A Novel Approach to Clean Tanning Technology

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Abstract

Traditional chrome tanning technology is still widely used today. In this technology, chrome shaving as well as chrome contained effluent in tanning and retanning processes is a big issue in the industry. Wet white tanning technology has been gaining in importance in recent years, but in general, the comprehensive performance of chrome-free tanned leather is not comparable with that of chrome tanned leather. In the present work, chrome-free tanning and chrome tanning are combined in a reversed procedure, which produces leather with chrome tanned leather quality without chrome tanned leather waste problems. In this procedure, a special chrome-free tanning agent TWT was used to tan delimed hides (no pickle) making wet white with shrinking temperature at 80-85°C. Then, new method called reversed tanning further process the wet white into chrome-tanned crust. In this reversed method, retanning, fatliquoring and coloring processes were carried out before chrome tanning. This technology eliminates chrome waste issue in tanning, shaving, post tanning processes. The chrome contained effluent is only concentrated in the last chrome tanning process. The leather made with this technology has complete conventional chrome-tanned leather quality. In this way, chrome leather quality without chrome waste problems was achieved. So it is a new clean tanning technology.

Key words: Chrome-free tanning, wet-white, reversed tanning process, chrome tanning, post tanning

1. Introduction

Up to now, chrome tanning is still the most important and most widely used tanning method in leather industry due to its outstanding leather quality and competitive price.[1-4] Approximately 90% raw hides and skins are tanned by chrome in the world.[5] However, Chrome tanning is controversial because of chrome waste pollution issue. In the conventional chrome tanning processes, only 60-70% of added chrome is absorbed by leather, the rest is discharged into waste effluent, which results in serious environment pollution.[6] Therefore, many tanners have focused on the improvement of chrome tanning technology in recent years, such as high chrome exhaustion systems,[7, 8] which can achieve a chrome absorption of 80-90%.[9] Recovery and reuse of chrome tanning wastewater are capable of effectively minimizing chrome discharge.[10, 11] However, chrome will be still released from wet blue in the post tanning processes such as setting out, washing, chrome retanning, neutralizing, retanning, dyeing, fatliquoring and so on. The study of Dr.Shi' s team shown that the effluent in each step contains different amount of chrome due to the existence of free and unstably combined chrome in chrome tanned leather.[12] Those chrome combined with fat compounds, retanning materials and dye stuff in the post tanning effluent make the effluent treatment very difficult and very cost[12]. Also the chrome tanned leather shaving, trimming materials are chrome contained waste. With respect to the disposal of these wastes, there are tightening

regulations in most countries, and it is increasingly difficult for leather industry to comply with the emerging regulations.[13] Chrome-free tanning technology has been gaining in importance in recent years. The chrome-free tanning agents commonly used are glutaraldehyde, modified glutaraldehyde, organic phosphonium salt, oxazolidine compounds and so on. However above tanning agents have various problems, such as pungent odor, high free formaldehyde content, low hydrothermal stability, yellowing, high price, etc. In addition**,** the tanning by above organic tanning agents increases the electronegativity of tanned leathers. This will hinder the uptake of anionic chemicals, such as dyestuffs and fatliquoring agents during post tanning processes and thus lead to poor quality of finished leather. So the comprehensive performance of chrome-free leather is not comparable with that of chrome leather.[14-16]

Aim to above problems of chrome-free tanning, Tingjiang New Material, Inc. produced a novel chrome-free tanning agent TWT which is an amphoteric organic compound. TWT can be used to tan delimed hides directly without pickling to produce wet white with shrinking temperature of 80-85°C. More importantly, wet white tanned by TWT possess moderate amphoteric property like wet blue, which makes the exhaustion of retanning agents, fatliquor and dye stuff very good during post tanning. The performance of TWT chrome-free leather is comparable with that of chrome leather but with a shrinkage temperature$<$90°C. Therefore, a navel approach, a reversed tanning process was carried out to improve the shrinkage temperature of TWT wet white.

In the present work, chrome-free tanning and chrome tanning are combined in a reversed procedure, which produces leather with chrome tanned leather quality without chrome tanned leather waste problems. In this reversed tanning procedure, TWT was firstly used to tan delimed hides to make wet white; then, shaving, washing, retanning, fatliquoring and coloring were followed. At the end, after acidification, wash, refloat and chrome tanned. This technology eliminates chrome waste issue in chrome tanning, shaving, and post tanning processes. The chrome contained effluent is only concentrated in the last process step. The amount of effluent is little and easy to collect and treat. The leather made with this technology has complete conventional chrome-tanned leather quality. In this study, the tanning performance of TWT was investigated to optimize the conditions of wet white tanning process. Then a novel reversed tanning technology was developed.

2. Experiments

2.1 Materials and instruments

Chrome-free tanning agent TWT was of commercial grade and produced by Tingjiang New Material, Inc. The other chemicals used for leather processing were of commercial grade. Instruments used for analysis were as below: Scanning Electron Microscope (SEM, JSM-7500F, JEOL, Japan), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 2100DV, PerkinElmer, USA), Yellowing Testing Machine (HT-8247A, Hung Ta Instrument Co. Ltd.,Taiwan).

2.2 TWT wet white tanning process

2.2.1 Effect of tanning pH on shrinkage temperature of wet white

Five pieces of pickled goat pelts were used to study the effect of tanning pH on shrinkage temperature of wet white. The offers of chemicals were based on lime weight, similarly hereinafter. The pelts were depickled in 100% pickle liquor at 20°C for 20min, and sodium bicarbonate or sodium carbonate was used to adjust the pH of float to 4, 5, 6, 7 and 8, respectively. Then tanning was carried out using 4% TWT for 2h. Then temperature rose to 40°C, and pH rose to 8.0. After running for 4h, the drums were stopped overnight. Next day, the shrinkage temperatures of wet whites were measured after running for 30min.

2.2.2 Effect of tanning temperature on shrinkage temperature of wet white

Eighteen pieces of pickled goat pelts were used for investigating the effect of tanning temperature on shrinkage temperature of wet white. The pelts were depickled in 100% pickle liquor at 20°C for 20min, and then pieces were divided into 6 groups, and pH was adjusted to 5.5, 6.0, 6.5, 7.0, 7.5 and 8.0, respectively. Then each group (three pieces) was tanned by 4% TWT for 2h. After that each group was divided into three once more, and the tanning temperature rose to 30, 35 and 40°C, respectively. Shrinkage temperatures of wet whites were measured after running for 4h.

2.2.3 Effect of tanning time on shrinkage temperature of wet white

A piece of limed goat pelt were delimed, bated and washed at first. Then it was tanned by 4% TWT in 50% float for 2h. After that 100% hot water was added, and the temperature rose to 40°C. The shrinkage temperature of wet white was measured every hour for 5 hours.

2.2.4 Effect of TWT dosage offer on shrinkage temperature of wet white

The limed goat and cattle pelts were delimed, bated and washed at first. Then they were separately tanned by using different dosage of TWT (2%, 3%, 4%, 5% and 6%, respectively) in 50% float. The duration was 2h for goat pelts and 4h for cattle pelts. After that100% water was added, and the temperature rose to 40°C. The shrinkage temperature of wet white was measured after tanning for 3hours.

2.3 Analysis of physicochemical properties of wet white

2.3.1 Acute oral toxicity of wet white

The test of acute oral toxicity in rat of wet white tanned by TWT was performed using standard method by College of Public Health at Sichuan University.

2.3.2 SEM analysis of wet white

The wet white was dried in the air. Then its grain and cross section were observed by using SEM.

2.3.3 Yellowing analysis of wet white

The yellowing property of wet white was measured by using yellowing testing machine, and the testing conditions were that wet white is under ultraviolet light at 56±1°C for 6h. The

resistance to yellowing grade was evaluated by using gray sample card(GB 250-1995; grade 5: best; grade 1: worst).

2.3.4 Storage stability of wet white

The wet white was stored in sealing bag, and the air was replaced for two times in every week. The shrinkage temperature of wet white was measured every 15 days.

2.4 Reversed tanning process

The cattle wet white tanned by 5% TWT was shaved to 1.0 mm. The reversed tanning was carried out as described in table I.

Table I Reversed tanning process of wet white

Process	Chemicals	Dosage (%, based on shaved weight)	Temperature (^oC)	Time (min)	Remarks
Washing	Water	200	R.T	10	
Rewetting	Water	150	40		
	Degreasing agent	1		30	pH 5.0-5.5, drain
Washing	water	200	R.T	10	
Retanning	water	100	35		
	Acrylic resin	6		60	
	Syntan 1	10		45	
	Syntan 2	6		45	
	Formic acid	1		30	pH 4.0
Dyeing	Water	100	50		
	Dye stuff	x		60	
Fatliquoring	Water	100	50		
	Fatliquoring agents	8			
	Formic acid	1		15×3	pH 3.4-3.6, drain
washing	water				Collect all water
Chroming	Refloat water	100	R.T		
	Chrome powder ($Cr_2O_3$24%)	6		90	
	Sodium formate	1		30	
Adjust Ph	$NaHCO_3$	1.2		Three feeds	pH 4.0
	Water	100	40	60	Next day run for 20 min and drain.

2.5 Determination of chrome concentration in wastewater

Wastewaters from tanning and post tanning processes were collected and filtrated. Then the chrome concentration was tested by using ICP-AES.

3. Results and discussion

3.1 TWT wet white tanning process

3.1.1 Effect of tanning pH on shrinkage temperature of wet white

Figure 1 shows the effect of tanning pH on shrinkage temperature of wet white. Obviously, the shrinkage temperature of wet white increases as pH rose. When the tanning pH was higher than 7, a shrinkage temperature around 90°C is achieved, indicating the strong tanning ability of TWT. The mechanism of tanning by TWT is that the aldehyde groups of TWT react with the amino groups on side chains of collagen to form effective cross-links between collagen fibers. The number of free amino groups on the side-chain of collagen increases as pH rose, which favors the tanning reaction of amino groups with TWT. Therefore, the optimal pH for tanning is 7-8 in terms of shrinkage temperature, which is just the pH of bated pelt. This fact makes it possible to perform non-pickling tanning by using TWT.

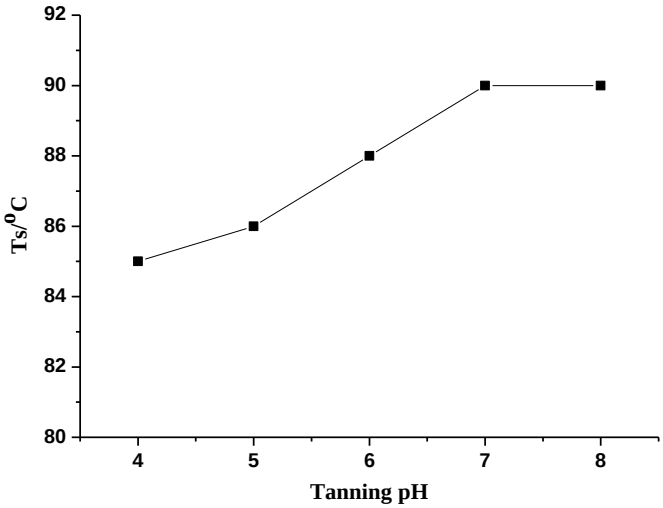


Figure 1. Effect of tanning pH on shrinkage temperature of wet white

3.1.2 Effect of tanning temperature on shrinkage temperature of wet white

Effect of tanning temperature on shrinkage temperature of wet white is shown in Figure 2. Tanning temperature also influences the shrinkage temperature of wet white significantly. When tanning temperature was increased from 30°C to 40°C, shrinkage temperature rose by 10°C under the same pH. This may be due to the fact that raising of tanning temperature could promote the motion of molecules of TWT and increase the reactivity of aldehyde group, and hence a higher shrinkage temperature was obtained. This fact also reveals that TWT is a temperature-controlled tanning agent. The bated pelt can be directly tanned by TWT under room temperature to make the tanning agent penetrate into fiber network, then rise the temperature to enhance the tanning ability of TWT. This novel tanning method is easy to operate and control. Meanwhile, neutral salts/chloride produced by pickling can be eliminated.

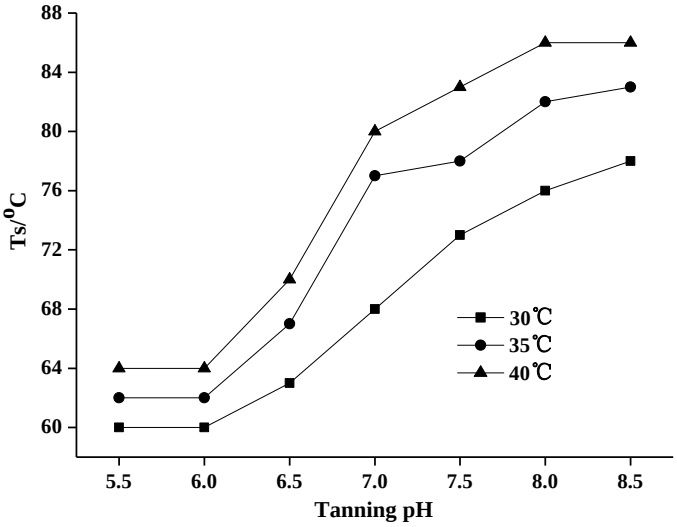


Figure 2. Effect of tanning temperature on shrinkage temperature of wet white

3.1.3 Effect of tanning time on shrinkage temperature of wet white

From Figure 3, we can see that the shrinkage temperature of wet white increases as the duration of tanning prolonged, and it remains stable after tanning for 3 hours. Therefore, the optimal duration of tanning is set to be 4-5 hours.

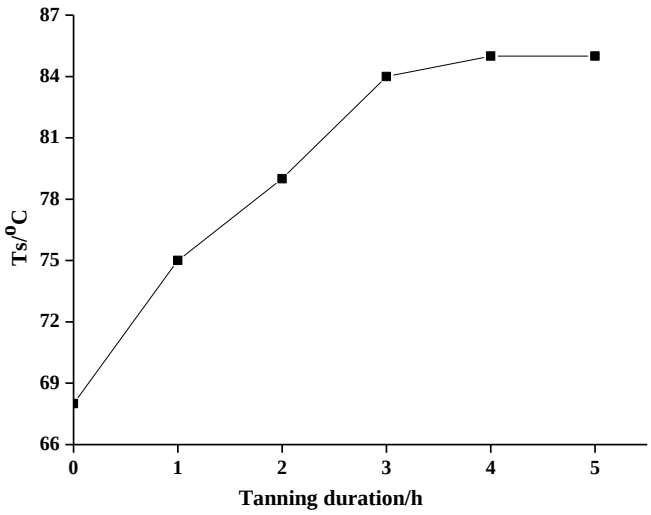


Figure 3. Effect of tanning duration on shrinkage temperature of wet white

3.1.4 Effect of TWT dosage offer on shrinkage temperature of wet white

The effect of TWT offer on shrinkage temperature of wet white is given in Figure 4. It can be seen that the shrinkage temperature of wet white increases with increasing the offer of TWT. It reaches 84 ^{o}C when the offer of TWT is 5% for goat skin, and 6% for cattle hide. The shrinkage temperature of cattle hide is lower than that of goat skin when the TWT offer was the same. This is because the fiber network of cattle hide is more compact than that of goat skin, so the penetration of macromolecular TWT in cattle hide is more difficult. In

consideration of both cost and tanning effect, the TWT offer is 4% for goat skin and 5% for cattle hide.

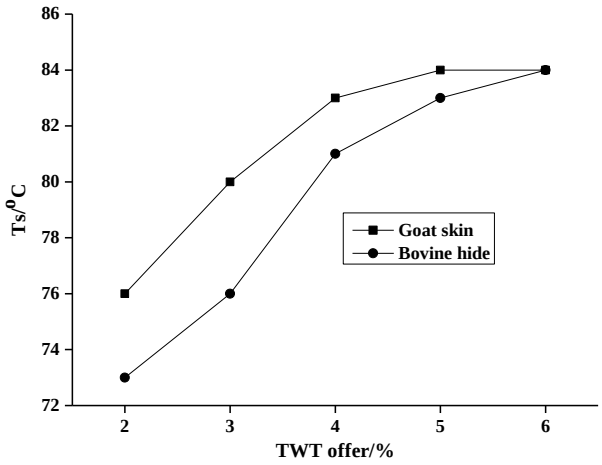


Figure 4. Effect of TWT offer on shrinkage temperature of wet white

3.2 The optimal TWT wet white tanning process

Based on the results above, the optimal tanning method by using TWT is summarized in Table II. It should be noted that TWT can be successfully used for non-pickling tannage. The shrinkage temperature of wet white was about 85°C. The handle of wet white was satisfactory in terms of grain smoothness, stability, fullness and softness.

Table II TWT wet white tanning process

Process	Chemicals	Dosage (%)	Temperature (°C)	Time (min)	Remarks
Tanning	Water	50	R.T.		pH:6-7
	Pre- Fat	0.5		20	
	TWT	4/5	R.T.	120/240	Goat skin: TWT 4%, 120 min Bovine hide: TWT 5%, 240 min
	NaHCO3			60	Adjust pH=7-8
	Hot water	100	38~40	120	Ts ≥ 80°C, drain
	water	100	R.T.		
	syntan	2		30	
	Preservatives	0.3		60	

3.3 Properties of wet white

3.3.1 Acute oral toxicity of wet white

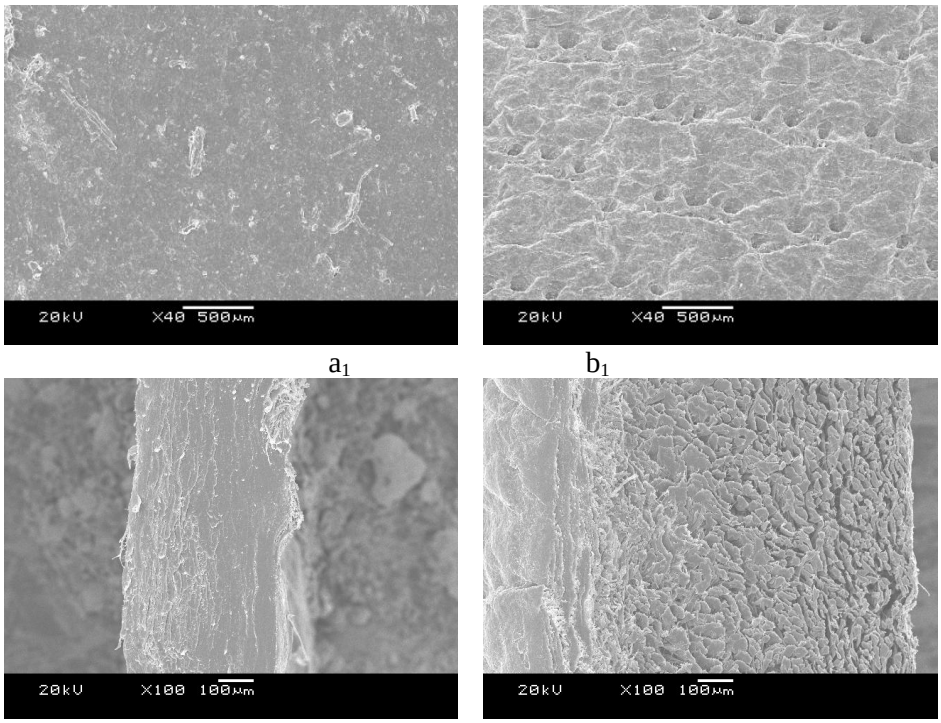
Table III shows that the wet white acute oral toxicity in rat, expressed as LD_{50}, is more than 5000 mg/kg. The rats were not poisoned or dead during experiment. This indicates that the wet white is low toxic, and the shavings derived from it can be recovered for producing industrial protein or other industrial products.

Table III Acute oral toxicity in rat of wet white

Gender	LD_{50} (mg/kg)
Male	>5000
Female	>5000

3.3.2 SEM analysis of wet white

From Figure 5, it can be seen that the significant differences between the bated pelt and wet white. After tanning by TWT, the pore on the grain layer is clearer than that before tanning (Figure 5 a_1 and b_1). The cross sections show that the fiber bundle is dispersed after tanning, whereas the fiber bundle of bated pelt before tanning is more compact. These facts indicate that TWT wet white leather has sufficient stability for splitting and shaving.



a_1 b_1 a_2 b_2

Figure 5. SEM images of cattle hide before and after tanning
(a_1: grain of bated pelt; b_1: grain after tanning; a_2: cross section of bated pelt; b_2: cross section after tanning)

3.3.3 Yellowing properties of wet white

In general, chrome-free leathers have no good resistance to yellowing. However, Table IV showed that the wet white tanned by TWT exhibit good result, the grade of resistance to yellowing reaches 4. So the wet white tanned by TWT can be used to produce white or pale colored leather.

Table IV Yellowing property of wet white

Kinds of wet white	Grade
Goat wet white	4
Cattle hide wet white	4

3.3.4 Storage stability of wet white

Wet white should have a good heat stability sufficient to allow splitting and shaving, and have sufficient mold resistance to permit short term storage.[17] The change of shrinkage temperature during storage was shown in figure 6, the shrinkage temperature of TWT wet white has no significant decline, and is higher than 80°C, and there is no obvious mold stain on surface of wet white. These phenomena indicate that TWT wet white possesses good storage stability.

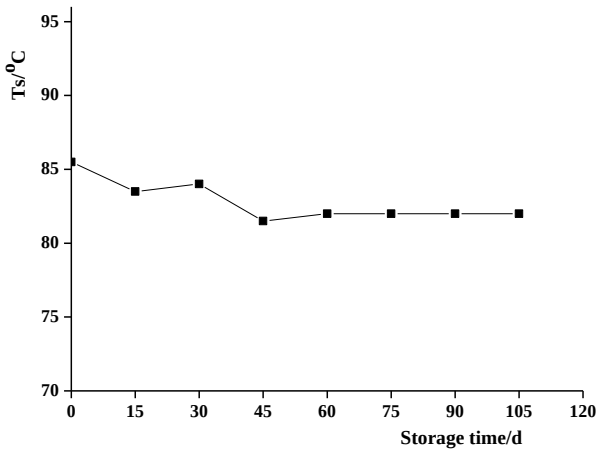


Figure 6. The effect of storage time on shrinkage temperature of wet white

3.4 Reversed tanning processes

In the reversed tanning processes, different kinds of retanning agents, filling agents, fatliquors and dye stuff and their combinations were applied to treat wet white to produce various type leather. Because of the amphoteric characteristics of TWT wet white, the exhaustion of those post tanning materials in the reversed tanning process were fairly good. Vegetable tannin materials show the best retanning filling, second is acrylic syntan, then, resin syntan ,e.g. Amino resin, phone resin, etc.. After wet-end process, the pH was adjusted to fix all anionic materials. Chrome tanning was followed. In the reversed tanning, chrome penetration, distribution and exhaustion and fixation were easy to control. The leather temper, softness, fullness, handles and feel can be adjusted according to different requests. The coloring process is trick. The color shade changed after chrome tanning in the reversed process. Different dyestuff showed different change pattern. The color fastness was slightly better compared with that of conventional chrome leather. Reversed tanned crust has stronger surface cationic charge characteristic than that of normal chrome crust. The adhesion of base coat on reversed tanned crust is slight better than that of normal chrome crust.

3.4.1 Basic comparison of two methods

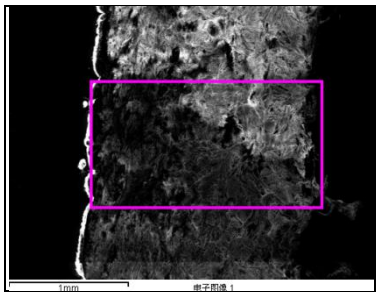
Table V Comparison of basic characteristics of two methods

Tanning methods	Chrome usage (Based on 100kg raw hide)	Ts	Content of Cr_2O_3 In effluent	Content of Cr_2O_3 in leather
Conventional Chrome tanning	8-10 kg	100-110℃	2~3 g/L	3.5~4.5%
Reversed Tanning	2.5-3.5 kg	＞100℃	0.4~0.6 g/L	1.8~2.2%

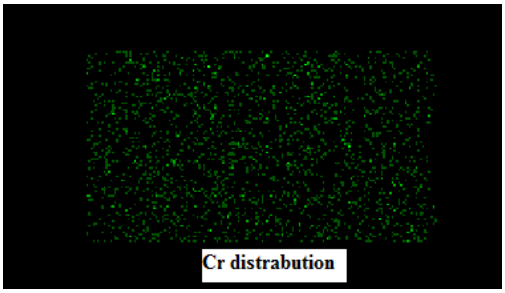
The basic characteristics of finished leathers are listed in table V. The Cr_2O_3 content in reversed tanned leather in lower than that in conventional chrome tanned leather. The amount of chrome powder usage in reversed tanning is about 35-40% of that in conventional chrome tannage. The shrinkage temperature of both leathers is close.

3.4.2 Chrome distribution inside finished leather

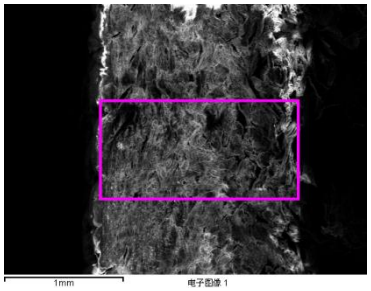
The scanning electron micrographs of leather cross section (a: conventional chrome tanning, b: reversed tanning) show both leathers present a compact fiber structure. Chrome distribution in conventional chrome tanning is much denser than that in reversed tanning. It can be seen that chrome distribution is uniform even though chrome usage is low and used at end of step in reversed tanning.



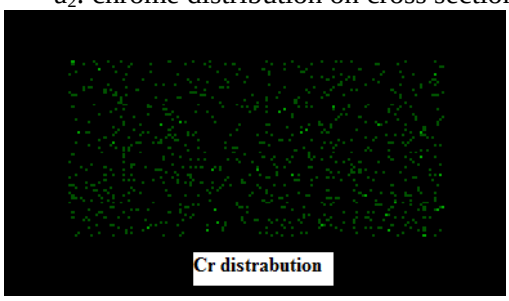
a_1: cross section



a_2: chrome distribution on cross section



b_1: cross section



b_2: chrome distribution on cross section

Figure 7. The cross section chrome distribution in finished leathers
(a: conventional chrome tanning; b: reversed tanning technology)

The analysis of chrome distribution inside leather is shown in the following Figure 8.

Figure 8 shows In the reversed tanning, chrome penetration is good and distribution is even. The flesh side has slight more chrome than middle and grain side, which is easy to explain. While, in conventional chrome tanning, middle section has more chrome content, which may be due to the retanning material on the surface more.

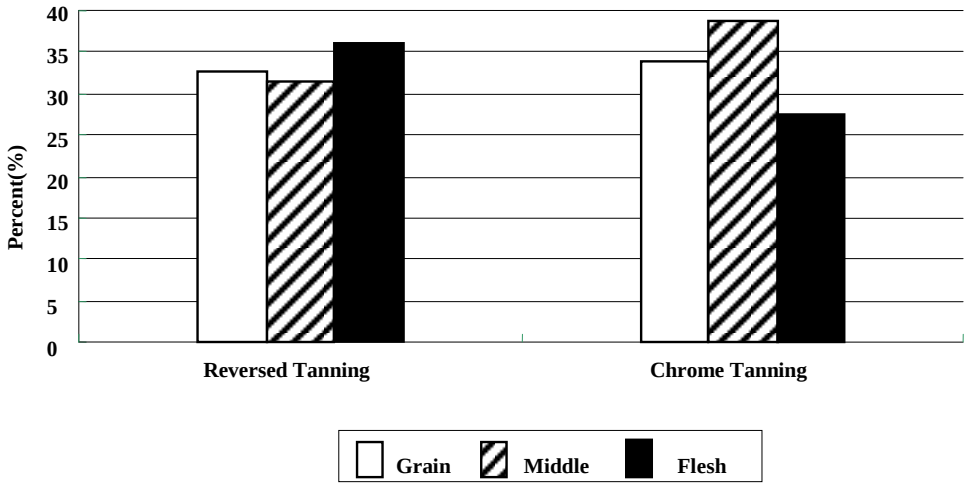


Figure 8 Chrome distribution inside leather (as Cr_2O_3%)

3.4.3 Comparison of mechanical properties

Table VI presents the mechanical properties of finished leathers. The results indicate that the mechanical properties of finished leather from reversed tanning are comparable with those of conventional chrome tanning.

Table VI Physical-mechanical properties of finished leathers

Sample	Tensile strength (M Pa)	Tear strength (N/mm)	Elongation at 10 N load (%)
Conventional chrome tanned	16.4	53.4	43.5
Reversed tanned	18.2	48.9	44.9

3.4.4 Evaluation of leathers

The assessment values of tanned leathers are shown in Figure 9. It can be seen that the fullness and grain smoothness of leather from reversed tanning are superior to that of conventional tanning. The conventional tanned leather has slight better break. In all, the general properties of leather made with reversed tanning are comparable to that of leather made with conventional tanning.

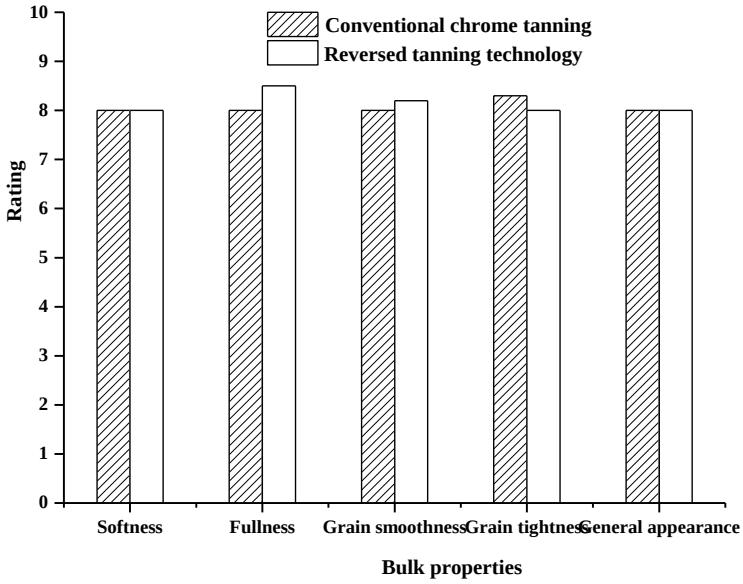


Figure 9. Evaluation of leather

3.4.5 Chrome distribution in the waste of tanning and post tanning processes

Table VII shows chrome distribution in the waste of tanning and post tanning processes of conventional chrome tannage and reversed tanning process. For conventional chrome tanning, tanning-rewetting processes contributed about half of the chrome released, and chrome concentration in chrome retanning wastewater was also quite high (2052 mg/L). In addition, the effluent from retanning, dyeing and fatliquoring processes contains different amount of chrome, which makes the effluent treatment very difficult. In contrast, In reversed tanning procedure, TWT was firstly used to tan delimed hides to make wet white; then, retanning, fatliquoring and coloring processes were carried out; in the end, chrome tanning was carried out. Therefore, The chrome contained effluent is only concentrated in the last process step, and chrome content is low (240 mg/L).

Table VII Chrome distribution in wastewater of tanning and post tanning processes (mg/L)

Process	Conventional chrome tanning[12]	Reversed tanning
Tanning	3446	0
Washing	805	0
Rewetting	659	0
Rechroming	2052	/
Neutralization	768	/
Washing	495	0
Retanning	200	0
Dyeing and fatliquoring	90	0
chroming	/	240

4. Conclusions

TWT wet white tanning optimal conditions are: offer dosage: 4-6% (based on delimed hides weight); float pH 7-8; Tanning time: 3-5 hours; float temperature: first room temperature for 2-3 hours, then 38-40°C for 2-3 hours;

TWT wet white has shrinkage temperature about 85°C, has amphoteric characteristics, fairly good resistance to heat and UV light, is low toxic, LD_{50} (mg/kg)>5000;

TWT wet white has good stability to shaving and splitting, good resistance to fungus and bacteria, has shelf life three to six months;

Reversed tanning process is a novel approach to clean tanning technology. Chroming was carried out in the last step of wet-end process. In the reversed tanning, chrome penetration, distribution and exhaustion are very good. This technology eliminates chrome waste in chrome tanning, shaving, trimming, and post tanning processes. The chrome contained effluent is only concentrated in the last process step. The amount of effluent is little and easy to collect and treat;

This process is flexible, versatile and easy to control. The leather performance is comparable to that of normal chrome leather and the leather characteristics can be tailored to specific requests.

This is likely to be an effective and feasible way to achieve clean chrome tanning.

5. Acknowledgments

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