CLEANER CHROME TANNING-TECHNOLOGY OF LOW-CHROME TANNING WITHOUT SALT, PICKLING AND SHORT PROCEDURE

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Abstract. Tannery effluent with high salinity and chromium have a serious environmental impact. The traditional chrome tannage that involved the use of sodium chloride, acid and chromium is one of the main origins of salt and chromium pollution. In this study, a non-pickling, chrome-less tanning technology was developed. The novel Chrome-free agent SL can be directly employed to tan bated bovine hide and the wet white was obtained. Then the shaved wet white was pre-treated by Poly-carboxylate auxiliary agent PAA and tanned by chrome powder. It was tested that the shrinkage temperature of the wet white, the initial pH of chrome tanning, the consumption of chrome powder, the shrinkage temperature of the chrome-tanned leather, the content of Cr_2O_3 in effluent, the absorption of chromium and the other properties of the chrome-tanned leather. It was found that the shrinkage temperature of the wet white tanned by SL reached over 80°C, the optimal consumption of Poly-carboxylate auxiliary agent was 2wt% based on the weight of the shaved wet white, the better chrome-less tanning conditions were that the wet white was tanned by 3-4wt% chromium powder for 150～180min at room temperature when the initial pH value was 3.0-3.5. The next processes were same as traditional chrome tannage. Meanwhile, the shrinkage temperature of the leather tanned by the chrome-less tannage reached more than 95°C, the absorption of chromium was 96%, the content of Cr_2O_3 in the effluent was under 200mg/L. For the chrome-less tanned leather, the absorption of dyestuff, fat-liquor reached 99.5%, 82.5% respectively. Compared with the traditional chrome tanned process, not only the conventional pickling process was eliminated, the process was been shorten and reduce the pollution of sodium chloride, but it can reduce 50% of the consumption of Chrome powder, improve the absorption of chromium and can reduce content of Cr_2O_3 in effluent.

1 Introduction

As we know, Chrome-tanned & finished leathers have good comprehensive properties such as high hydrothermal stability, softness, etc, so the Chrome tanning agents is considered as the best mineral tanning agent among the tanning agents used in the leather industry. Therefore most of all the tanneries in the world have now adopted chrome tanning. But the absorption level of chromium is only 60-80% during the traditional chrome tanning so that the tannery effluent contains chromium and waste containing chromium is produced[1]. How to reduce or abolish the disadvantage of the Chromium tanning agent is always one of important topics in the leather industry. The key problem is to improve the absorption level in order to overcome the valid absorption and reaction between collagen and Chrome tanning agent. So many technologists have many research and obtain some results in the field of high absorptive chrome tannage, chrome-less tannage and non-chrome tannage. Based on the needs and trends of leather products of markets, Chrome-tanned leather and non-chrome tanned leather will be co-existed for a long time[2]. Therefore in order to meet the demands of markets and environmental protection, the best way is to reduce the dosage of Chrome tanning agent and improve the absorption level of chromium in the tanning process. So chrome-less tannage is one of cleaner chrome tanning technologies.

Of existing chrome-less tannage, one way is that some organic tanning agent or other mineral tanning agent was adopted to achieve the combination tanning with Chrome tanning agent[3,4,5]. The other way is that pelt was tanned by new chrome tanning agent modified by other mineral tanning agents[5]. In recent years, in order to improve the effect of less chrome tanning, the chrome-less

tannage based on wet white is studied, that is, the pelt is pre-tanned by Alumium tanning agent or aldehyde tanning agent to obtain the wet white, then the shaving wet white is tanned by Chrome tanning agent[6,7]. But the appearance, softness and other properties of the chrome-less tanned leather less than that of traditional chrome tannage, the chrome-less tannage need be further studied.

Based on the new technology of non-chrome tanning agents in recent years, the purpose of our research is to develop new chrome-less tannage without salt, Pickling and short procedure which can remove the pickle, achieve the chrome-less tannage and match the quality of the leather tanned by traditional chrome tanning.

2 Experimental procedures

2.1 Materials

Bovine pickled hide (pH 2.6-3.0) and bated bovine hide (pH 7.5-8.0) were used as raw materials. The novel chrome-free agent SL prepared on laboratory scale is an amphoteric organic compound (approximately a 45% solution w/v; pH 2.5-4.0). The novel chrome-free agent SL prepared on laboratory scale is an amphoteric organic compound (approximately a 45% solution w/v; pH 2.5-4.0). The poly-carboxylate auxiliary agent PAA prepared on laboratory scale is an compound with more carboxyl groups (approximately a 35% solution w/v; pH 5.0-5.5; M_n 24344). TRUPON SWS, TRUPON DB were obtained from TRUMPLER Chemicals s.p.a, Germany. All chemicals used for leather processing were of commercial grade.

2.2 Tanning properties of the novel chrome-free agent SL

As we know, the novel chrome-free agent SL was synthesized by the radical co-polymerisation reaction with acrolein and diallyl dimethyl ammonium chloride, whose structure is shown in Fig. 1[8]. The tanning process of SL is shown in Table 1. The Six pieces of bated bovine hide (30cm×20cm, pH 7.0-7.5) were put in the stainless steel drums (50cm diameter) and the float was 100%. The offer of SL is 2%, 4%,5%, 6%,8%,10% (based on 150% times of the weight of bated pelt) respectively The time of penetration is 4 hours. Then the pH was adjusted to 7.0～7.5. Then the temperature of the float was raised to 40°C, the float ratio was adjusted to 2.0 and running continued for 5hours. The pH of the tanning float and the shrinkage temperature of the leather were measured the next day.

2.3 The properties of wet white tanned by the novel chrome-free agent SL

The five pieces of the wet white tanned by the novel chrome-free agent SL(2cm×10cm, pH 7.0-7.5) were put in the 250mL cone bottle and the water was 100mL. Then the cone bottles were put in the Water bath oscillator (25°C, 140rpm) and were operated for 2, 4, 6, 8, 10 hours. The shrinkage temperature of the leathers were measured. In addition, The seven pieces of the wet white tanned by the novel chrome-free agent SL (2cm×10cm, pH 7.0-7.5) were put in the 250mL cone bottle and the water was 100mL whose pH was adjusted to 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 respectively. Then the cone bottles were put in the Water bath oscillator (25°C, 140rpm) and were operated for 2 hours. The shrinkage temperature of the leather were measured.

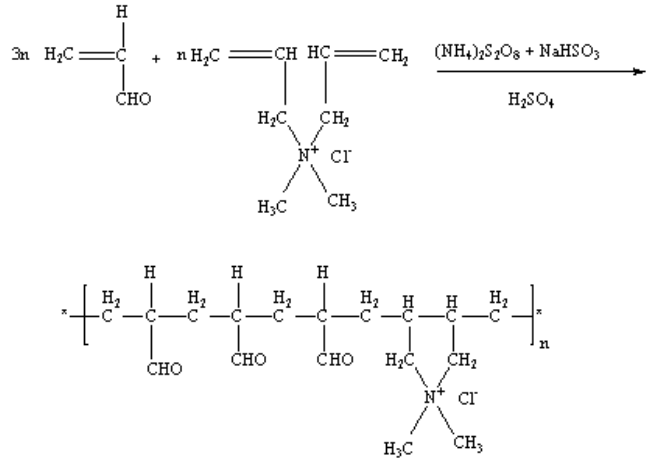


Fig. 1. The synthesis of the novel chrome-free agent SL.

Table 1. The procedures of tanning with SL based on the bated bovine hide.

Process	chemicals	Offer/%	T/°C	t/min	pH	Remarks
Wash	Water	200	25	15	7.0-7.5	3times,drain
Tanning	Water	100	18-22			
	SL	X*		240		
Basification	$NaHCO_3$	0.6		30		
	$NaHCO_3$	0.6		30	7.5-8.0	
	Water	100	50	300	7.0-7.5	

*X=2、4、5、6、8、10

2.4 Optimization of the initial pH in tanning process

The six pieces of the shaved wet white tanned by the novel chrome-free agent SL (30cm×20cm, pH 7.0-7.5, 0.9-1.0mm) were put in the stainless steel drums (50cm diameter) and the float was 60%. The offer of Chrome tanning agent is 5% (based on the weight of the shaved wet white). The initial pH of the tanning float is adjusted to 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 respectively. The tanning process was shown in Table 2. The time of penetration, the shrinkage temperature and the state of leather, the content of Cr_2O_3 in the effluent and the absorption of Chrome tanning agent were measured respectively.

Table 2. The chrome tanning process of the shaved wet white tanned by SL.

Process	Chemicals	Offer/%	T/°C	t/min	pH	Remarks
Re-wetting	Water	200	35			
	BCN 60	0.3		30	7.0	
Wash	Water	200	18-22	15		Twice, drain
Tanning	Water	60	18-22			
	Formic acid	0.5-2.5		20	Y*	
	Chrome powder	5		120		Check the penetration
Basification	Sodium formate	1				
	Sodium bicarbonate	0.8		30		
	Sodium bicarbonate	0.6		60	3.8-4.0	
	Water	150	50	300	3.8	Horse up

*Y=2.5, 3.0, 3.5, 4.0, 4.5, 5.0

2.5 Optimization of the offer of Chrome tanning agent in tanning process

The five pieces of the shaved wet white tanned by the novel chrome-free agent SL (30cm×20cm, pH 7.0-7.5,0.9-1.0mm) were put in the stainless steel drums (50cm diameter) and the float was 60% whose pH was adjusted to 3.5. The offer of Chrome tanning agent is 2%, 3%, 4%, 5%, 6% (based on the weight of the shaved wet white) respectively. The tanning process was showed in Table 3. The time of penetration, the shrinkage temperature and the state of leather, the content of Cr_2O_3 in the effluent and the absorption of Chrome tanning agent were measured respectively.

Table 3. Chrome tanning process of the shaved wet white tanned by SL under the different consumption of Chrome tanning agent.

Process	Chemicals	Offer/%	T/°C	t/min	pH	Remarks
Re-wetting	Water	200	35			
	BCN 60	0.3		30	7.0	
Wash	Water	200	18-22	15		Twice, drain
Tanning	Water	60	18-22			
	Formic acid	1.0-1.2		20	3.5	
	Chrome powder	Z*		120		Check the penetration
Basification	Sodium formate	1				
	Sodium bicarbonate	0.8		30		
	Sodium bicarbonate	0.6		60	3.8-4.0	
	Water	150	50	300	3.8	Horse up

*Z=2.0, 3.0, 4.0, 5.0, 6.0

2.6 The properties of Poly-carboxylate auxiliary agent in the less-chrome tanning

As we know, the reaction between collagen and Chrome tanning agent is carboxyl groups of collagen enter the inner boundary of Chromium and achieve the chemical coordination, whose bond energy is equivalent to that of covalent bond[9]. Therefore the number of carboxyl groups can increase the absorption and fixation of chromium. So the poly-carboxylate auxiliary agent PAA was synthesized by the radical co-polymerisation reaction with acrylic acid, maleic anhydride, itaconic acid, whose reaction and structure is shown in Fig. 2[10].

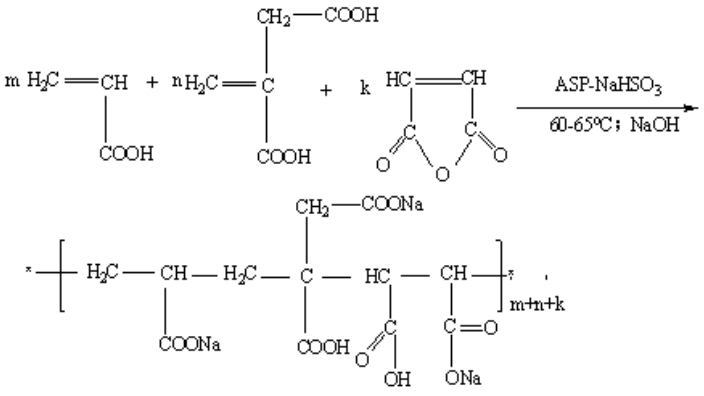


Fig. 2. Schematic diagram of the synthetic reaction of poly-carboxylate auxiliary agent PAA

Table 4. Chrome-less tanning process of the shaved wet white tanned by SL under the poly-carboxylate auxiliary agent (PAA).

Process	Chemicals	Offer/%	T/°C	t/min	pH	Remarks
Re-wetting	Water	200	35			
	BCN 60	0.3		30	7.0	
Wash	Water	200	18-22	15		Twice, drain
Pre-treation	Water	100	35			
	PAA	M*		40		
Wash	Water	200	18-22	15		drain
Tanning	Water	60	18-22			
	Formic acid	1.0-1.2		20	3.5	
	Chrome powder	4		120		Check the penetration
Basification	Sodium formate	1				
	Sodium bicarbonate	0.8		30		
	Sodium bicarbonate	0.6		60	3.8-4.0	
	Water	150	50	300	3.8	Horse up

*M=0, 0.5, 1.0, 1.5, 2.0, 2.5

In order to increase the absorption of chromium, the poly-carboxylate auxiliary agent PAA was used to pre-treat the shaved wet white. The six pieces of the shaved wet white tanned by the novel chrome-free agent SL(30cm×20cm, pH 7.0-7.5,0.9-1.0mm) were put in the stainless steel drums (50cm diameter) and the float was 100%. The wet white was pre-treated by the poly-carboxylate auxiliary agent PAA, whose offer is 0%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5% (based on the weight of the shaved wet white) respectively. The tanning process was showed in Table 4. The time of penetration, the shrinkage temperature and the state of leather, the content of Cr_2O_3 in the effluent and the absorption of Chrome tanning agent were measured respectively.

2.7 Contrast experiment between less-chrome tanning and traditional chrome tanning

A piece of bated bovine pelt (approximately 50 square foot, pH 7.0-7.5) was cut into two pieces along the backbone line. The left half was directly tanned by SL, then was shaved, pre-treated by the poly-carboxylate auxiliary agent PAA and less-chrome tanning. The right half (control) was pickled, chrome tanning according to traditional process. They were separately put in the stainless steel drums (1000cm diameter). The recipes of tanning the subsequent processes are given in Table 5, 6.

The shrinkage temperature, the content of Cr_2O_3 in the effluent, the absorption of Chrome tanning agent softness and state of the leathers were measured. At the same time, samplers of the leathers were cut from the official sampling position[11]. The cross sections of the samples were observed by Scanning Electron Microscope (JSM-5900LV, JEOL Ltd., Japan). The micrographs at a magnification of 100 were obtained with an accelerating voltage of 20KV.

2.8 Piolt production of Leather tanned by chrome-less tannage

Sixty pieces of bated bovine pelt (approximately 50 square foot, pH 7.0-7.5) were directly tanned by SL, then were shaved, pre-treated by the poly-carboxylate auxiliary agent PAA, less-chrome tanning. The recipes of tanning the subsequent processes are given in TABLE V, VI. The shrinkage temperature, the content of Cr_2O_3 in the effluent, the absorption of Chrome tanning agent softness and state of the leathers were measured.

Table 5. The procedures of tanning with novel Chrome-less tannage and traditional chrome tanning.

Process	Chrome-less tannage		Traditional chrome tanning		t/min	Remarks
	Chemicals	%	Chemicals	%		
Wash	Water, 25°C	200	Water, 25°C	200	15	3 times, drain
Pickling	/	/	Sodium Chloride	8	20	
	/	/	formic acid	0.6	15	
	/	/	Sulfuric acid	1.1-1.2	120	pH 2.8-3.0
De-acidification	/	/	HCOONa	1.5		
	/	/	$NaHCO_3$	2.5	150	pH 6.0-7.0
Wash	/	/	Water, 25°C	200	15	2 times, drain
Tanning	SL	5	Chrome tanning agent	8	300	
Basification	$NaHCO_3$	1.2	$NaHCO_3$	1.2	60	pH 7.0-8.0
	Water, 55°C	100	Water, 55°C	100	300	pH 7.0-7.5
Out of drum and piled down. Wring, shaving to 1.0mm, weight						
The chrome-less tannage based on the shaved wet white is done according to Table 4.						

Table 6. The procedures of dyeing or fat-liquoring of the leathers tanned by Chrome-less tannage and traditional chrome tanning.

Process	Chemicals	%	Time(min)	Remarks
Re-wetting	Water,35°C	200		
	BCN 60	0.3		
	Formic acid	0.8	30	pH 5.8
Wash	Water,25°C	200	15	drain
Dyeing/Fat-liquoring	Water,50°C	200		
	dyestuff	2	30	
	TRUPON SWS	12		
	TRUPON DB	5	90	
	Formic acid	0.6		
	Formic acid	0.6		pH 3.8
Wash	Water,25°C	200	15	
Out of drum and horsed overnight, Vacuum and hang dry, vibration staking & milling				

3 Results and Discussion

3.1 Analysis of Tanning properties of the novel chrome-free agent SL and its leather

Relation between the shrinkage temperature of the leather tanned by SL and its offer is shown in Fig 3. The shrinkage temperature of the leathers rise as the offer increases when the offer of SL is 2%-5%, when the level of tanning agent reacting with the collage increases as the offer increases and the shrinkage temperature of the leather rises greatly. The change of the shrinkage temperature of the leather is less when the offer of SL is 6%-10%, which show that the amino groups of the fiber collage almost entirely react with SL. Therefore the optimal offer of SL is 5% based on the weight of bated pelt. The shrinkage temperature of the leather is 85.7°C, whose color is white and has fine grain.

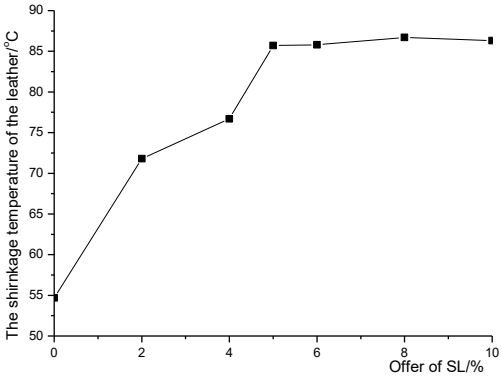
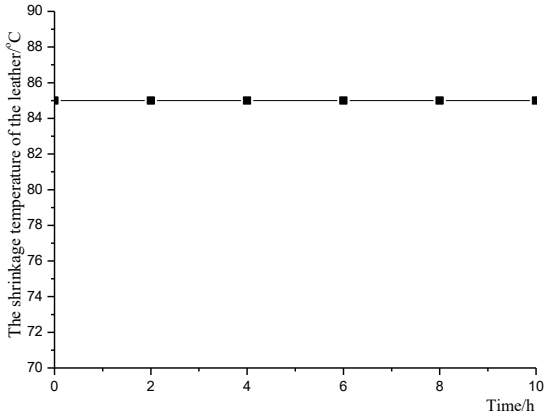


Fig. 3. Relation between the shrinkage temperature of the leather tanned by SL and its offer.

The properties of de-tanning resistance of SL-tanned wet white leather during washing with water and acid solution are shown in Fig 4. The shrinkage temperature of the SL-tanned leather has no change after it is washed with water, which show that the SL-tanned leather has good de-tanning resistance in the water. In addition, the shrinkage temperature of the SL-tanned leather is affected to a certain extent by acid solution with different pH. The change of the shrinkage temperature of the SL-tanned leather low when the pH of acid solution is changed from 5.5 to 2.5. But the range of the change of the shrinkage temperature of the SL-tanned leather less, which shown that the SL-tanned leather has good de-tanning resistance in the acid solution.



A

B

Fig. 4. The properties of de-tanning resistance of SL-tanned wet white leather during washing with water and acid solution (A: washing with water for different time B: washing with acid solution of different pH).

3.2 Optimum the initial pH of Chrome tanning agent in shaved wet white

The chrome-tanned effect of the shaved SL-tanned wet white under the different initial pH is shown in Table 7. The initial pH of float and wet white can affect the time of penetration of Chrome tanning agent, the shrinkage temperature and the state of Leather. The time of penetration of Chrome tanning agent increases along with the rise of pH of float. The reason is maybe that the more carboxyl group is transformed to ionic state and fixed with Chrome tanning agent under the condition of higher pH so as to penetrate slowly in the wet white. In addition the shrinkage temperature of Leather increases along with the rise of pH of float, which higher than 95°C. The color and the grain of Leather are from light blue to dark blue, from fine to coarse. So the initial pH of float is 3.5 based on the effect of tanning.

Table 7. The chrome-tanned effect of the shaved SL-tanned wet white under the different initial pH.

Initial pH	Time of penetration/h	Ts/°C	Color of Leather	State of Grain
2.5	2	100	Light blue	fine
3.0	2	103	Light blue	fine
3.5	2.5	105.5	Blue	fine
4.0	2.5	106	Dark blue	Coarse
4.5	3	108.5	Dark blue	Coarse
5.5	3	109.6	Dark blue	Coarse

3.3 Optimum the offer of Chrome tanning agent in shaved wet white

The chrome-tanned effect of the shaved SL-tanned wet white under the different offer of Chrome tanning agent is shown in Table 8. The offer of Chrome tanning agent can affect the time of penetration of Chrome tanning agent, the shrinkage temperature and the state of Leather. The time of penetration of Chrome tanning agent decreases along with the offer of Chrome tanning agent. The shrinkage temperature of Leather increases along with the rise of the offer of Chrome tanning agent, which higher than 95°C. But the color of Leather are from light blue to dark blue, which maybe that more Chrome tanning agent is fixed on the surface of Leather so as to darker than before. In addition, the absorption level of Chromium decreases along with the rise of the offer of Chrome tanning agent so as to the rise of the content of Cr_2O_3 of the effulent. So the offer of Chrome tanning agent is 3-4% based on the effect of tanning including the shrinkage temperature and the state of Leather, the content of Cr_2O_3 of the effulent and Absorption level.

Table 8. The chrome-tanned effect of the shaved SL-tanned wet white under the different offer of Chrome tanning agent.

Offer of the Chrome tanning agent/wt%	Time of penentration/h	Ts/°C	Color of Leather	Content of Cr_2O_3 in the effulent/mg/L	Absorption Level/%
2	2.5	96	Light blue	48	98
3	2	100	Light blue	145	96
4	2	103	Blue	225	95.3
5	1.5	104.8	Dark blue	384	93.6
6	1.5	108	Dark blue	554	92.3

3.4 Optimum the offer of the poly-carboxylate auxiliary agent PAA in less-chrome tanning of shaved wet white

Effect of different offer of the poly-carboxylate auxiliary agent PAA on less-chrome tanning was shown in Table 9. The trends of the absorption level of Chromium is from increase to decrease along with the

rise of the offer of the poly-carboxylate auxiliary agent PAA, that is, the absorption level of Chromium increase in the range of 0 and 2%, but the absorption level of Chromium decrease when the offer of the poly-carboxylate auxiliary agent PAA is bigger than 2%. In addition, the time of penetration of Chrome tanning agent and the state of Leather are also affected based on the offer of the poly-carboxylate auxiliary agent PAA. Therefore the optimal offer of the poly-carboxylate auxiliary agent PAA is 1.5-2%.

Table 9. Effect of different offer of the poly-carboxylate auxiliary agent PAA on less-chrome tanning.

Offer of PAA/wt%	Time of penentration/h	Color of Leather	Content of Cr_2O_3 in the effulent/mg/L	Absorption Level/%	State of Grain
0	2	blue	225	95.3	fine
0.5	2	blue	190	96	fine
1.0	2	blue	134.5	97.2	fine
1.5	2	blue	67.0	98.6	fine
2.0	2.0	Dark blue	96	98	Coarse
2.5	2.5	Dark blue	182.2	96.2	Coarse

3.5 Comparison chrome-less tannage and traditional chrome tanning

The status of the leathers tanned by chrome-less tannage and traditional chrome tanning is shown in Table 10. Both of the shrinkage temperature of Leathers are above 95°C. The leather has a fine grain, good softness and fullness. The offer of Chrome tanning agent in chrome-less tannage less than that of traditional chrome tanning. In addition, the absorption level of Chromium is up to 98% so that the content of Cr_2O_3 in the effulent also less than that of traditional chrome tanning. Furthermore the content of Cl^- is zero in the effulent so as to reduce the pollution of the content of chloride ion.

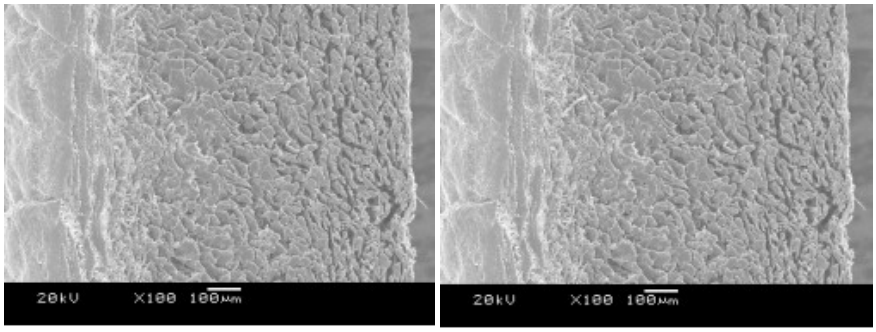
The scanning electron micrographs of sections of the leather samples are presented in Figure 8. The fiber bundles of the leather tanned by less-chrome tannage are well dispersed, which is on a par with the one of the leather tanned by traditional chrome tanning.

3.6 The properties of Leather tanned by less-chrome tannage from Piolt production

Sixty pieces of bated bovine pelt were tanned by the less-chrome tannage in the tannery. The properties of Leathers are shown in Table 11. The shrinkage temperature, the content of Cr_2O_3 in the effluent, the absorption of Chrome tanning agent softness and state of the leathers are satisfied and equal to that of traditional chrome tanning.

Table 10. The properties of Leathers tanned by less-chrome tannage and traditional chrome tanning.

Item	Leather tanned by less-chrome tannage	Leather tanned by traditional chrome tanning
Ts/°C	103	105
Color of Leather	Blue	Blue
Content of Cr_2O_3 in the effulent/mg/L	67	1200
Absorption level/%	98.6	75
State of Grain	Fine	Fine
Offer of Chrome tanning agent/%	4 (based on the weight of Shaved wet white)	6 (based on the weight of limed split)
Content of Cl^- in the effulent /mg/L	0	4000
Fullness	Full	Full
Softness	6.0	6.0
absorption of dyestuff/%	99.5	96
absorption of fat-liquor/%	82.5	85



a b

Fig. 8. Scanning Electron Microscopic photograph (×100 magnification) of the leathers tanned by less-chrome tannage and traditional chrome tanning (a: The leathers tanned by less-chrome tannage ; b: the leathers tanned by traditional chrome tanning).

Table 11. The properties of Leathers tanned by less-chrome tannage from Piolt production.

Item	Leather tanned by less-chrome tannage
Offer of Chrome tanning agent/%	4 (based on the weight of Shaved wet white)
Ts/°C	105
Color of Leather	Light blue
Fullness	Full
Softness	6.2
State of Grain	Fine
Content of Cr_2O_3 in the effulent/mg/L	65
Absorption level/%	98.8
Content of Cl^- in the effulent /mg/L	0

4 Conclusions

A non-pickling, chrome-less tanning technology was developed. The novel Chrome-free agent SL can be directly employed to tan bated bovine hide and the wet white was obtained. The shrinkage temperature of the wet white tanned by SL reached over 80°C and has good de-tanning resistance in water and the acid solution.

The shaved wet white was pre-treated by 1.5-2wt% Poly-carboxylate auxiliary agent and tanned by chrome powder.The better chrome-less tanning conditions were that the wet white was tanned by 3-4wt% chromium powder for 150～180min at room temperature when the initial pH value was 3.0-3.5. The next processes were same as traditional chrome tannage. Meanwhile, the shrinkage temperature of the leather tanned by the chrome-less tannage reached more than 95°C, the absorption of chromium was 98%, the content of Cr_2O_3 in the effluent was under 200mg/L. For the chrome-less tanned leather, the absorption of dyestuff, fat-liquor reached 99.5%, 82.5% respectively. Compared with the traditional chrome tanned process, not only the conventional pickling process was eliminated, the process was been shorten and reduce the pollution of sodium chloride, but it can reduce 50% of the consumption of Chrome powder, improve the absorption of chromium and can reduce content of Cr_2O_3 in effluent.

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