PROCEEDINGS OF THE 11th WORLD RABBIT CONGRESS
Qingdao (China) - June 15-18, 2016
ISSN 2308-1910

Session
Fur & Wool

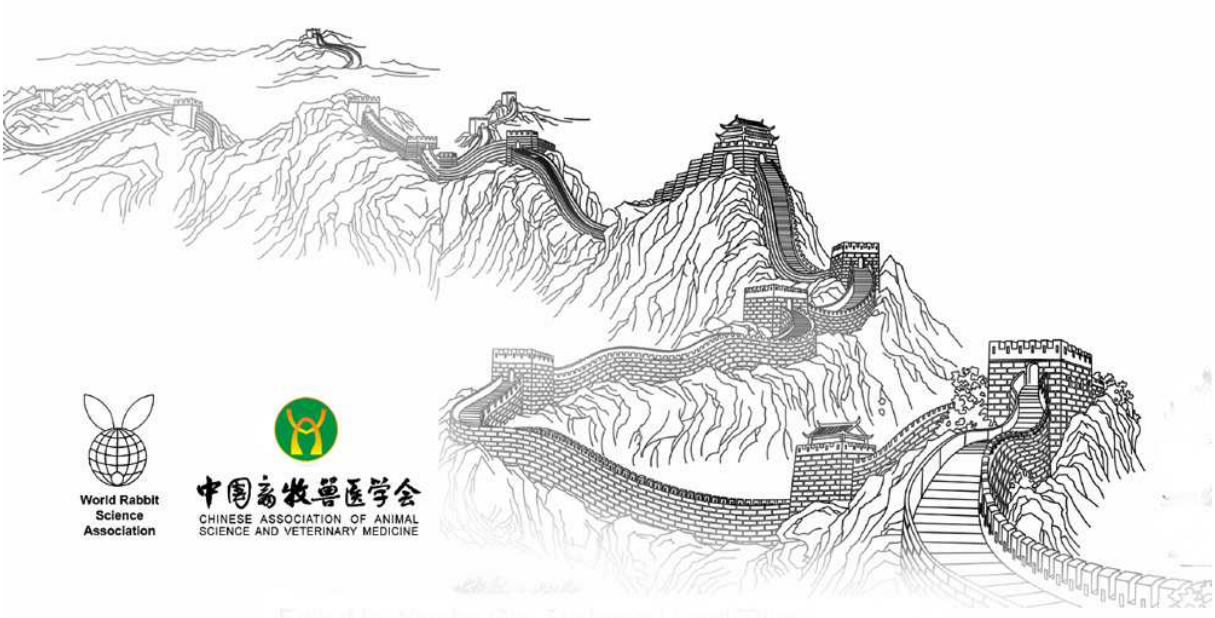
Liu H., Liu H.Y., Chen Y.Y., Li S.L., Zhang Z.C.

THE FORMALDEHYDE-FREE TANNING METHOD OF REX SKIN BASED ON ZIRCONIUM-ALUMINUM COMPLEX TANNING AGENT.

Full text of the communication

How to cite this paper :
Liu H., Liu H.Y., Chen Y.Y., Li S.L., Zhang Z.C., 2016 - The formaldehyde-free tanning method of rex skin based on Zirconium-Aluminum complex tanning agent. *Proceedings 11th World Rabbit Congress - June 15-18, 2016 - Qingdao - China, 845-848.*

.



THE FORMALDEHYDE-FREE TANNING METHOD OF REX SKIN BASED ON ZIRCONIUM-ALUMINUM COMPLEX TANNING AGENT

Liu Han[1], Liu Hongyan[2], Chen Yinyin[2], Li Shuangli[1], Zhang Zongcai[1,2]*

[1]The Key Laboratory of Leather and Engineering of Ministry of Education, Sichuan University, 610065, Chengdu, China
[2]National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, 610065, Chengdu, China
*Corresponding author: Zhang Zongcai, professor, email: zhang508@scu.edu.cn

ABSTRACT

This paper studied the effect of different ratio of zirconium and aluminum salt, dosage of tanning agent and masking agent on tanning results. The result showed that the shrinkage temperature was 70.9 ^{0}C when the total dosage of tanning agent was 10 g/L and ZrO_2:Al_2O_3=1:0.5. Masking agent can significantly improve the penetration and absorption of the tanning agent. The shrinkage temperature of the pelt could reach to 80.1°C which was masked with lactic acid, and it showed preferable in the softness, hand feel, strength and washable resistance.

Key words: zirconium-aluminum complex tanning, Rex fur, masking agent, formaldehyde-free tanning

INTRODUCTION

Nowadays, environmental protections have become one of the most concerned issues in global industrial activities. And the cleaner fur processing towards a greener environment is the current theme for sustainable fur industry. Rex skin has been one of the most important raw fur skins for its flat, homogeneous, fine and dense fur. However, the rabbit skin tanning method is still dominated by formaldehyde or formaldehyde-aluminum tanning. And the enormous amounts of emissions of formaldehyde in conventional formaldehyde or formaldehyde-aluminum tanning process are a longstanding old problem that has never been resolved satisfactorily before. Besides, the great deal of free formaldehyde in the fur productions which are tanned with formaldehyde has raised a serious threat to fur sector. In order to overcome the problems, a novel formaldehyde-free tanning method of rex skin based on zirconium-aluminum complex tanning agent was developed and optimized (Fathima *et al.*, 2003; Lan, 2009).

MATERIALS AND METHODS

Main equipments and materials

AZ-7000S Electronic Universal Testing Machine (GAOTIE Polytron Technologies Inc); Leather Softness Testing Instrument (GAOTIE Polytron Technologies Inc); RiteColor Premier 8200(X-Rite Inc.); Inductively Coupled Plasma Emission Spectrometer (AES-ICP, 2100DV, Perkin Elmer Inc. America); Desktop Scanning Electron Microscope (Phenom Pro, Phenom World Inc., Netherland).
The pickled rex skins used in this experiment were processed by means of routine processing technic of Rex, and the process was: soaking, fleshing, resoaking, degreasing, bating, pickling. The pH of pickled pelt is 2.0. Zirconium sulfate and ammonium aluminum sulfate are industrial grade.

Tanning scheme

The composition of tanning liquid: water: 2 L/piece of skin; NaCl: 50 g/L; tanning agent: 10 g/L (except No. 8 and No. 9). The pickled pelts were tanned for 6 h, and then basified to pH3.5, overnight. The tanning liquid was basified to pH4.0 with sodium bicarbonate next morning, and heated up to

40°C. After 6 h, the pelts were taken out. The ratio of zirconium and aluminum salt, dosage of tanning agent, type of masking agent (Liu *et al.*, 2012) of the 16 different experiments were shown on Table 1.

Table 1: Tanning experimental scheme.

number	The ratio of zirconium and aluminum salt		Note
	ZrO_2	Al_2O_3	
1	0.25	1	
2	0.5	1	
3	0.75	1	
4	1	1	
5	1	0.75	
6	1	0.5	
7	1	0.25	
8	1	0.5	8 g/L of the dosage of tanning agent
9	1	0.5	12 g/L of the dosage of tanning agent
10	1	0.5	Masking with Sodium formate
11	1	0.5	Masking with Sodium citrate
12	1	0.5	Masking with Sodium formate and Sodium citrate
13	1	0.5	Masking with lactic acid
14	1	0.5	Masking with Sodium citrate and lactic acid
15	1	0.5	pickling with Aluminum salt
16	1	0.5	pickling with Zirconium salt

Analytical method

Mechanical property

The thickness of the pelt was measured on the basis of Leather-Physical and mechanical tests-Determination of thickness [QB/T 2709-2005]. The tensile strength, tear strength and load stretch rate were measured on the basis of Leather-Physical and mechanical tests-Determination of tensile strength and percentage extension [QB/T 2710-2005] and Leather-Physical and mechanical tests-Determination of tear load-Double edge tear [QB/T 2711-2005].

Whiteness of the pelt (flesh side) and fur

The whiteness was determined according to the following equation:

$$W_H = 100 - \sqrt{(100-1)^2 + a^2 + b^2}$$

(L, a, b are the brightness index and color index of the sample in the lab system)

RESULTS AND DISCUSSION

The tanning effect of different ratio of Zr and Al and dosage of tanning agent

As shown in Table 2, the shrinkage temperature was 70.9°C when the total dosage of tanning agent was 10 g/L and ZrO_2:Al_2O_3=1:0.5, and the pelt showed better softness, hand feel and strength. Although the shrinkage temperature is higher when the ratio of zirconium and aluminum salt was ZrO_2:Al_2O_3=1:0.5, the pelt was hard. So the ratio of zirconium and aluminum salt ZrO_2:Al_2O_3=1:0.5 was chosen for the next experiments.

Table 2: The tanning effect of different ratio of Zr and Al and dosage of tanning agent.

Number	Ts (°C)	Softness	Tear strength (N/mm)	Tensile strength (Mpa)	Stretched rate (%)	Thickening (%)
1	61.7	6.69	35.956	12.955	17.574	53.97
2	62.9	6.86	40.255	13.377	21.995	59.21
3	64.7	6.74	39.715	12.558	28.406	63.88
4	66.5	6.32	41.466	14.331	17.951	67.57
5	68.6	6.26	38.022	10.243	21.109	68.26
6	70.9	6.26	37.707	10.570	19.746	72.61
7	74.8	6.07	35.512	11.570	17.675	72.70
8	66.3	6.43	35.475	9.500	19.162	--
9	74.4	6.35	32.075	10.212	26.413	--

The influence of masking agent on tanning

Table 3: Physical properties of the pelts tanned with different kinds of masking agents.

Number	Ts (°C)	Softness	Tensile strength (Mpa)	Stretched rate (%)	Whiteness of fur	Whiteness of pelt
10	75.3	6.092	12.800	30.409	90.838	89.512
11	74.3	7.376	14.775	32.561	91.203	89.591
12	73.8	8.006	11.937	33.104	92.737	90.911
13	80.1	6.930	13.328	34.71	92.375	91.035
14	74.8	7.600	14.091	39.741	90.831	90.099

The masking agents in tanning liquid turn into the interior of zirconium and aluminum complexes, substitute acid radicals or unstable H_2O, form a new coordination compounds with H_2O, OH^- and acid group, change the composition, molecular size, charge and component content, the content of hydrated metal ions of the tanning liquid. Thus the tanning performance of the tanning liquid is changed. Adding masking agent can significantly improve shrinkage temperature, feel and strength of the pelt (Li *et al.*, 2015). The pelt showed the highest shrinkage temperature when it was masked with lactic acid, and it showed better in the softness, hand feel and strength. So the lactic acid was added for the next experiments as masking agent (Table 3).

To determine the content of Zr and Al in pelt by using Inductive Coupled Plasma Emission Spectrometer, the pelt was digested. The results were shown in Figure 1. The content of Zr and Al in the pelt which was tanned with masking agent increased significantly, and it was the highest when the pelt was tanned with lactic acid as masking agent.

Masking agents may also have a great impact on the fiber loose situation of the pelt. The dispersion of the fibers was characterized by SEM on fracture section of the pelt, as shown in Figure 2.

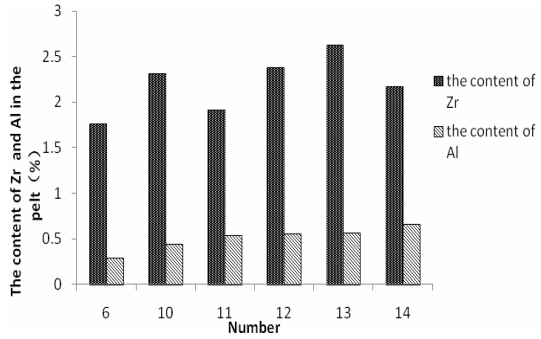


Figure 1: The content of Zr and Al in pelt

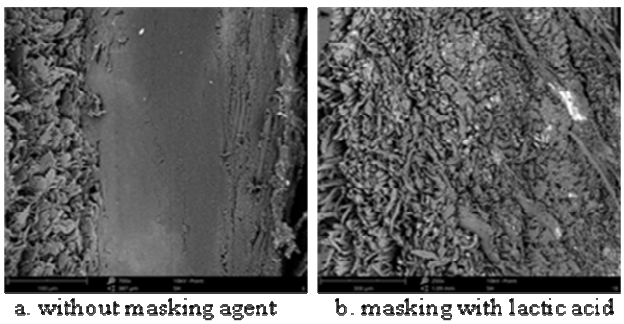


Figure 2: The dispersion of the fibers

Washable resistance of the pelt

The traditional aluminum tanning leather was not washable. The shrinkage temperature of the pelt which was washing for 1 h was reduced by 14 degrees (Table 4). The pelt tanned with zirconium-aluminum complex tanning agent had excellent washable resistance, and the shrinkage temperature of the pelt which was washing for 3h was not obviously decreased.

Table 4: The shrinkage temperature of the pelts washed with water

time	Traditional aluminum tanning	No. 6	No.10	No. 11	No. 12	No. 13	No. 14
Washing 0h	64.8℃	70.9℃	75.3℃	74.3℃	73.8℃	80.1℃	74.8℃
Washing 1h	50.8℃	70.9℃	75.1℃	74.3℃	73.7℃	80.1℃	74.5℃
Washing 2h	50.0℃	70.6℃	75.1℃	74.0℃	73.7℃	80.1℃	74.5℃
Washing 3h	50.0℃	70.6℃	75.1℃	74.0℃	73.7℃	80.1℃	74.5℃

CONCLUSIONS

The results show that the shrinkage temperature of the pelt will be higher with the increasing content of Zr in the tanning float, and it can reach to 70℃ when the total dosage of tanning agent was 10 g/L and ZrO_2:Al_2O_3=1:0.5. Adding masking agent can improve shrinkage temperature, feel and strength of the pelt significantly. The pelt showed the highest shrinkage temperature when it was masked with lactic acid, and showed better softness, hand feel, strength and washable resistance.

ACKNOWLEDGEMENTS

This work was supported by the earmarked fund for China Agriculture Research System (CARS-44-D-3) and the Project of Key technology research integration and industrialization demonstration of modern industrial chain for rabbit (2016 NZ002).

REFERENCES

Fathima N.N., Balaraman M., Rao J.R. 2003. Effect of zirconium (IV) complexes on the thermal and enzymatic stability of type I collagen. *Journal of Inorganic Biochemistry, 95, 47-54*.

Lan Y., Xu X., Zhou Jianfei. 2009. Research on tanning mechanism and developing prospects of zirconium salt. *Leather Science and Engineering, 04, 21-27*.

Li F., Yang X., Dan W. 2015. Fe-Zr-Al complex tanning agent and application on goat upper leather tanning process. *China Leather, 16, 16-20*.

Liu T., Lan Y., Zhang J.. 2012. Study on infiltration and combination of metal zirconium tanning with inhibitor. *Leather Science and Engineering, 06, 16-21*.

QB/T 2709-2005. 2005. Leather-Physical and mechanical tests-Determination of thickness. *The light industry standard of the people's Republic of China.*

QB/T 2710-2005. 2005. Leather-Physical and mechanical tests-Determination of tensile strength and percentage extension. *The light industry standard of the people's Republic of China.*

QB/T 2711-2005. 2005. Leather-Physical and mechanical tests-Determination of tear load-Double edge tear. *The light industry standard of the people's Republic of China*.

==========