technology.[a]

Sample of effluent	Chrome conc. in various offers (mg/L)				Amount of effluent (ton)	Chrome output in various offers (g/ton shaved wet white)			
	0.5%	1.0%	1.5%	2.0%		0.5%	1.0%	1.5%	2.0%
Chrome tanning	27	92	131	275	2.0	54	184	262	550
Washing	15	53	74	158	2.0	30	106	148	316
Total					4.0	84	290	410	866

[a]Using chrome powder of 33% basicity.

REFERENCES

1. Suparno O., Covington A. D., Evans C. S.; Novel combination tanning using diphenols and oxazolidine for high stability leather. *J. Soc. Leather Technol.Chem.* **91**, 188-192, 2007.
2. Nishad Fathima N., Madhan B., Raghava Rao J., *et al.*; Mixed metal tanning using chrome-zinc-silica: A new chrome-saver approach. *JALCA* **98**, 139-146, 2003.
3. Zhou, J., Hu, S. X., Wang, Y. N., *et al.*; Release of chrome in chrome tanning and post tanning processes. *J. Soc. Leather Technol.Chem.* **96**, 157-162, 2012.
4. Kakakhel L., Lutfullah G., Bhanger M. I., *et al.*; Electrolytic recovery of chromium salts from tannery wastewater. *J. Hazardous Mater.* **148**, 560-565, 2007.
5. Nishad Fathima N., Prem Kumar T., Ravi Kumar D., *et al.*; Wet white leather processing: A new combination tanning system. *JALCA* **101**, 58-65, 2006.
6. Madhan B, Rao J. R., Nair B. U.; Tanning agent based on mixed metal complexes of aluminum and zinc. *JALCA* **96**, 343-349, 2001.
7. Fan, H. J., Li, L., Shi, B., *et al.*; Characteristics of leather tanned with nano- SiO_2. *JALCA* **100**, 22-28, 2005.
8. Fan, H. J., Shi, B., He, Q., *et al.*; Tanning characteristics and tanning mechanism of nano- SiO_2. *J. Soc. Leather Technol. Chem.* **88**, 139-142, 2004.
9. Gregori J., Marsal A., Manich A. M., *et al.*; Optimization of the chrome tanning process: influence of three types of commercially available masking agents. *J. Soc. Leather Technol.Chem.* **77**, 147-150, 1993.
10. Wu, C., Zhang, W. H., Liao, X. P., *et al.*; Transposition of chrome tanning in leather making. *JALCA* **109**, 176-183, 2014.
11. Shi, B., Li, J., Wang, Y. N., *et al.*; A novel wet white technology based on an amphoteric organic tanning agent. Taipei: 9th AICLST Congress, 1-18, 2012.
12. Zhang, M. R., Chen, W. Y.; Tanning chemistry. Beijing: China Light Industry Press Inc., pp. 51-53, 1999. (In Chinese)
13. Sun, Q. Y., Wang, Y. N., Liao, X. P., *et al.*; SDBS Adsorption method: a new method for determination of isoelectric point of skin and leather. *China Leather* **42**, 9-18, 2013. (In Chinese)