Chrome-reduced Combination Tanning for Cleaner Dyed Sheep Fur Processing

by

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Abstract

Chrome tanning is essential for conventional processing of dyed sheep fur as it can provide fur with high hydrothermal stability suitable for dyeing of wool at a temperature around 70°C. However, a long float length and a big offer of chrome tanning agent (16 g/L) are required for the tanning process, which lead to poor uptake of chrome and excessive discharge of chrome in wastewater. In this study, reduction of chrome offer in dyed sheep fur production was investigated to develop a cleaner tanning technology. It was found that the even distribution of chrome and satisfactory dispersion of fur collagen matrix were achieved even though chrome tanning agent offer was reduced to 2 g/L and 4 g/L. But the shrinkage temperature of the furs was only 79°C and 85°C, respectively, which resulted in a sharp area shrink of fur in following high temperature dyeing. In the combination tannage using 10 g/L amphoteric organic tanning agent (TWT) and 2 g/L or 4 g/L chrome tanning agent, the shrinkage temperature of fur was higher than 90°C accompanied by a higher utilization of chrome. These combination tanned furs were capable of enduring dyeing process at 68°C for 8 h, and presented a high uptake of post tanning chemicals because they had an isoelectric point close to that of chrome tanned fur. More importantly, the physical properties of the combination tanned dyed furs were comparable to the dyed fur made by conventional chrome tanning using 16 g/L chrome tanning agent.

Introduction

In fur industry, dyeing of wool at a high temperature for a long time (about 70°C, 6-8 h) is commonly performed in the production of dyed sheep fur. Thus, the shrinkage temperature (Ts) of tanned sheep fur is required to be higher than 90°C in order to avoid the shrink of fur and damage to collagen fiber during dyeing.[1] Chrome tannage is regarded as the dominant tanning method of dyed sheep fur because it endows fur with high hydrothermal stability. However, a large quantity of chrome tanning agent (12-16 g/L) is often used in conventional fur tanning process. In addition, a long float length (6-10) is applied to prevent wool from felting. Therefore, a low uptake rate of chrome (usually less than 30%) is presented due to osmotic balance. A large amount of chrome remained in wastewater. It will lead to environmental pollution and waste of chrome if the wastewater is not properly disposed.

In consideration of the characteristics of dyeing sheep fur (e.g. high Ts, large area yield, softness and lightness), none of the existing chrome free tanning technology is qualified when singly used. It seems that chrome is essential for the tanning process of sheep fur. Accordingly, for the purpose of reducing chrome offer and discharge, it is meaningful to develop a combination tanning method using an appropriate chrome-free tanning agent and a small quantity of chrome tanning agent. Organic tanning agents such as aldehyde and phosphonium, rather than mineral tanning agents or vegetable tannins, could give the fur softness and lightness according to practical experience. Moreover, it has been reported that these organic tanning agents could improve the uptake of chrome and enhance the crosslink between collagen fibers.[2-4] In our previous studies, an amphoteric organic tanning agent (named TWT) was developed and its adaptability in combination tanning with chrome in leather processing had been proved.[5, 6] Besides the common characteristics of organic tanning agent as mentioned above, TWT showed better compatibility with post tanning chemicals (such as fatliquor and dyestuff) compared with other organic tanning agents due to its amphoteric charge property.[5] This suggests the prospect of TWT in chrome-reduced combination tannage for producing quality dyed sheep fur.

In this study, the effects of chrome tanning agent offer on tanning and dyeing processes of dyed sheep fur processing were firstly investigated, so as to find the feasible degree of chrome reduction. Then, based on the acceptable reduced offer of chrome, a combination tanning of TWT and chrome was explored. The chrome content, Ts and area yield of fur

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were measured to evaluate the performances of the combination tanning. In addition, the release of chrome during dyeing, the uptake of fatliquor and dyestuff as well as the physical properties of the dyed fur were determined to further evaluate the adaptability of the novel tannage.

EXPERIMENTAL

Materials

Pickled sheep skins were supplied by Zhejiang Zhonghui Fur & Leather co., LTD. (Tongxiang, China). Amphoteric organic tanning agent (TWT) was supplied by Sichuan Tingjiang New Material Co., LTD. (Shifang, China). The other chemicals used in fur making were of commercial grade. The chemicals used for analysis of fur and wastewater were of analytical grade.

Conventional Chrome Tanning of Sheep Fur

Pickled sheep skins were tanned by the conventional chrome tanning method as shown in Table I.

Chrome-reduced Combination Tanning of Sheep Fur

Pickled sheep skins were tanned by TWT at first, and then chrome tanning was conducted. The chrome-reduced combination tanning processes were shown in Table II.

TABLE I
Conventional Chrome Tanning of Sheep Fur.

Process/Chemicals	Offer (%)	Conc. (g/L)	T (°C)	t (min)	Remarks
Repickling					
Water [a]	800		28		
NaCl		60			
Formic acid		5		240	pH=2.5-2.8
Tanning (in repickling bath)					
Chrome tanning agent (Cr_2O_3 24%)		X	30	180	X=2, 4, 8, 12, 16
Sodium formate		2	32	60	
Chrome tanning auxiliary		2		90	Overnight
Basification (in tanning bath)					
$NaHCO_3$		3.5-6	32	15×5+60	pH=3.8-4.0
			38	120	Overnight
Washing					
Water	1000		25		
Formic acid		0.5			
Degreasing agent		5		120	Drain
Washing					
Running water			25	10	Drain
Horsed up for 24 h and wrung.					

[a] The offer of water was based on the weight of pickled sheep skin.

TABLE II
Chrome-reduced Combination Tanning of Sheep Fur.

Process/Chemicals	Offer (%)	Con. (g/L)	T (°C)	t (min)	Remarks
Depickling					
Water	800		25		
NaCl		60			
$NaHCO_3$		4		5	pH=6.8-7.5
Organic tanning (in depickling bath)					
TWT tanning agent		10	25	240	
$NaHCO_3$		4		240	pH=7.6-7.8
			40	240	Overnight
Next day ran for 30 min and drained. Horsed up for 24 h and wrung.					
Chrome tanning					
Water	800		32		
NaCl		20			
Formic acid		1			
Non-ionic surfactant		0.5		120	pH=3.4-3.6
Chrome tanning agent		X		360	X=2, 4 Overnight
Basification					
$NaHCO_3$		1-2	35	15×4+60	pH=3.8-4.2
			38	180	Drain
Washing					
Water	1000		25		
Formic acid		0.5			
Degreasing agent		5		30	Drain
Washing					
Running water			25	10	Drain
Horsed up for 24 h and wrung.					

Post Tanning Processes of Sheep Fur

Post tanning processes of sheep fur were performed according to the recipe shown in Table III.

Determination of Chrome Content in Sheep Fur and Dyeing Wastewater

Wool on the chrome tanned sheep fur was completely shaved. Then the fur was split into three layers (grain layer, middle layer and flesh layer) using a freezing microtome (Leica CM1950, Leica, Germany). After drying to a constant weight, the fur samples were digested by using concentrated nitric acid and hydrogen peroxide (2:1, v/v). The digestion liquor was filtered and then diluted with deionized water, and the concentration of chrome was determined by ICP-AES (inductively coupled plasma atomic emission spectrometry, 2100 DV, PerkinElmer, USA). Chrome content of the fur was calculated by following equation.

Chrome content = (weight of Cr_2O_3/weight of dried sheep fur) × 100%

Dyeing wastewater was digested at first, and then the chrome concentration was determined as above.

TABLE III
Post Tanning Processes of Sheep Fur.

Process/Chemicals	Offer (%)	Con. (g/L)	T (°C)	t (min)	Remarks
Neutralization					
Water	800		35		
Sodium formate		2			
$NaHCO_3$		2		120	pH=6.0-6.5
Washing	Running water		25	10	Drain
Fatliquoring					
Water	800		50		
Fatliquor		6		120	
Formic acid		1.0		30×2	pH=3.8-4.0
Washing	Running water		25	15	Drain
Horsed up for 24 h and wrung.					
Dyeing					
Water	800		68		
Ammonia water		1		30	
Black dyestuff		4		420	
Formic acid		0.5		30×2	pH=3.8-4.0
Washing					
Running water			25	10	Drain
Horsed up for 24 h and wrung.					

Scanning Electron Microscope (SEM) Analysis of Sheep Fur
The tanned sheep fur was lyophilized after shaving of wool. Then wool and the cross section of the fur were observed using SEM (JSM-7500F, JEOL, Japan).

Estimation of Area Yield of Sheep Fur
Sheep fur was wrung to control its moisture content around 65%. Then, the area yield of sheep fur was measured by using grid counting method (1 cm^2/grid unit).

Uptake of Fatliquor and Dyestuff in Post Tanning Processes
Total Organic Carbon (TOC) concentrations of fatliquoring emulsion before and after fatliquoring were determined by TOC analyzer (LiquiTOC, Elementar, Germany). The uptake rate of fatliquor was calculated according to the measured TOC values. The uptake rate of dyestuff was determined by spectrophotometry.[6]

Determination of Isoelectric Point of Sheep Fur
The isoelectric points of sheep furs tanned by different tannages were determined using a method based on the adsorption of sodium dodecyl benzene sulfonate (SDBS) on collagen fiber.[7] The mechanism of adsorption is electrostatic interaction. 0.200 g sheep fur powder without wool (conditioned at 20°C under 65% RH for 48 h) was added into 100 mL SDBS solution (0.5 mg/mL) with different pH values. Then adsorption of SDBS on fur powder was conducted at 30°C for 4 h. The concentrations of SDBS solution before and after adsorption were determined by spectrophotometry to calculate the adsorption capacity of SDBS in fur. The effect of pH on adsorption capacity was fitted with competitive binding model. The $LogIC_{50}$ value of fitting curve was recognized as the isoelectric point.[7]

Determination of Physical Properties of Fur
The dyed sheep furs after shaving of wool were conditioned for 24 h at 20°C and 65% RH, and then their tensile strength, tear strength and elongation at break were tested according to standard method.[8,9]

Results and Discussion

Effect of Reduction of Chrome Offer on Tanning Performance
Pickled sheep skins were tanned with different concentrations of chrome tanning agent (from 2 g/L to 16 g/L). As shown in Table IV, the chrome content and Ts of the fur increased with increasing chrome offer. It is well known that a high concentration of chrome tanning agent favors penetration of chrome into sheep skin and improves fixation of chrome on collagen fiber. However, it was found in our experiments that chrome was evenly distributed in each layer of the furs after tanning with different concentrations of chrome tanning agent (Figure 1). SEM analysis also demonstrated that collagen fiber of sheep fur was well opened up and fixed even though the concentration of chrome tanning agent was reduced to 2 g/L (Figure 2). The uptake rate of Cr was significantly reduced with increasing chrome offer (Table IV), and reduced to as less as 24.4% when 16 g/L chrome tanning agent was used due to the long float length. An undesirable area shrink of fur was observed (see Table IV) as the concentration of chrome tanning agent increased. This can be explained by the astringency of chrome tanning agent.[10] In general, it seems that the reduction of chrome offer did not affect the tanning performances except hydrothermal stability of sheep fur.

Effect of Reduction of Chrome Offer on Dyeing Performance
Sheep furs tanned by different dosages of chrome tanning agent were then treated according to the recipe shown in Table III. Dyeing of wool was conducted at 68°C for 8 h in order to open up the scale layer.[1] Such a severe condition may lead to release of chrome from fur as well as the shrink of fur.

TABLE IV
Chrome Content, Shrinkage Temperature and Area Yield of Chrome Tanned Sheep Fur.

Chrome tanning agent offer (g/L)	Cr_2O_3 content (%)	Uptake of Cr (%)	Ts (°C)	Area Yield (%)
2	0.73	53.2	78.9	102.53
4	1.47	53.6	85.0	100.00
8	2.22	40.5	90.0	95.07
12	2.51	30.5	95.0	93.53
16	2.67	24.4	100.5	91.85

Table V shows that chrome concentration in dyeing wastewater of each group was actually very low (1-4 mg/L), which indicated that most of the chrome in the fur was effectively fixed with collagen fibers.[11] However, the Ts of fur decreased by 3-5°C after dyeing. It was also observed that the area yield reduced dramatically when the fur was tanned with 2 g/L or 4 g/L chrome tanning agent. Therefore, the fur with relatively low hydrothermal stability was not able to resist shrink and damage of collagen fibers during dyeing process. An essential shrinkage temperature, i.e. higher than 90°C, is required for the manufacture of dyed fur. These results suggested that the application of combination tannage was necessary for enhancement of Ts when chrome tanning agent concentration was reduced to 2-4 g/L.

Chrome-reduced Combination Tanning using TWT

Combination tanning was conducted according to Table II. Pickled sheep skins were firstly tanned by 10 g/L TWT tanning agent, and then tanned by 2 g/L or 4 g/L chrome tanning agent. TWT is an amphoteric organic macromolecular compound with multiple functional groups including aldehyde, amino and carboxyl groups.[5] The aldehyde groups imparted moderate tanning power to TWT, resulting in a Ts of fur around 86°C (Table VI). Moreover, the sheep fur did not shrink after TWT tanning in terms of area yield (Table VI). SEM analysis also showed that collagen fibers of TWT tanned fur were well dispersed, and the scale layer of the wool exhibited no sign of damage (Figure 3 A-1 and A-2). These facts demonstrated that the first step of tanning by TWT brought positive effect for fur making. Then a small quantity of chrome tanning agent (2-4 g/L) was added to further raise the Ts and enhance the tanning effect. The results in Table VI indicated that Ts of the combination tanned fur was higher than 90°C, which might meet the requirement of subsequent dyeing. It was found that the chrome content of combination tanned fur as well as the uptake rate of Cr was 10%-30% higher than those of single chrome tanned fur (see Table IV).

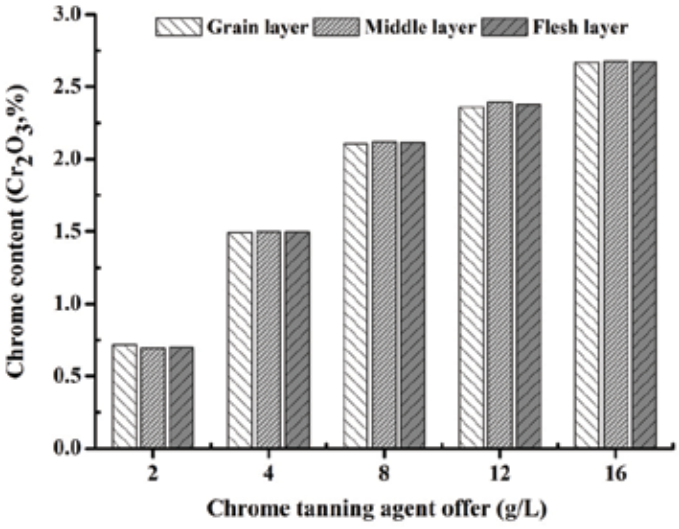

Figure 1. Chrome distribution in chrome tanned sheep fur.

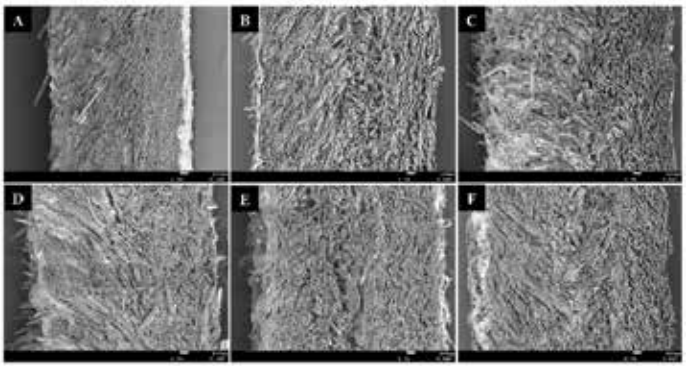

Figure 2. SEM images of the cross section of fur before and after chrome tanning. (A: pickled sheep skin; B, C, D, E, F: tanned by 2 g/L, 4 g/L, 8 g/L, 12 g/L and 16 g/L chrome tanning agent, respectively.)

TABLE V
Effect of Chrome Offer on Dyeing Performance of Chromed Tanned Sheep Fur.

Chrome tanning agent offer (g/L)	Chrome conc. in dyeing wastewater (mg/L)	Shrinkage temperature (°C)		Area yield (%)	
		before dyeing	after dyeing	before dyeing	after dyeing
2	1.43	75.3	69.8	108.94	46.99
4	1.72	83.0	80.0	108.33	83.33
8	2.15	91.6	88.9	100.40	101.29
12	2.51	100.5	97.5	97.71	102.72
16	3.32	102.8	98.5	94.72	103.33

As we know, the prior organic tanning can fix collagen fibers and thus improve penetration and distribution of following chrome tanning agent.[3, 4] This fact is confirmed by the results in Figure 4 that the layer distribution of Cr in the combination tanned fur was quite even. More importantly, the carboxyl groups of TWT could coordinate with chrome complexes just as the carboxyl groups on the side chains of collagen do, so that the absorption of Cr in fur was enhanced and the emission of Cr into wastewater was reduced. In addition, good tanning performance was achieved in terms of area yield (Table VI) and morphology of fur (Figure 3). It can be inferred that the combination tanned fur was suitable for the following fatliquoring and dyeing processes.

Dyeing Performance of Chrome-reduced Combination Tanned Fur

The effects of dyeing on chrome release, Ts and area yield of the combination tanned fur were investigated. Chrome released from the fur during dyeing (Table VII) was much less than that from the conventional chrome tanned fur (see Table V) under the same offer of chrome tanning agent. This means that the combination tanning using TWT enhanced the fixation of Cr due to the fact that more carboxyl groups were introduced onto collagen fibers. Table VII also shows that the Ts did not decrease remarkably after dyeing. Meanwhile, the area yields of the fur even increased slightly. These results suggested that the combination tanned fur was capable of enduring high temperature dyeing process. Furthermore, the uptake rates of fatliquor and dyestuff in the combination tanned fur were found to be higher than those in chrome tanned fur under the same offer of chrome tanning agent (Table VIII). In fact, they were comparable to those of conventional chrome tanned fur using 16 g/L chrome tanning agent. This can be explained by the isoelectric point (pI) of fur shown in Table VIII. It is known that the pI of fur or leather is in relation to the penetration and fixation of anionic fatliquors and dyestuffs in the post tanning processes.[12] Higher pI brings about stronger fixation of anionic chemicals at a pH lower than pI. The pI of conventional chrome tanned fur using 16 g/L chrome tanning agent was 8.18, which resulted in an excellent absorption of anionic fatliquor and dyestuff at the end of post tanning processes (around pH 4.0). However, the pI

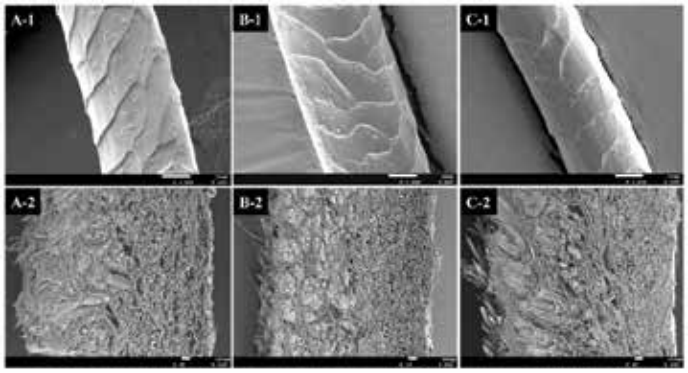

Figure 3. SEM images of wool and cross section of TWT tanned and combination tanned furs. (A: 10 g/L TWT tanning; B: 10 g/L TWT + 2 g/L chrome tanning agent; C: 10 g/L TWT + 4 g/L chrome tanning agent.)

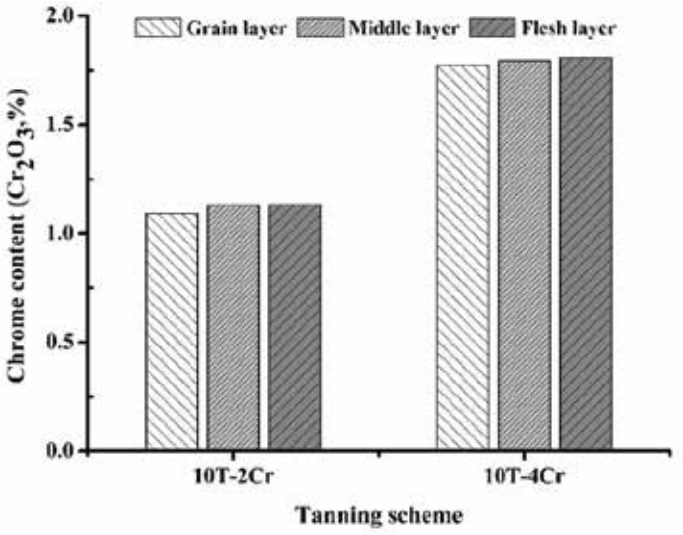

Figure 4. Chrome distribution in the combination tanned sheep fur. (10T-2Cr: 10 g/L TWT + 2 g/L chrome tanning agent; 10T-4Cr: 10 g/L TWT + 4 g/L chrome tanning agent.)

TABLE VI
Chrome Content, Shrinkage Temperature and Area Yield of the Combination Tanned Sheep Fur.

Tanning scheme	Cr_2O_3 content (%)	Uptake of Cr (%)	Shrinkage temperature (°C)	Area yield (%)
10 g/L TWT	—	—	86.3	100.59
10 g/L TWT + 2 g/L chrome tanning agent	1.12	81.5	92.0	105.68
10 g/L TWT + 4 g/L chrome tanning agent	1.81	66.0	103.2	102.63

of furs tanned by 2 g/L and 4 g/L chrome tanning agent was reduced to 7.62 and 7.71, respectively, due to less chrome complexes and more unsealed carboxyl groups in the fur, as indicated in Table IV. The use of TWT in combination tanning raised the pI of fur through introduction of amino groups in TWT and increase of chrome binding capacity (see Table VI), which is beneficial for the uptake of post tanning chemicals.

The high utilization of chrome in the combination tanning and well uptake of post tanning chemicals in the combination tanned fur achieved satisfactory physical properties of the resultant fur. As shown in Table IX, physical properties of the combination tanned dyed fur were comparable to that made by conventional chrome tanning using 16 g/L chrome tanning agent, even though 2 g/L chrome tanning agent was used in the combination tanning.

TABLE VII
Dyeing Performance of Chrome-reduced Combination Tanned Sheep Fur.

Tanning scheme	Chrome conc. in dyeing wastewater (mg/L)	Ts (°C)		Area yield (%)	
		before dyeing	after dyeing	before dyeing	after dyeing
10 g/L TWT + 2 g/L chrome tanning agent	0.88	91.2	92.9	106.14	107.56
10 g/L TWT + 4 g/L chrome tanning agent	0.70	105.8	101.5	104.15	112.51

TABLE VIII
Uptake of Fatliquor and Dyestuff in the Tanned Sheep Fur.

Tanning scheme	Uptake of fatliquor (%)	Uptake of dyestuff (%)	Isoelectric point of fur
2 g/L chrome tanning agent	54.85	96.90	7.62
10 g/L TWT + 2 g/L chrome tanning agent	58.98	99.62	7.75
4 g/L chrome tanning agent	56.23	98.84	7.71
10 g/L TWT + 4 g/L chrome tanning agent	59.53	99.68	7.82
16 g/L chrome tanning agent	58.67	99.49	8.18

TABLE IX
Physical Properties of Dyed Fur.

Tanning scheme	Tensile strength (N/mm^2)	Tear strength (N/mm)	Elongation at break (%)
10 g/L TWT + 2 g/L chrome tanning agent	18.47	52.48	83.43
16 g/L chrome tanning agent	13.27	49.67	80.73

CONCLUSIONS

The combination tanning of amphoteric organic tanning agent TWT and chrome can meet the needs of dyed sheep fur processing. This tannage can largely reduce the dosage of chrome tanning agent, and produce dyed fur with the physical properties and area yield comparable to those of the fur made by conventional chrome tanning. The use of amphoteric organic tanning agent in the combination tanning is the key point that brings about high utilization of chrome and high uptake of post tanning chemicals, so as to produce satisfactory resultant fur.

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REFERENCES

1. Cheng, F. X., Zhang, D. M., Wang, X. C.; Theory and technology of fur processing. Chemical Industry Press, Beijing, China, 2005.
2. Luo, J. X., Li, J., Liao, X. P., *et al*.; Cleaner chrome tanning-A non-picking process using an aliphatic aldehyde as pre-tanning agent. *J. Soc. Leather Technol. Chem*. **96**, 21-26, 2012.
3. Fathima, N. N., Rao, J. R., Nair, B. U.; Studies on phosphonium based combination tanning: less chrome approach. *JALCA* **106**, 249-256, 2011.
4. Plavan, V.; Chrome tanning improvement by chitosan application. *J. Soc. Leather Technol.Chem*. **96**, 89-93, 2012.
5. Shi, B., Li, J., Wang, Y. N., *et al*.; A novel wet white technology based on an amphoteric organic tanning agent. Taipei: 9th AICLST Congress, 1-18, 2012.
6. Wu, C., Zhang, W. H., Liao, X. P., *et al*.; Transposition of chrome tanning in leather making. *JALCA* **109**, 176-183, 2014.
7. Sun, Q. Y., Wang, Y. N., Liao, X. P., *et al*.; SDBS Adsorption Method: A New Method for Determination of Isoelectric Point of Skin and Leather. *China Leather* **42**, 9-13, 2013.
8. IUP 6, Measurement of tensile strength and percentage elongation, 2011.
9. IUP 8, Measurement of tear load – Double edge tear, 2002.
10. Li, G. Y., Luo, Y.; High exhaustion chrome tanning mechanism and its technology (II): study of chrome tanning technology at high pH value. *China Leather* **29**, 20-22, 2000.
11. Zhou, J., Hu, S. X., Wang, Y. N., *et al*.; Release of chrome in chrome tanning and post tanning processes. *J. Soc. Leather Technol.Chem*. **96**, 157-162, 2012.
12. Guthrie-Strachan, J., Flowers, K.; Protein and leather charge. *World Leather* **19**, 19-23, 2006.