

Minimization of Chromium Discharge in Leather Processing by using Methanesulfonic Acid: A Cleaner Pickling-masking-Chrome Tanning System

by

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Abstract

Chrome tanning is the most important and widely used tanning method in leather manufacture hitherto. However, chromium discharge may be a serious environmental concerned pollutant in leather processing, which originates from both chrome tanning and post-tanning operations. In order to minimize the emissions of chromium from the whole leather processing, a novel leather processing method integrating high chromium exhaustion and low chromium leaching-out based on the application of methanesulfonic acid (MSA) was designed and optimized. The results indicated that, being superior to the conventional processes, the chrome tanning and retanning processes with MSA were conducted at a high beginning pH (5.0) smoothly and the total chromium utilization ratio was increased to 95.8% from 81.0% in the novel processes. Accordingly, the total Cr dosage was decreased by 26.7% around, the residual Cr concentrations in each chrome-containing wastewater was decreased by 44%-85%, varying with the operations, and the total Cr discharge generated in the whole leather processing was reduced by 83.8% around, from 2.737 kg/t salted-wet hide to 0.443kg/t salted-wet hide before next chrome precipitation treatment. The area yields, mechanical properties and organoleptic properties of the leather from the new method were comparable with that from conventional processes.

Introduction

Chrome tanning is the technology of using a chrome tanning agent, basic chromium sulfate (BCS), to convert the pelts to leathers. Conventionally, in order to achieve good penetration of chromium into pelts, a “pickling-masking-tanning” process is adopted. The pelts are acidified to pH 2.5-3.2 with formic acid and sulfuric acid in slat solution before tanning, named pickling, to lower the reactivity of the carboxyl groups of collagen, and chromium complexions are also modified by added ligands, typically carboxylates, to reduce the affinities of them towards collagen, named masking.^{1,2} The relative affinities of ligands to chrome ions from potential masking agents are listed as follows: hydroxide > oxalate > citrate > lactate > malonate > maleate > phthalate > glycolate > tartrate > succinate > adipate > acetate > carboxyl of collagen > formate > sulfite > sulfate > chloride > nitrate > chlorate.¹ According to the above list, the affinity of formate to chromium ion is a little weaker than that of the carboxyl of collagen, so it is chosen as the dominant masking agent. However, only 60%-80% of the offering chrome is effectively utilized in the conventional chrome tanning process. As a result, the chrome concentration in spent float is in a range of 1,000-3,000mg/L,³ causing a significant disposal problem. Therefore, cleaner chrome tanning processing, i.e., maximizing the chrome uptake and minimizing the residual amount of chrome in floats, is a matter of great concern to all tanners.

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The low chrome utilization ratio in the conventional chrome tanning process can be probably attributed to that the lower affinity of the masked chromium complex ions with carboxyls of collagen side chain. The adding of organic acids in pickling and carboxylates during tanning introduces relatively large quantities of carboxylates into the tanning float, which may produce rather strong masking effects to chromium ions, resulting from the strong coordinating ability of carboxylates with chromium ion. Hence, the possibility of carboxyls of collagen entering into the inner spheres of chromium complex ions to substituted existing organic ligands is decreased accordingly. The uptake ratio of chrome is kept a rather low level. Many researches on optimizing masking agents have been done. Carboxylates with different molecular structure, including aliphatic and aromatic dicarboxylates,^{4,5} low molecular weight polyacrylates,⁶ and so on, were chosen as masking agents. Though these kinds of masking agents can increase the chromium exhaustion to a certain degree, it is difficult to achieve the chromium utilization ratio beyond 85%, and the leather is often negatively affected by the irrelevant application of the additives. Therefore, it may be deduced that the current pickling-masking-tanning system is not beneficial to high-exhaustion of chrome.

Theoretically, taking every effort to promote the reaction activity between chrome and collagen can improve the tanning effectiveness. For example, resulting from the increase of both the dissociation degree of carboxyl of collagen side chain and the hydrolyzation degree of chromium ion at a high pH, it is beneficial to the uptake of chromium by collagen when the bated pelts are directly chrome tanned or after preprocessed with syntans at a high beginning pH over 6.0,⁷⁻⁹ called non-pickling chrome tanning. However, the excessive fast combination of chromium on pelt surface will cause difficult penetration of chromium and bad hand feeling of leather when tanning at the high initial pH. Hence, to find a new kind of acid with weaker affinity to chromium than formic acid to establish a novel pickling-masking-chrome tanning system, which can well balance the competing process rates of Cr penetration and reaction with collagen when chrome tanning is conducted at a reasonably highly initial pH value, will be a possible approach to achieve high-exhaustion of chrome and minimize chrome discharge in chrome tanning.

Methanesulfonic acid (MSA) is a kind of organic strong acid. For there is an electron donor, methyl, connecting directly with sulfur atom, its pKa value (-0.6) is higher than sulfuric acid (pKa=-3.0), and much lower than formic acid (pKa=3.68) and acetic acid (pKa=4.76)¹⁰, thus the acidity of MSA is weaker than common inorganic acids, and stronger than most of organic acids. MSA has been used in electroplate industry to substitute sulfuric acid as it is considered as a "green acid" due to its environmental advantages: far less corrosive and easily

biodegradable.¹¹ Though the structure and geometric parameters of the Cr (III) complex ions of sulfate and methanesulfonate are rather similar, forming Cr (III) complexes is more easily in methanesulfonate solution than sulfate solution,¹² and Cr (III) complex ions in methanesulfonate are more stable.¹³⁻¹⁵ Therefore, the coordination ability of methanesulfonate toward Cr(III) is stronger than sulfate. It can be deduced that pickling with MSA has the potential to well balance the contradiction of the high-exhaustion and penetration of chromium during chrome tanning, theoretically.

According to the above analysis, a novel pickling-masking-chrome tanning system based on the application of MSA was designed to achieve the high-exhaustion of chrome. The process parameters were optimized, such as initial tanning pH value, dosage of chrome, and the leather quality was evaluated. The chrome discharge in the whole leather processes was also traced.

Experimentals

Materials and Instruments

Salted-wet cattle hides from Sichuan, China, were purchased from a local tannery (Chengdu Xinshi Leather Industry Co., Ltd.). Methanesulfonic acid (MSA, 70%) was offered by BASF-AE. Chromium (III) sulfate hydrate ($\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$, CP) was purchased from Aladdin Co.. Chromosal B (a chromium tanning agent with 33% of basicity and 26% of Cr_2O_3 content) was purchased from LANXESS Inc. The following applied leather chemicals, including syntans, fatliquors, polymers, filling agents, etc. were industrial grade and from Sichuan Dowell Science & Technology Co., Ltd. The other chemicals were analytic grade.

Ultraviolet and Visible Spectrophotometer (TU-1810PC, Beijing Purkinje General Instrument Co., LTD, China), Stainless Experimental Drum (GSD400-4, Wuxi Xinda Light Industry Machinery Co., Ltd. China), Inductively Coupled Plasma Emission Spectrometer (AES-ICP, 2100DV, Perkin Elmer Inc. America), Precision Slice Machine (C520L, Camog (a) Inc., Italy), Desktop Scanning Electron Microscope (Phenom Pro, Phenom World Inc., Netherland).

Evaluation of the Masking Effect of MSA to Chromium Ion

The appropriate chromium(III) sulfate hydrate (11.6g) was dissolved in deionized water (250.00ml) to get a solution with Cr concentration of was 0.2mol/L. Samples (20.00ml) were removed and mixed with MSA at different ratios. As a control, the molar ratio of formic acid to chromium was 1:1. The solutions were then aged by standing at room temperature (20-22°C) for 3 hours. A solution of NaHCO_3 (5%, w/w) was added slowly with magnetic stirring for 30min to adjust the pH to 4.0. The total volumes were diluted to 100.00ml respectively. Have been aged

for 12 hours at 40°C, the ultraviolet-visible spectrum analysis was conducted at the wave lengths from 700nm to 350nm at 0.5nm interval respectively.

Substituting Sulfuric Acid and/or Formic Acid with MSA in Pickling

Salted-wet cattle hides were conducted soaking, fleshing, liming, splitting, deliming and bating procedures as normal processes. A whole grain-layer limed cattle hide with thickness of 3.0 mm after splitting was divided into pieces adjacently and symmetrically, and they were distributed to different tanning groups for evaluating and comparing tanning effects. The bated pelts were put into drums and soaked in 50% of water at 23°C (based on the weight of limed hides, the same below) and pickled to pH 2.9 around with a certain amount of MSA, the mixtures of formic acid and MSA, or sulfuric acid and MSA, respectively, in the presence of 6.0% (w/v) of NaCl. After pickling overnight, 6.0% Chromosal B together with 1.0% of sodium formate was added into each drum. When chrome completely penetrated into hide inner-layer after running for about 180min at 23°C, the pH was basified to around 4.0 with NaHCO₃ solution carefully. Then a certain amount of hot water (60°C) was added to make the total water offer be total 200% of limed hide weight. After running for another 120 min at 40°C, the drums were stayed overnight. The next day, the pH of tanning liquors was adjusted to 4.0±0.1 once more. The Cr contents in spent tanning liquors were determined.

Optimization of Processing Parameters of MSA Pickling-Chrome Tanning

The adjacent and symmetrical bated pelts were prepared and pickled to different pH with varying amounts of MSA. After pickling overnight, chrome tanning was carried out with a varying offer amount of Chromosal B, with or without using sodium formate. All other operations were the same as above. As a control, two groups of pelts were pickled as per the conventional method (formic acid 0.5% and sulfuric acid 1.0-1.2%) and were tanned with 6.5% of Chromosal B alone or the combinations of 5.0% of Chromosal B and 0.5% of sodium formate respectively. The Cr contents in spent tanning liquors were determined. Cr distribution, shrinkage temperature values (Ts) and the appearances of the chrome-tanned leather were determined and compared.

Tracing Chrome Discharge in Whole Leather Wet-end Processing Based on MSA Pickling-chrome Tanning

Bated pelts were divided into two groups. Among them, a whole piece of grain-layer limed cattle hide was cut into two half sides along with the backbone line, symmetrically, and they were distributed to different tanning groups for evaluating and comparing tanning effects. As shown in Table I, the two groups of pelts were chrome tanned with a conventional pickling-chrome tanning process (No. i) and MSA pickling-chrome tanning process (No. ii), respectively. After stacked and aged for

7 days, the tanned leathers were carried out sammying, shaving (thickness 1.1-1.2 mm), and wetting as the normal operations. Then the shaved tanned leathers were put in drums and conducted with a normal (No. i) and a modified (No. ii) chrome retanning processes correspondingly. Then the chrome retanned leathers were neutralized, retanned with syntans, dyed and fatliquored as the normal procedures for shoe upper leather, and was also used to substitute formic acid to fix syntans, dyestuff and fatliquors in No. ii process. The chromium concentrations in chromium-containing wastewaters were analyzed and the main leather properties were also measured.

Determination of Chromium Concentration in Spent Tanning Liquors

The spent tanning liquors were filtered with 100 mesh filter cloth and digested with the mixture of hydrochloric acid and nitric acid at 120°C for 120min. The digestion solutions were appropriately diluted and their chromium concentrations were measured with AES-ICP. The chromium concentrations of spent tanning liquors were calculated.

Determination of Chromium Content and Distribution in Leather

The chrome-tanned leather samples of each tanning group were taken out in the adjacent and symmetrical parts of the same hide, and washed thoroughly to remove uncombined chromium salt. Then the samples were freeze-dried at -55°C and 20pa vacuum for 24hours. The dried leathers were averagely split into three layers using Precision Slice Machine. A certain quantity of the dried leather sample was completely digested with the mixture of nitric acid and chloride acid at 120°C for 120min. The digestion solutions were appropriately diluted and their chromium concentrations were measured with AES-ICP. The chromium content in each layer of the leather was calculated.

Scanning Electron Microscopy (SEM) Analysis

The samples of the dried crust leathers of each tanning group were viewed microscopically using Desktop Phenom Pro Desktop Scanning Electron Microscope. Then the pattern of both the grain on the surfaces and the collagen fibril on the section were evaluated.

Test of Physical and Mechanical Properties of Crust Leather

Dried crust leather samples of each tanning group were taken out in the adjacent and symmetrical parts of the same hide for testing physical and mechanical properties. The dichloromethane extracts were evaluated as per ISO 4048-2008. Samples were conditioned as per IUP method (IUP 2, 2000). Physical properties such as tensile strength, elongation at break, tear strength and bursting strength were examined as per the standard procedures (IUP 6, 2000; IUP 8, 2000; IUP 9, 1996).

Table I
Leather making processes for shoe upper leather.

Operations	Chemicals	Dosages (%)	Parameters	Comments
Bating				
Pickling	Water	50	23°C	
	NaCl	6.0	10 min	
No. i	HCOOH	0.5	30 min	
	H ₂ SO ₄	1.1	180 min	
No. ii	MSA	0.9	180 min	
Overnight				No. i pH 2.96; No. ii pH 4.86
Cr- tanning				
No. i	Chromosal B	6.5		
	HCOONa	0.5	180 min	Cr penetrate evenly
No. ii	Chromosal B	4.5	180 min	Cr penetrate evenly
Basifying	NaHCO ₃	X	180 min	30 min interval
	Water (60°C)	150	120 min	Stable at 40°C
Overnight				
Draining				Cr sewage 200%
Stacking			7 days	
Sammying				Cr sewage 20%
Shaving				Thickness 1.1-1.2 mm
Wetting	Water (40°C)	200		
	Nonionic wetting agent	0.3		
	Nonionic degreasing agent	0.1		
	NaHCO ₃	0.3	120 min	pH 4.5
Draining				Cr sewage 200%
Cr-retanning	Water (40°C)	200		
No. i	HCOOH	0.5	120 min	pH 3.5 around
	Chromosal B	3.5		
	HCOONa	0.5		

Table I continued on following page.

Table I continued.

	NaHCO ₃	X	120 min	pH 4.2 around
No. ii	Chromosal B	3.5		
	MSA-Na	0.5	90 min	
	NaHCO ₃	X	120 min	pH 4.2 around
Overnight				
Draining				Cr sewage 200%
Neutralizing	Water	150	40°C	
	Neutralizing Syntans	1.5	30min	
	NaHCO ₃	1.0	90min	pH 5.1
Draining				Cr sewage 150%
Organic retanning/ Filling	Water	150	40°C	
	Synthetic Fatliquor	2.0	30min	All the chemicals were diluted with 3 times hot water
	Polyacrylate Retanning Agents	9.0	60min	
	Polysulfone Syntan	4.0		
	Polynaphthalene Sulphonate	2.0		
	Melamine Resin	3.0		
	Protein Filling	3.0		
	Vegetable Tannin	3.0	90min	
No. i	HCOOH	0.5		
No. ii	MSA	0.5	30min	pH4.5 around
Draining				Cr sewage 200%
Washing	Water	200	10min	Cr sewage 200%
Fatliquoring/ Dyeing	Water	150	55°C	
+	Dyestuffs	3.0	30min	All chemicals were diluted with 3 times hot water
+	Mixture of Fatliquors	10.0		
No. i	HCOOH	1.5	90min	pH3.6 around
No. ii	MSA	1.8	90min	pH3.6 around
Draining				Cr sewage 200%

Vacuum Drying, Hanging Drying, Stacking as conventional methods

Results and Discussions

The Masking Effect of Methanesulfonic Acid (MSA) on Chromium Ions

UV-Vis is the most common technique for characterizing Cr(III) species. The positions of the two peaks are changeable depending on ligands associated to chromium ion, and the slight variations in the wavelengths are attributed to the fact that Cr(III) reacted with different ligands.¹⁶ In order to evaluate the masking effect of MSA towards chromium ions, UV-Vis spectral studies of chromium sulfate solutions with different ratios of MSA at pH 4.0 were conducted, and the results are showed in Figure 1 and Table II.

Two fairly strong absorptions of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ complex are known in the visible and near-ultraviolet region from 700nm to 350nm. These peaks correspond to two transitions from ground states to the excited states: ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$.¹⁷ The spectrum is the characteristic of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ complex in which Cr(III) ion is octahedral, and the water molecules in this complex could be replaced by various ligands present in the solution, resulting the color change of the solution from green to blue.¹⁵ The results in Figure 1 and Table II indicate that the two peaks are slightly shifted to the blue region by 0.5nm to 1.5nm, varying with the concentrations of MSA, meaning that one or more water molecules in the inner sphere of Cr(III) complex are replaced with MSA, forming the MSA-complexes of Cr(III). Therefore, the affinity of MSA to Cr(III) is stronger than that of sulfuric acid. But the peaks in formic acid solution are obviously shifted by 3.5nm and 7.0nm respectively, indicating the formation of the stronger formic acid-complexes of Cr(III), for the affinity of carboxyl is much stronger than that of methanesulfonate to Cr(III). Therefore, the masking effect of MSA on chromium ions is between sulfate and formate.

The Influence of Pickling with MSA on Chrome Tanning

In order to pre-search the possibility of establishing a new pickling-chrome tanning system, MSA was used to completely

or partially substitute sulfuric acid and/or formic acid in pickling process, and the influences of pickling methods on chrome tanning effects were examined firstly. The results are shown in Table III.

The results in Table III show that MSA pickling can increase chromium uptake to a certain degree, comparing with conventional pickling. The improving effect of replacing sulfuric acid with MSA on chromium exhaustion, i.e. combining MSA and formic acid in pickling (No.2), isn't as evident as substituting formic acid (No.3). The chromium uptake arrives at 79% when pickling with MSA alone. The reason may be ascribed to the strong masking effect of formate toward Cr(III) ions as the results above (Figure 1 and Table II). Although there is no adding of formic acid in pickling method No.3 and No.4, the added 1.0% of sodium formate in tanning processing still produces enough masking effect toward Cr(III), which significantly negatively influences the complex ability of masked chromium ions with collagen carboxyls. In order to illustrate the impact of masking effect on chromium uptake, only MSA was used in pickling without adding formic acid and formate (No.5), and the result shows that the chromium uptake is remarkably raised to

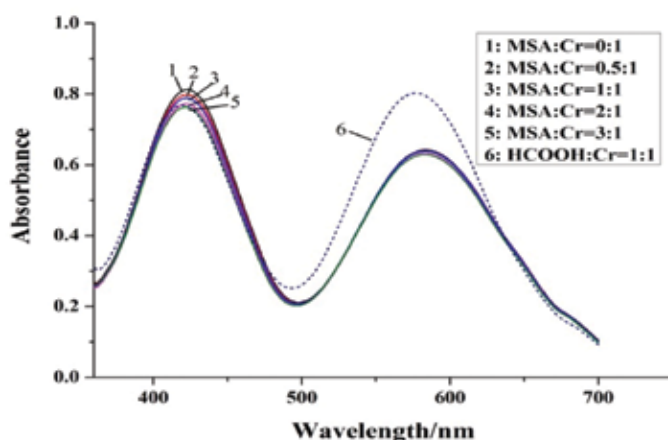


Figure 1. UV-Vis spectrum of chromium (III) ion in different concentrations of ligands.

Table II
Measured wavelength of the two peaks in the UV-Vis spectrum of chromium solutions with different concentrations of ligands.

Ratio of masking agent to chromium (mol/mol)	MSA					HCOOH
	0:1	0.5:1	1:1	2:1	3:1	1:1
$\lambda_{\text{max},1}$	423.0	422.5	422.5	422.0	421.5	419.5
$\lambda_{\text{max},2}$	583.5	583.0	583.0	583.0	583.0	576.5

86%, whilst the residual chromium concentration is decreased to 335mg/L. The results indicate that the excessively strong masking effect toward chromium ion from an overdose of formate is not beneficial to the combination of chrome by collagen, and MSA pickling exhibits good effect on improving the high exhaustion of chrome in the case of no addition of any other masking agents.

Optimizing of Parameters of MSA Pickling-chrome Tanning Process

According to the above results (Table III), the application of MSA can promote the absorption of chromium, hence, aiming at minimizing chromium discharge to a maximum degree, the main control parameters of MSA pickling-chrome tanning process, including pickling pH, masking agent and chrome offers, were further investigated. The results in Table IV show that, though the Cr offer is raised by about 30% in method No.6, from 0.89% to 1.16%, comparing with method No.7, the Cr uptake ratio is increased to 80% from 75% of method No.7, in which (No.7) 0.5% of sodium formate is added together with chrome powder. This further illustrates that the strong masking effects from formate to Cr(III) ion negatively influence the combination of chrome by collagen. The only difference between methods No.8 and No.6 is the kind of used acid in pickling, but the Cr uptake ratio in methods No.8 is much higher, which further indicates that MSA pickling can promote chrome exhaustion. This advantage can be mainly ascribed to the moderate masking effects of MSA towards Cr(III) ion. In order to minimize chromium discharge to a maximum degree, the initial tanning pH is raised to 5.0, and the offer is reduced to

0.81% (method No.9) in consideration of the much enough Cr content in the leather from MSA process with a regular Cr offer (method No.8). As expected, the Cr exhaustion is further enhanced to 95%, and the shrinkage temperature (Ts) reaches to 107°C, which can satisfy the requirement of chrome tanning standard accordingly, the residual Cr concentration in wastewater is further reduced to 115mg/L from 372mg/L. However, combining formic acid even at a rather low level of 0.15% in method No.10 makes more Cr resided in wastewater than in method No.9. This indicates the negative effects of formate on chromium absorption over again.

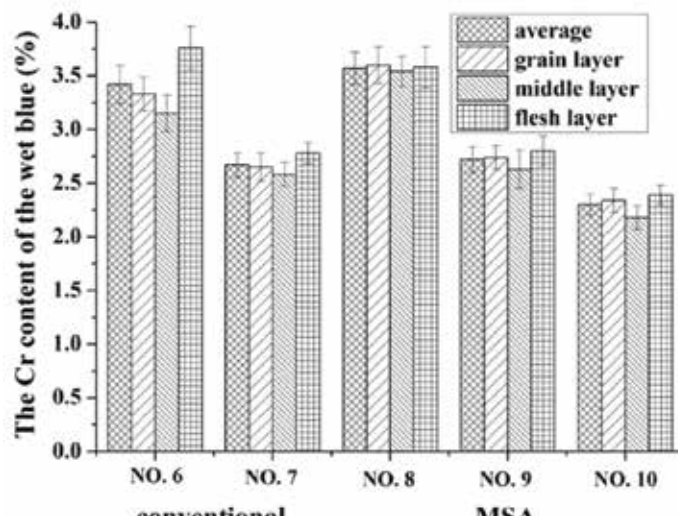


Figure 2. Cr contents and distributions of chrome tanned leathers with different pickling methods.

Table III
Influence of pickling with different acids on chrome uptake.

Pickling methods	No.1 FA ^a +SA ^b	No.2 MSA+FA	No.3 MSA+SA	No.4 MSA-I	No.5 MSA-II
Acid dosage (%)	FA a 0.6, +SA b 0.9	MSA 2.2, +FA 1.2	MSA 1.5, +SA 0.5	MSA 3.1	MSA 3.1
Pickling pH	2.9±0.1	2.9±0.1	2.9±0.1	2.9±0.1	2.9±0.1
Tanning end pH	4.1±0.1	4.1±0.1	4.1±0.1	4.1±0.1	4.1±0.1
Cr offer (%)	1.07	1.07	1.07	1.07	1.07
Sodium formate offer ^c (%)	1.00	1.00	1.00	1.00	0
Cr in waste bath (mg/L)	1074±10	1040±10	914±8	799±8	335±5
Cr uptake ratio (%)	72	73	77	79	86

^aFA-formic acid; ^bSA-sulfuric acid; ^cSodium formate was added together with chrome powder.

As mentioned before, there is a worry about Cr penetration into the inner layer of pelts when chrome tanning conducted at a high initial pH and with a low offer of Cr, hence, the chromium contents and distributions in chrome-tanned leathers from the above methods in Table IV were further investigated. The results are illustrated in Figure 2.

Figure 2 indicates that the Cr content of chrome-tanned leather is consistent with the corresponding calculated value according to the data in Table IV. The addition of sodium formate in conventional process can improve the uniformity of Cr distribution in leather, but the combined Cr amount is decreased obviously, comparing method No.6 and No.7. In the MSA pickling process, being attributed to the moderate masking effect of MSA towards Cr(III) ions, there is no negative influence on the penetration and distribution of chromium in the leather. Chrome tanning at a high initial pH of about 5.0 with MSA, the penetration of chromium is not hindered, and the “excessive surface tanning effect” is not observed, and the addition of other masking agents is not necessary. Hence, raising initial tanning pH and appropriate reduction Cr offer in MSA pickling-tanning process is a practicable approach to further decrease chromium discharge.

Tracing Chrome Discharge in Whole Leather Wet-end Processing

The efficiency of the novel pickling-chrome tanning method with MSA was further evaluated on improving chrome tanning

and leather quality in comparison with the conventional process. Because chrome in wet-blue leather will also leach out at varying levels in the following post-tanning operations, including wetting, neutralizing, organic retanning/filling and dyeing/fatliquoring, the emission of chromium was also traced in whole leather wet-end processing.¹⁸

In the novel process, the pelts was pickled with MSA to a relatively high pH value of about 4.9 and tanned with a reduced Cr offer and without adding any other masking agent, and then

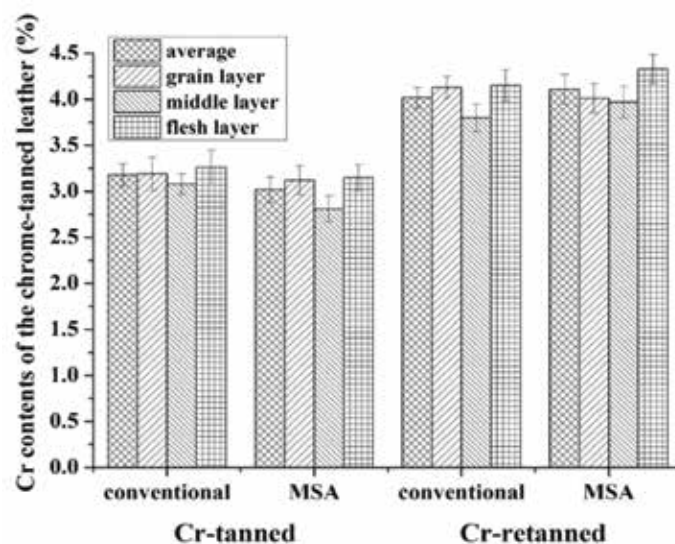


Figure 3. The effectiveness of the novel process on improving Cr distribution.

Table IV
Influence of pickling pH and Cr offering in MSA pickling on chrome tanning.

Pickling methods	Conventional		MSA		
	No.6	No.7	No.8	No.9	No.10
Acid dosage (%)	FA ^a 0.50 +SA ^b 1.10	FA 0.50 +SA 1.00	MSA 3.00	MSA 1.00	FA 0.15 +MSA 0.70
Pickling pH	2.9±0.1	2.9±0.1	2.9±0.1	5.0±0.1	5.0±0.1
Basification pH	4.1±0.1	4.1±0.1	4.1±0.1	4.1±0.1	4.1±0.1
Chromosal B (Cr) offer (%)	6.5 (1.16)	5.0 (0.89)	6.5 (1.16)	4.5 (0.81)	4.0 (0.72)
Sodium formate offer ^c (%)	0	0.50	0	0	0
Cr in waste water (mg·L ⁻¹)	864±8	802±8	372±4	155±3	224±3
Cr uptake ratio (%)	80	75	91	95	91
Shrinkage temperature (°C)	120±2	112±1	118±2	107±2	107±1

^aFA-formic acid; ^bSA-sulfuric acid; ^cSodium formate was added together with chrome powder

retanned with 0.63% of Cr offer and 0.5% of sodium methanesulfonate to substitute sodium formate at pH 4.5. The tanning effects are shown in Table V and Figure 3.

The results show that the novel chrome tanning process is going well at a high beginning pH of 4.9. As shown in Table V, the Cr absorption ratio in the novel process is increased to 94% from 75% in the conventional process, and the residual Cr in spent tanning float is reduced to 166.6mg/L from 1076.6mg/L (see Table VI), correspondingly, which are consistent with the results of No.9 method in Table IV. On basis of the novel pickling-chrome tanning, the next chrome retanning operation was a little modified, i.e., wet-blue leather was conducted retanned with methanesulfonate as the masking agent at initial pH 4.5 around. Further, the chrome uptake rate is increased to 96% from 76% in the conventional retanning process. All in all, both the novel tanning and retanning process with MSA exhibit obvious effectiveness on increasing chrome exhaustion.

As shown in Figure 3, though the total Cr offer was reduced by 30% (from 1.16% to 0.81%) in the novel MSA pickling-tanning process, the average Cr content of the chrome tanned leather is only a little lower than that from the conventional tanning process, and there is no obvious difference in the average Cr contents and Ts of the retanned leather between the two processes. This can be ascribed to the high exhaustion of chrome in the novel processes. Therefore, the total Cr offer can be obviously decreased. The Cr distribution in the vertical section

of the leather retanned with novel process is more uniform than that in the leather from conventional retanning process, and the Cr content in the grain layer is not remarkable higher than in the middle layer. This once again proves that chromium penetrating into the inner layer is not hindered when tanning at the high beginning pH in the novel process. The area yield of leather is also not diminished (see Table V); hence no excessive tanning effectiveness has happened in the novel process.

As mentioned before, besides the high-concentration chrome-containing effluents from tanning, sammying and chrome retanning, all the spent liquors from following post-tanning operations contain chrome resulting from the releasing of chrome from leather. All the chrome-containing effluents should be treated to decrease the Cr concentration to lower than 1.5mg/L before discharged into sewage system in China, according to the strict statutory limits. Hence, the chrome discharge in whole leather wet-end processing was traced.

Generally, a certain amount of formic acid is added to lower pH to promote the combination and fixation of anionic chemicals, such as anionic syntans, dyestuffs and fatliquors, in the post-tanning processes. MSA was also used to substitute formic acid in the post-tanning processes of wet-blue leather from the novel pickling-chrome tanning and retanning methods, and the Cr concentrations of the spent liquors from main wet-end processes are shown in Table VI.

Table V
Effects of MSA pickling to a high pH on chrome tanning and retanning.

Operations	Pickling methods	Acid dosage (%)	Pickling pH	Cr offer (%)	Ts (°C)	Cr uptake rate (%)	Yield of leather ^a (sq.ft/kg)
Cr-tanning	Conventional	FA 0.5; SA 1.1; Na-FA ^b 0.5	2.9±0.1	1.16	118±2	75	3.10
	MSA	MSA 0.9	4.9±0.1	0.81	107±2	94	3.10
Cr- retanning	Conventional	FA 0.5; Na-FA ^b 0.5	3.5±0.1	0.63	124±2	76	7.54
	MSA	Na-MSA ^c 0.5	4.5±0.1	0.63	121±2	96	7.52

^a yield of leather in Cr tanning=areas of wet-blue (sq.ft)/weight of limed hide (kg);

yield of leather in Cr retanning=areas of final leather (sq.ft)/ weight of shaved leather (kg).

^bNa-FA: sodium formate; added together with chrome powders.

^cNa-MSA: sodium methanesulfonate; added together with chrome powders.

It can be seen that the chromium concentration of each wastewater is decreased by 46.1%-84.5%, the total chromium discharge amount is reduced by 83.8%, and the total Cr utilization ratio is increased to 95.8% from 81.0% in the novel technology of integrating application of MSA in pickling-chrome tanning and post-tanning processes, comparing with the corresponding one from the conventional processes. Not only does the novel leather making process using MSA increase chromium exhaustion during chrome tanning and retanning, but also decrease chromium leaching out in post-tanning operations effectively, hence, the total Cr discharge is minimized.

Table VI
Tracing Cr discharge in whole leather wet-end processing ^a

Operations	No. i ^a Conventional (mg·L ⁻¹)	No. ii ^a Novel (mg·L ⁻¹)	Decrease rate (%)
chrome tanning	1076±10	167±2	84.5
Samming	465±3	107±3	77.0
Wetting	16±2	7±1	58.9
Chrome retanning	541±6	88±2	83.7
Neutralizing	18±2	7±2	62.7
Washing	9±2	5.0±1	43.8
Organic retanning/ Filling	29±2	12±1	57.3
Washing	15±2	8±1	46.1
Dyeing/Fatliquoring	41±2	15±2	64.2

The input and output of the Cr in whole process
(kg/t salted-wet hide) ^b

Total Cr offer	14.411	10.561	26.7
Total Cr discharge	2.737	0.443	83.8
Total Cr utilization ratio (%)	81.0	95.8	-

^aThe process parameter of No. i and No. ii seen Table I;

^b1.0t salted-wet hide was changed into 1.1t limed hide and 0.262t shaved grain chrome-tanned leather, and the samming water amount is 200 kg/t.

Moreover, considering that the residual Cr concentration was very low in the spent tanning liquor, it can be recycled directly in pickling process after simply filtrated. It is expected that the main problems of recycling the conventional spent chrome tanning liquor, such as dark color and rough grain of chrome tanned leather, from the high-concentration residual chromium will be overcome. Also, the chrome-containing sludge generated from alkali-precipitation of low concentration chrome-containing wastewater from post-tanning processes will be dramatically decreased. The further research is ongoing.

Comparison of Leather Properties

One of the main factors affecting the acceptability of a novel leather making method by tanners is whether it can improve or at least keep the original properties of the final leather. Hence the main properties of the leathers from the adjacent and symmetrical parts of a same hide respectively conducted the processing procedures of No. i and No. ii in Table I were evaluated by scanning electron microscope, and the results are shown in Figure 4.

As mentioned before, excessive binding and depositing of chrome on the surface of leather resulting in wrinkled grain is a potential risk for tanning at a high initial pH. The electron micrographs illustrate that the grain pattern is a little smoother of the leather from MSA processing than conventional processing, and there is no any deposition of chromium on surface and inside the hair pores, hence, the excessive tanning effect in leather surface does not happen. The fiber bundles are well separated and their diameters are finer, and there is less

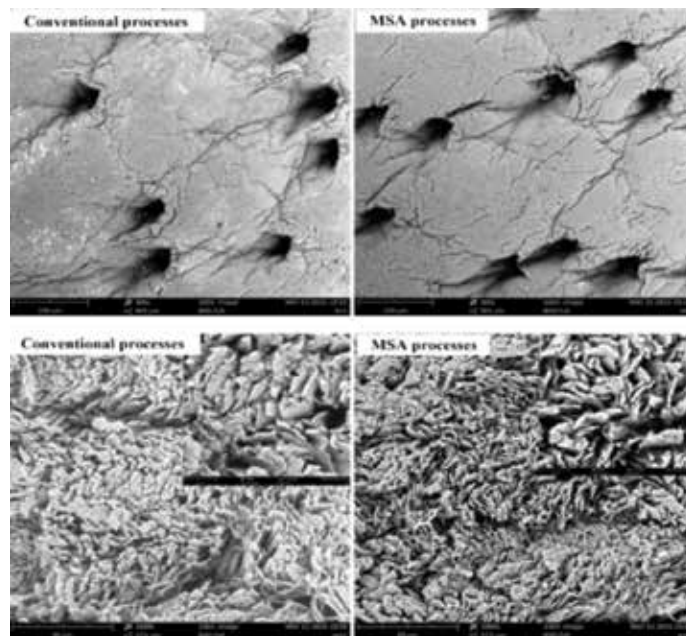


Figure 4. SEM images of the grain pattern (×300) and vertical sections (×1000, ×5000) of the crust leather.

densely blocky adhesion between fibers of the leather from MSA processing than the other one, which can be attributed to that the inner layer is well tanned, and the chemical used in post-tanning processing are well absorbed and penetrate into the inner layer.

Actually, it is found that the absorptions of anionic chemicals, especially dyestuffs and fatliquors, were obvious improved in the novel processing through observing the color depths and the turbidities of spent floats. The content of fatliquor in leather is higher and the distribution is more even as illustrated in Figure 5. The higher fatliquor content in middle layer may result from higher content of chrome (see Figure 4). Hence, the leather is softer and with better physical-mechanical performances, as shown in Table VII.

The Pilot-scale Experiment Results

In order to verify the acceptability of the novel pickling-chrome tanning method with MSA, the pilot-scale experiments were conducted in Tongtianxing Leather Co., which is the biggest furniture leather plant in China. Bating pelts of Ireland cowhides

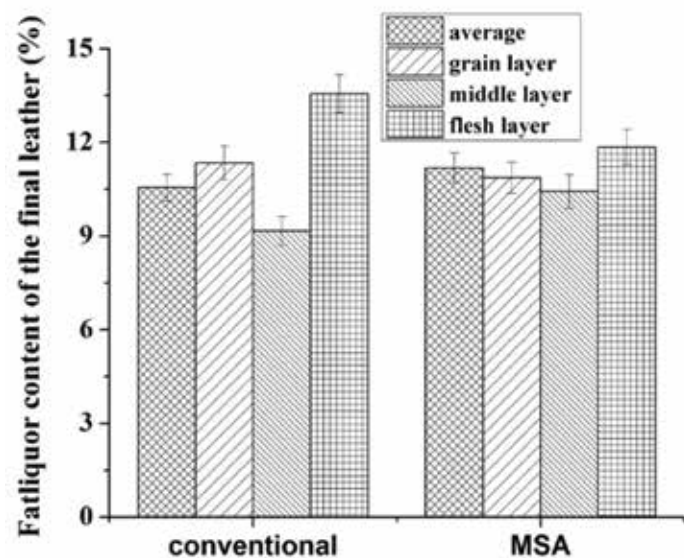


Figure 5. Fatliquor content in the final leather (dichloromethane extracts).

Table VII
Physical properties of crust leathers.

Samples	Tensile strength (N/mm ²)	Tear strength (N/mm)	Elongation at break (%)
Conventional	7.5±1.2	25.6±5.7	45.7±4.7
MSA	7.9±0.9	32.0±3.4	56.7±3.2

were taken out from the tannery production line of furniture leather, and conducted pickling with 1.0% MSA to pH of 4.5, and then tanning with 0.85% of Cr offer based on the weight of limed pelts of 2.5-2.8mm thickness. Satisfactorily, the same results with laboratory experiments were obtained. The twice repeated results indicated that the residual Cr concentration in the spent tanning liquor was 270mg/L. As the control, it was 2608mg/L from the tannery tanning float, tanning with 1.16% Cr offer as per conventional methods. The Cr content in leather was 3.15%, a little lower than the control, 3.31%, and the shrinkage temperature reached to 95°C, in the case of Cr offer decreased by 26.7%.

The wet-blue leathers were post-tanned and finished as per the tannery's furniture leather procedures. The resultant leathers passed through the examination of the quality inspectors from the tannery. Skilled tanners commented that, in the aspects of organoleptic properties comparing with the tannery products, the leather was more stretching, the fullness and softness were better, and the grain pattern of the final leather was more uniform. In their opinions, pickling-tanning method with MSA is interesting and commercially acceptable.

Conclusion

The novel pickling-masking-chrome tanning system with MSA can remarkably increase the chromium exhaustion without impairing Cr penetration in both chrome tanning and retanning, resulting from the suitable and moderate masking effect of the MSA ligand towards Cr(III) ion. Accordingly, the total chrome offer can be reduced by about 26.7%, and the total Cr utilization ratio can be increased to 95.8% from 81.0% around, resulting in the total chromium emission in the whole leather processing is reduced by 83.8%, comparing with the conventional process. The area yield, physical and organoleptic properties of the leather are comparable with those from conventional processes.

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References

1. Anthony, D.C.; Tanning chemistry: the science of leather, *RSC Publishing*, Cambridge UK, pp.177-258, 2011.
2. Anthony, D.C.; Modern tanning chemistry. *Chem. Soc. Rev.* **26**, 111-126, 1997.

3. Sundar, V. J., Rao, J.R. and Muralidharan, C.; Cleaner chrome tanning-emerging options. *J. Clean. Prod.* **10**, 69-74, 2002.
 4. Chen, W.Y., Li, G.Y.; Tanning chemistry, *China Light Industry Press*, Beijing China, pp. 85-89, 2001.
 5. Gregori, J., Marsal, A., Manich, A.M. and Cot, J.; Optimization of the chrome tanning process – influence of 3 types of commercially available masking agents. *JSLTC.* **77**, 147-150, 1993.
 6. Luan, S.F., Liu, Y., Fan, H.J., Shi, B. and Duan Z.J.; A novel pre-tanning agent for high exhaustion chromium tannage. *JSLTC.* **91**, 149-153, 2007.
 7. Thannikaivelan, P., Kanthimathi, M., Rao, J.R. and Nair, B.; A novel formaldehyde-free synthetic chrome tanning agent for pickle-less chrome tanning: comparative study on syntan versus modified basic chromium sulfate. *JSLTC.* **97**, 127-136, 2002.
 8. Chen, J.P., Gong, Y. and Chen, W. Y.; Study on the softness of pickle and pickle-less chrome tanning leather. *7th Asian International Conference of Leather Science and Technology*, Chengdu China, 675-678, 2006.
 9. Suresh, V., Kanthimathi, M., Thanikaivelan, P., Raghava, J.R. and Unni, B.N.; An improved product-process for cleaner chrome tanning in leather processing. *J. Clean. Prod.* **9**, 483-491, 2001.
 10. Bnownstrin, S., Stillman, A.E.; Proton resonance shifts of acids in liquid sulfur dioxide. *J. Phys. Chem.* **63**, 2061-2062, 1956.
 11. Michael, D., Gernon, Min, W., Thomas, B. and Patrick J.; Environmental benefits of methanesulfonic acid: comparative properties and advantages. *Green Chemistry.* **1(3)**, 127-140, 1999
 12. Kityk, A.A., Protsenko, V.S. and Danilov, F.I.; Voltammetry Study of Cr(III)/Cr(II) system in methanesulfonate and sulfate solutions: temperature dependences. *J. Electroanal. Chem.* **689**, 269-275, 2013.
 13. Protsenko, V., Danilov, F.; Kinetics and mechanism of chromium electrodeposition from formate and oxalate solutions of Cr(III) compounds. *Electrochimica Acta* **54**, 5666-5672, 2009.
 14. Protsenko, V.S., Kityk, A.A. and Danilov, F.I.; Kinetics and mechanism of chromium electrodeposition from methanesulfonate solutions of Cr(III) Salts. *Surf. Eng. Appl. Ekect.* **50**, 384-389, 2014.
 15. Protsenko, V.S., Kityk, A.A. and Danilov, F.I.; Voltammetry study of Cr(III)/Cr(II) system in aqueous methanesulfonate solutions. *J. Electroanal. Chem.* **661**, 213-218, 2011.
 16. Maher, J., Fathi, A., Safa, S. and Awni, K.; Monitoring chromium of content in tannery wastewater. *J. Argent. Chem. Soc.* **97**, 77-87, 2009.
 17. Protsenko, V.S., Kityk, A.A. and Danilov, F.I.; Electroreduction of Cr(III) ions in methanesulphonate solution on Pb electrode. *E-J CHEM* **8**, 1714-1719, 2011.
 18. Zhou, J., Hu, S.X., Wang, Y.N., He, Q., Liao, X.P., Zhang, W.H. and Shi, B.; Release of chrome in tanning and post tanning processes. *JSLTC.* **96**, 157-161, 2011.
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