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Release of chrome in leather production with less chrome tannage and less chrome retannage

Zhou Jian[1,2]

[1]College of Life Science and engineering, Southwest University of Science and Technology, Mianyang 621 010, P. R. China
[2]National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610 065, China
E-mail: zhoujian@swust.edu.cn

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High chrome concentration in wastewater of traditional chrome tannage has attracted increasing attentions，and the distribution of chrome in wastewater in the processes of less chrome tanning and less chrome retanning has investigated. The results indicate that the residual chrome in chrome tanning and chrome retanning wastewater is still the main origin of chrome in effluent, but the decrease of chrome concentration in wastewater is found to be significant. It is interesting that the properties of leathers including shrinkage temperature and mechanical properties do not decrease sharply along with the decrease of chrome offer. This fact demonstrates that the chromes that effectively react with collagen have not been decreased although reducing the chrome offer. Therefore, the development of technologies of less chrome tannage and less chrome retannage that can reduce chrome offer might be an important direction in alleviation of chrome discharge in tannery.

Keywords: Less chrome tannage, Less chrome retannage, Chrome release, Traditional tanning techniques, Effective.

Chrome tanning plays an important role in leather industry[1]. At the same time, a large amount of chrome is remained in the wastewater of chrome tanning and chrome retanning[2]. There is an average estimation that only 50%~70% of the chrome added is absorbed by leather in the conventional chrome tanning and chrome retanning processes[3].

With the environmental concerns and legislation request, the wastewater generated in the chrome tanning and chrome retanning processes cannot be discharged directly without effective treatments because of high content of chrome[4]. Thus, various efforts have been made to develop novel techniques to reduce the release of chrome. Recovery and reuse[5] of chrome from chrome tanning wastewater is capable of effectively minimizing the discharge of chrome, but the properties of final leather are difficult to control because of the complexity of reused wastewater including chrome and various chemical reagents[3]. The chrome absorptivity can be increased with processes improvement in chrome tanning and chrome retanning such as tanning with smaller liquid ratio, higher temperature, lengthening time as well as improving *p*H value[6]. However, chances are those measures have some side effect on the final leather, such as grain coarsening and green leather[7-9]. Auxiliary agentsfor chrome tanning and chrome retanning including carboxylate[10], acrylic acid[11] and amino resin[12] are usually used to improve the chrome absorptivity since the effect of crosslink of auxiliary agents between single-point combined chrome and collagen fiber[13]. Therefore, it is essential for tannery to reduce the release of chrome on the premise of maintaining qualities. It was found that, however, the researches about the reasons of chrome release and the influence of chrome release on leather quality were limited. Therefore, in our former research[14], the distribution of chrome in the wastewaters from chrome tanning and post tanning processes was investigated and the possible improvement for reducing the release of chrome with less-chrome tanning and less-chrome retanning was suggested.

In the present work, a new procedure of less chrome tanning and less chrome retanning was investigated according to the results of former research. The wastewaters of post chrome tanning processes were collected and their chrome concentration was determined. Various physical and chemical effects, such as shrinkage temperature of leathers were also measured after each process to reflect the influence of less chrome tanning and less chrome retanning. Based on all the data obtained a new procedure for reducing the release of chrome with less chrome tanning and less chrome retanning were discussed.

Experimental Section

Materials

Conventionally processed pickled goat skins (*p*H=2.8) were used as the raw material for tanning trials. All the operations were carried out in drums (Φ400mm×150mm) equipped with automatic controls of speed and temperature. The chemicals used for leather processing were of commercial grade, and the chemicals used for chrome content determination were of analytical grade. The Cr_2O_3 content and alkalinity of chrome tanning agent is 20.61 and 33%, respectively.

Methods

Chrome tanning and post tanning processes

Pickled goatskins were tanned by chrome powder using the conventional method. Each wet blue was divided into four pieces along the core and the backbone for subsequent operations from chrome tanning to neutralization (including the processes of less-chrome tanning, wring-shaving, washing-1, acidification, less-chrome retanning, washing-2 and neutralization). The amount of chrome tanning agent was listed in Table 1.

Chrome concentration in wastewater

Wastewater from each process was collected and the volume was measured. Then the chrome concentration in wastewater was tested by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 2100DV, Perkin-Elmer, USA) after filtration and dilution. Then, the content of total chromium left or released in wastewater can be calculated.

Table 1 — The amount of chrome tanning agent in the processes of less chrome tanning and less chrome retanning

Processes	Amount of Chrome tanning agent	
	chroming (base of 150% pickled goatskins)	Re-chroming (base of 100% wet blue)
Less chrome tanning	4%	4%
	5%	4%
	6%	4%
	7%	4%
	8%	4%
Less chrome retanning	4%	0
	4%	1%
	4%	2%
	4%	3%
	4%	4%
A cenrtain percentage of chrome tanning agent	3%	5%
	5%	3%
	7%	1%

Chrome content in leather

Leather samples collected along the backbone after each process were dried to constant weight at 102°C. After cooling in desiccators for 30 minutes, about 0.1g of dried leather was weighed and then digested by microwave digestion system (MDS-8, Sineo, China). The total chromium content in digestion solution was determined by ICP-AES and then the content of Cr_2O_3 in leather was calculated.

Determination of leather properties

The shrinkage temperature of leathers after various processes was determined in glycerol by HG shrinkage temperature recorder. Leather samples were stored at 20±2°C and 65±2% RH for 48 hr, and then used for the measurements of tensile and tear strengths and break elongation with a GT-Al-7000s tester.

Results and Discussion

Release of chrome in less chrome tanning processes

Previous investigations manifested that the total chrome concentrations in the wastewater maintains a high concentration of 3446 $mg.L^{-1}$ in the process of chrome tanning and chrome is actually released in all the processes from chrome tanning to neutralization[14]. Therefore, the alleviation of chrome discharge is of great concern to tanners. In the present work, reducing the offer of chrome tanning agent was investigated from chrome tanning to neutralization to reduce the discharged chrome. 8% chrome tanning agent (base of 150% pickled goatskins) is usually used in the traditional chrome tannage. Therefore, less chrome tannage with 4, 5, 6, 7 and 8% chrome tanning agent (base of 150% pickled goatskins) are designed to investigate the release of chrome.

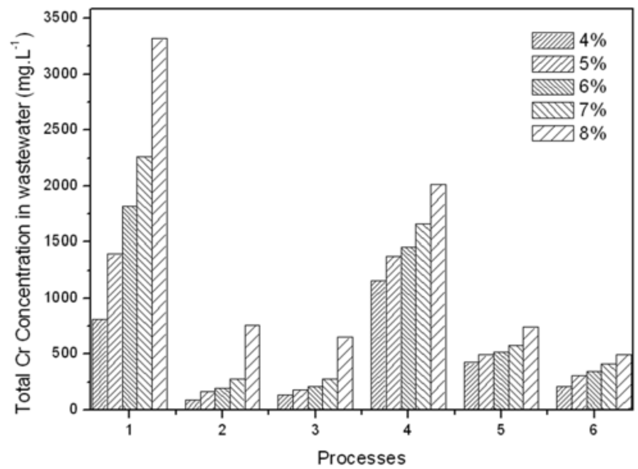
The total chrome concentrations in the wastewaters from chrome tanning to neutralization processes are presented in Fig.1. As can be seen, the chrome concentrations in the wastewater from chrome tanning to neutralization all increases evidently with increasing chrome tanning agent offer. It should be noted that most of released chrome is still discharged in the processes of chrome tanning and chrome retanning, but there appeared an obvious decrease.

Chrome concentration in the wastewater was reduced to 809.2 mg.L^{-1} with 4% chrome tanning agent offer (base of 150% pickled goatskins). Released chrome during the processes of washing-1, washing-2 and neutralization decreased apparently, mostly because of the decreasing of unfixed chrome in leather. These results indicated that the decreasing of chrome tanning agent offer should be the main reason for reductive chrome concentration in the wastewater. Furthermore, the lowest chrome concentration of 809.2mg.L^{-1} in chrome tanning wastewater indicated that the dynamic equilibrium of chrome ion in tanning system including leather and solution is responsible for the incomplete absorption and cross-linking of chrome.

The total chrome left or released in wastewater was calculated and the released ratio of chrome was presented in Fig. 2. It was found that the released ratio of chrome increased to 53.70% from 30.89% with the increasing chrome tanning agent offer. Above results meant that the released ratio of chrome is responsible for the addition of chrome tanning agent. In addition, it can be inferred that there is a great deal of incomplete absorbed chrome existed in the tanning solution and a great deal of unfixed chrome existed in leather because of the excessive addition of chrome tanning agent. So a conclusion might be that the excessive addition of chrome tanning agent is the main reason of high chrome concentration in wastewaters.

The shrinkage temperature of leathers is dependent on the amount of cross-linking chrome between collagen fibers. The shrinkage temperatures of leathers tanned by various offer of chrome tanning agent are displayed in Table 2. The shrinkage temperatures of leathers shows a little variation (110.2 to 116.2°C) after chrome tanning even though the chrome tanning agent offer varying from 4 to 8%, which suggested that the content of cross-linking chrome between collagen fibers do not decreased even though reducing the amount of chrome tanning agent. Furthermore, the excessive addition of chrome tanning agent mainly added the amount of incomplete adsorbed or unfixed chrome, which did not really contribute to the hydrothermal stability of leather.

Mechanical properties analysis was carried out and the results are given in Table 3. In comparison with the traditional chrome tanned leather, the tensile strengths and tear strength of less chrome tanned leather decrease insignificantly, and are superior to the Chinese standards for goatskin garment leather. Furthermore, the break elongation of leather tanned



1-chrome tanning; 2-washing-1; 3-acidification; 4-chrome retanning; 5-washing-2; 6-neutralization

Fig. 1 — Total chrome concentrations in wastewaters after chrome tanning with different chrome tanning agent offer (base of 150% pickled goatskins)

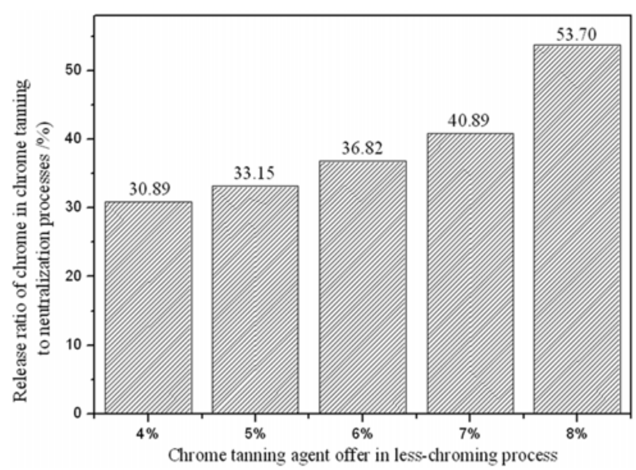


Fig. 2 — The released ratio of chrome in chrome tanning to neutralization processes after tanning with different chrome tanning agent offer (base of 150% pickled goatskins)

Table 2 — Shrinkage temperature of leathers in chrome tanning to neutralization processes after tanning with different chrome tanning agent offer (base of 150% pickled goat skins)

Processes	Shrinkage temperature(°C)				
	4%*	5%	6%	7%	8%
Chrome tanning	110.2	111.8	113.9	115.7	116.2
Shaving	112.9	113.5	116.4	117.3	115.3
Washing-1	109.6	109.8	110.4	111.8	110.7
Acidification	105.4	105.6	106	108.2	106.6
Rechroming	115.7	114.6	114.7	116.3	115.6
Washing-2	116.9	116.4	116.9	117.4	115.7
Neutralization	115.6	115.3	115.7	116.6	117

*4%-8% is the chrome tanning agent offer in less-chroming process by less chrome improved. These results indicate that the cross-linked chrome in collagen merely decreased with less chrome tannage.

Release of chrome in less chrome retanning processes

Chrome tanning and chrome retanning are the input processes of chrome in traditional tanning system. In this part, less chrome retannage with 0, 1, 2, 3 and 4% chrome tanning agent (base of 100% wet blue) are designed to investigate the release of chrome. Total chrome concentrations in wastewaters after chrome retanning with different offer of chrome tanning agent (base of 100% wet blue) are shown in Fig. 3.

As can be seen from the results, chrome concentrations in wastewaters in the processes of chrome retanning, washing-2 and neutralization increased with increasing offer of chrome tanning agent. Particularly, only 192.8 mg/L of chrome concentration exists in chrome retanning wastewater while no chrome tanning agent is added, but 1159 mg/L for chrome tanning agent offer of 4% (base of 100% wet blue). An interesting phenomenon is that, unlike with less chrome tanning process, the released ratio of chrome decreased with increasing offer of chrome tanning agent. The released ratio of chrome was calculated and presented in Fig. 4. About 58.82% of added chrome was discharged in wastewater with the chrome tanning agent offer of 1% (base of 100% wet blue), but decreased to 43.03%, 41.18% and 35.78% with the chrome tanning agent offer of 2%, 3% and 4%, respectively. This might be due to the reason of chrome osmotic pressure in chrome tanning system.

This fact suggests that a cenrtain offer of chrome tanning agent is necessary in the process of chrome retanning to make sure that the chrome osmotic pressure is positive from chrome retanning bath to collagen fibers.

The shrinkage temperature of leathers retanned by less-chrome tanning agent is presented in Table 4.

Table 3 — Mechanical properties of leather with less chrome tannage

Processes	Amount of chrome tanning agent	Mechanical properties of leather in chrome reduced tanning		
		Tensile strengths/N. mm^{-2}	Break elongation/%	Tear strengths/N.m^{-1}
Less chrome tanning	4%	19.14	79.35	36.32
	5%	22.56	73.25	36.10
	6%	23.16	68.55	38.50
	7%	24.32	65.65	41.09
	8%	24.86	60.54	42.87
Standard for goatskin garment leather (China)	/	>6.5	25-60	>18

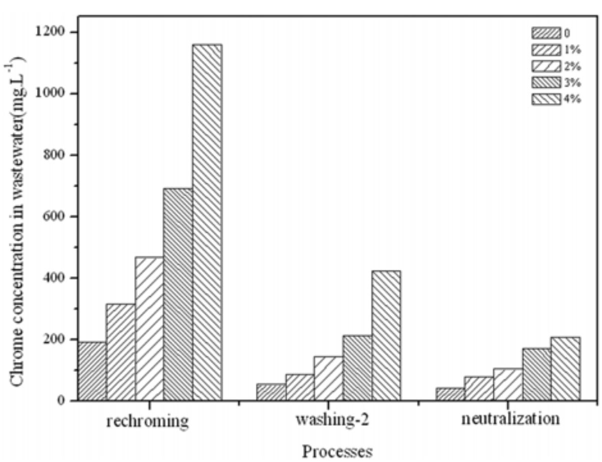


Fig. 3 — Total chrome concentrations in wastewaters after retanning with different chrom.etanning agent offer (base of 100% wet blue)

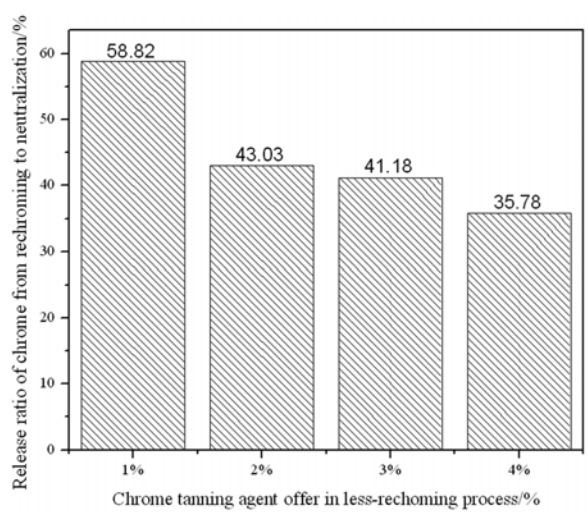


Fig. 4 — Release ratio of chrome in rechroming to neutralization processes after retanning withdifferent chrome tanning agent offer (base of 100% wet blue)

Table 4 — Shrinkage temperatures of leathers in rechroming to neutralization processes after retanning with different chrome tanning agent offer (base of 100% wet blue)

Processes	Shrinkage temperature/°C				
	0*	1%	2%	3%	4%
Rechroming	99.3	106.2	107.5	109.3	115.7
Washing-2	104.1	106.5	108.6	111.7	116.9
Neutralization	103.4	106.6	109.5	112.3	115.6

*0-4% is the chrome tanning agent offer in less-chrome retanning process

The results indicated that chrome retanning has little effect on the rise of shrinkage temperature. Taking the chrome tanning agent offer of 3% as example, only an improvement of 10°C for the shrinkage temperature of leather is achieved. The performance of mechanical properties for leather retanned by less chrome retannage is consistence with less chrome tanned leather (Table 5). These results indicated that the cross-linked chrome increased with the process of chrome retannage and the mechanical properties of less chrome retanned leather are sanctified the Chinese standard for goatskin garment leather.

Release of chrome in chrome tanning and chrome retanning processes with a cenrtain percentage offer of chrome tanning agent

As has been argued, a large amount of incomplete adsorbed chrome is remained in wastewater with traditional chrome tannage. A new chrome addition style with less chrome tannage and less chrome retannage has been mentioned and discussed. Therefore, the total percentage of chrome tanning agent (base of pickled goatskin) and chrome retanning agent (base of wet blue) was set to a definite value (Table 2) and the release of chrome was analyzed. Total chrome concentration in wastewater with a cenrtain percentage offer of chrome tanning agent is presented in Fig. 5.

As can be seen from the results, the total chrome concentration in wastewater before the chrome retannage with acenrtain percentage offer of chrome tanning agent is agreement on that with the less-chrome tannage, and that after chrome retannage is agreement on that with less-chrome retannage. The total chrome left or released in wastewater and the released ratio of chrome was calculated (Table 5). It was found that almost half of added chrome (48.1%) was left or released in wastewater with the chrome tanning agent offer of "7%+1%". The excessive chrome tanning agent (7%) in the process of chrome tanning result to a great deal of incomplete absorbed and unfixed chrome is discharged into wastewaters. Furthermore, the chrome concentration in chrome retanning bath is not high enough with 1% chrome retanning agent and result to low chrome osmotic pressure. Therefore, the offer of chrome tanning agent should be decreased and the offer of chrome retanning agent should be increased to reduce the chrome concentration in wastewater, as the results showed in Table 6 (3%+5%).

The shrinkage temperature of leathers from the processes of chrome tanning to neutralization with a cenrtain percentage offer of chrome tanning agent were showed in Fig. 6. The shrinkage temperature of leathers increased with the increasing offer of chrome tanning agent, and it keep step with less-chrome tannage. Significantly, the shrinkage temperature of leathers reached 104°C with the offer of 3% chrome tanning agent in the process of chrome tanning. This fact demonstrates that the effective cross-linking between collagen fibers and chrome complexes is strong enough. Furthermore, the mechanical properties (Table 7) of leathers tanned with a certain percentage offer of chrome tanning agent are superior to the Chinese standards for goatskin garment leather.

Table 5 — Mechanical properties of leather with less chrome retannage

Processes	Amount of chrome retanning agent	Mechanical properties of leather in chrome reduced tanning		
		Tensile strengths/N.mm^{-2}	Break elongation/%	Tear strengths/N.m^{-1}
Less chrome retanning	0	15.79	92.3	31.55
	1%	17.42	88.3	34.74
	2%	16.69	87.5	35.44
	3%	17.86	80.35	36.14
	4%	19.14	79.35	36.32
Standard for goatskin garment leather (China)	/	>6.5	25-60	>18

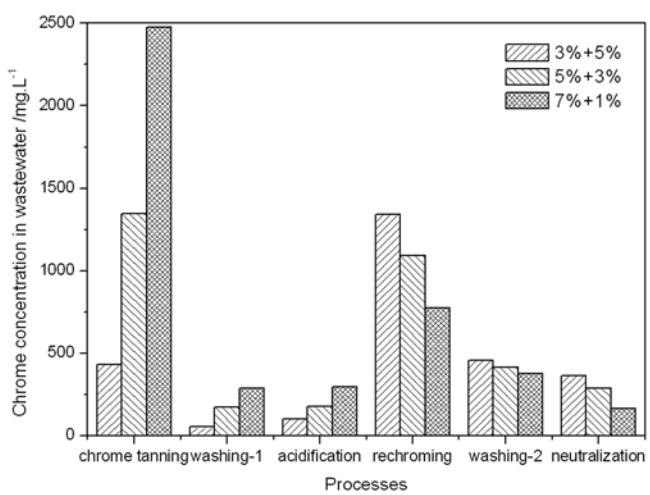


Fig. 5 — Total chrome concentration in wastewater with a cenrtain percentage offer of chrome tanning agent

Table 6 — Release ratio of chrome in chrome tanning to neutralization processes with a cenrtain percentage offer of chrome tanning agent

Processes	Release ratio of chrome /%		
	3%+5%	5%+3%	7%+1%
Chrome tanning to neutralization	30.44	39.35	48.10

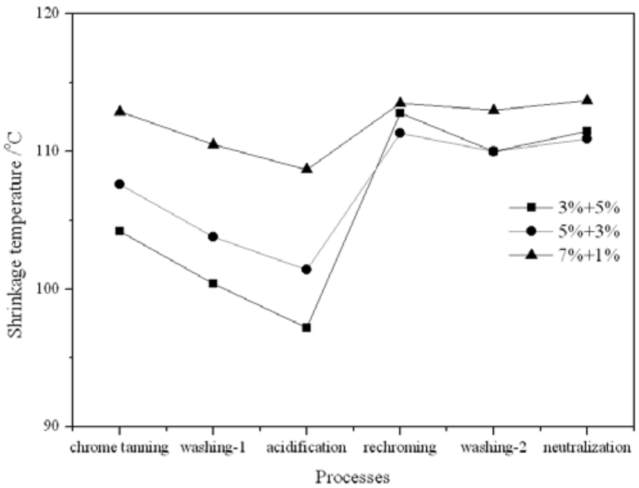


Fig. 6 — Shrinkage temperature of leathers in chrome tanning to neutralization processes with a cenrtain percentage offer of chrome tanning agent

Table 7 — Mechanical properties of leather in chrome reduced tanning

Processes	Amount of chrome agent	Mechanical properties of leather in chrome reduced tanning		
		Tensile strengths/N.mm^{-2}	Break elongation /%	Tear strengths/N.mm^{-1}
A cenrtain percentage of chrome tanning agent	3%+5%	23.00	41.7	34.87
	5%+3%	26.24	51.1	35.23
	7%+1%	32.57	75.5	36.98
Standard for goatskin garment leather (China)	/	>6.5	25-60	>18

Conclusions as a result, it is feasible that the new addition style of chrome tanning agent can decrease the release ratio of chrome and immune to the shrinkage temperature of leathers.

Conclusion

Nowadays, for most tanneries, traditional chrome tanning method (150% pickled goat skins offer of chrome tanning agent) is still used, and a great deal of incomplete absorbed and unfixed chrome is discharged into wastewaters. Investigation reveals that the amount of effective cross-links between collagen fibers and chrome complexes by less chrome tanning and less chrome retanning keeps agreement with that tanned by traditional chrome tanning. The excessive addition of chrome tanning agent improves the amount of incomplete adsorbed or unfixed chrome rather than the effective cross-linking. Compared with the traditional alleviation measures for chrome discharge, such as recovery and reuse of chrome from chrome tanning wastewater as well as high chrome exhaustion systems, less chrome tanning and less chrome retanning system will effective decreases the concentration of chrome in wastewater and eases the processing difficulty of wastewater. Furthermore, about 50% chrome tanning agent will be saved in the process of less chrome tanning and less chrome retanning without the decrease of the hydrothermal stability of leathers obviously. Therefore, the developed less chrome tanning technologies that can decrease the concentration of chrome in wastewater with reducing chrome offer might be a practical direction in alleviation of chrome discharge in tanneries. It is suggested that the development of less-chrome technologies that can decrease the concentration of chrome in wastewater and reducing chrome offer might be an important direction in alleviation of chrome discharge in tanneries.

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References

1 Covington A D, *J Am Leather Chem Assoc*, 107 (2011) 258.
2 Covington A D, *Leather Sci Eng*, 12 (2002) 3.
3 Kanagaraj J, Babu N K & Mandal A B, *J Clean Prod,* 16 (2007) 1807.
4 Taylor M M, Lee J & Bumanlaq L P, *J Am Leather Chem Assoc*, 106 (2011) 35.
5 Mella B, Glanert A C & Gutterres M, *Proc Saf Environ Prot*, 95 (2015)195.
6 Zhang C X, Xia F M & Peng B Y, *J Am Leather Chem Assoc*,12 (2016) 435.
7 Li G Y, Luo Y & Zhang M R, *China leather*, 29 (2000) 20.

8 Li G Y, Luo Y & Zhang M R, *China leather*, 29 (2000) 20.
9 Wu C, Zhang W H & Liao X P, *J Am Leather Chem Assoc*, 109 (2014)176.
10 Luan S F, Liu Y & Fan H J, *J Soc Leather Technol Chem.*, 91 (2007) 149.
11 Kanagaraj J & Gupta S, *J Am Leather Chem Assoc*, 103 (2008) 36.
12 Kanagaraj J, Sadulla S & Jawahar M, *J Soc Leather Technol Chem*, 89 (2005) 18.
13 Tao E, Ma H R & Hao C, *J Soc Leather Technol Chem*, 98 (2014) 63.
14 Zhou J, Hu S X &Wang Y N, *J Soc Leather Technol Chem*, 96 (2012) 157.