Phosphonium-Aluminum Combination Tanning For Goat Garment Leather

by

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Abstract

A new tetrakis hydroxymethyl phosphonium sulphate (THPS)-aluminum combination tanning system has been developed. The optimum dosage of THPS was 2.0%. The amount of THPS and basic aluminum chloride was optimized at 2.0% and 3.0% (basing on the weight of pelt). The influence of ligands on the shrinkage temperature (Ts) of leathers was also studied and the Ts of THPS-aluminum combination tanned leathers was above 88°C. Color fastness to dry/wet rub of THPS-aluminum combination tanned leathers was much better than the relevant color fastness to dry/wet rub of leathers tanned with THPS alone. Scanning electron microscopic studies showed that the fiber weave of THPS-aluminum combination tanned leather was much closer than leathers tanned with THPS alone and the fiber weave of THPS-aluminum combination tanned leather was closer(tighter) with an increase of amount of basic aluminum chloride. Hence, with the increase of the amount of basic aluminum chloride, the reactive ability of basic aluminum chloride with collagen fiber was stronger and the softness became worse. Degradation rate of soiling for the THPS-aluminum combination tanning leather was much quicker than that of chrome tanning leather. Through SEM analysis, the surface structure of leather which was not degraded was more regular than the leather degraded for 30 days. Meantime, the THPS-aluminum combination tanning leather degradated much more easily than the chrome leather, which suggested a benefit for the sustainable development of the leather industry in future.

Resumen

Un nuevo sistema de curtido combinado de sulfato tetrakis-hidroximetil-fosfonio (THPS)-aluminio se ha desarrollado. La dosis óptima de THPS fue de 2,0%. La cantidad de THPS y cloruro básico de aluminio fue optimizada en 2,0% y 3,0% (basándose en el peso de la piel). La influencia de los ligantes sobre la temperatura de encogimiento (Ts) del cuero, también fue estudiada y la Ts de los cueros curtidos con la combinación THPS-aluminio fue superior a 88°C. La solidez del color al frote seco/húmedo de los cueros curtidos con la combinación THPS-aluminio fue mucho mejor que la solidez en los cueros curtidos con THPS solamente. Los estudios realizados mediante el microscopio electrónico de barrido mostraron que el entramado de fibras de las pieles curtidas con la combinación THPS-aluminio fue mucho más cerrada que el de las pieles curtidas con THPS solamente y que el tejido de fibra de las pieles curtidas con la combinación THPS-aluminio fue más firme con un aumento en la cantidad de cloruro de aluminio básico. Por lo tanto, con el aumento de la cantidad de cloruro de aluminio básico, la capacidad de reacción del cloruro básico de aluminio con la fibra de colágeno es más fuerte y desmejora la suavidad del cuero. La tasa de degradación del manchado de los cueros curtidos con la combinación THPS-aluminio es mucho más rápida que el del cuero curtido al cromo. A través del análisis de SEM, la estructura de la superficie del cuero que no fue degradada, fue más regular que el cuero degradado por 30 días. Mientras tanto, los cueros curtidos con la combinación THPS-aluminio se degradó más fácilmente que un cuero curtido al cromo, lo que sugiere un beneficio para el desarrollosostenible de la industria del cuero en el futuro.

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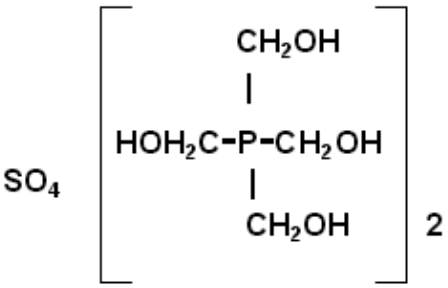
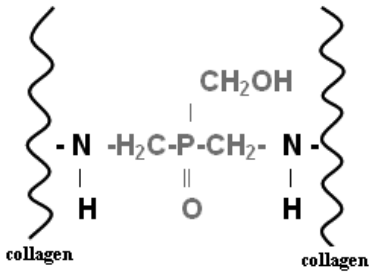
INTRODUCTION

With the development of science and technology and the consciousness of environment protection, the pollution caused by chrome tanning agent becomes a difficult problem. In order to overcome chrome related problems it is preferable to have a complete chrome-free tanning system. At present, the Ts of leather tanned by THPS or oxazolidines are more than 80ºC, so they are often used as tanning agent. THPS has many benefits such as low toxicity, low recommended treatment level, rapid breakdown in the environment, no bioaccumulation and reduced risk to both human health and environment.[1,2] The structural formula of THPS is as follows:



The hydroxymethyl groups in THPS can react with amino groups of collagen. The tanning mechanism is similar to that of the aldehyde tanning agent. They can firmly combine together and form short and strong cross linkage. [3,4] The reactive formulation is as follows:



The leather tanned by THPS which is called wet white leather has no metal ions and is electronegative. But for wet blue leather, the complexation is carried out between chrome and carboxyl and hydroxyl groups in collagen fibers. The electronegative wet white leather is completely different from wet blue leather, so its absorption and combination with retanning agent, dye, fatliquor and finishing agent is worse than wet blue leather. Since the combination points among wet white leather and chemicals is less, the fullness and dyeing properties of leather are bad. Therefore, combination tannage of THPS-mineral can effectively solve above problems. But the color of leather tanned by THPS-iron and THPS-tannin is deep, as a result, they are not suitable to produce leather with light color. In the study, the THPS-aluminum combination tanning for goat garment leather with light color is put forward. Dasgupta S. theoretically studied the effect of the THPS-aluminum combination tanning on the Ts of lambskins.[5,6] But no paper on the systematic research of the tanning goat garment leather with THPS-aluminum and the degradability of garment leather is present in literature. So in the study a THPS-aluminum tanning system for goat garment leather is put forward. Meantime, the tanning conditions, the effect of ligand on Ts, the optimization of the THPS-aluminum combination system in making garment leather, the degradability of garment leather and the physical mechanical properties of leather tanned with THPS-aluminum were researched.

EXPERIMENTAL

Materials

All materials used in leather processing were commercial grade. THPS (Commercial name is Granofin FCC) and basic aluminum chloride (Commercial name is Tanfix AL Powder) were provided by Clariant Company in Switzerland. Wet salted goatskins were supplied by Haining Shangyuan Leather Co., Ltd.

Determination of Ts

The Ts which was the hydrothermal stability of leather was determined with standard shrinkage meter (MSW-YD4). Each repeated triplicate and the average were recorded as the result.

Optimization of the dosage of THPS

Eight wet salted goatskins were pickled by conventional method, and then two pickled goatskins were used for each trial. 1.5%, 2.0%, 2.5% and 3.0% THPS (basing on the weight of limed skins) were used and tanning procedure was shown in TABLE I. Then the Ts of wet leather were measured.

THPS-aluminum combination tanning

Wet salted goatskins were pickled by conventional method. The pickled skins at a pH of 3.5 were taken and basifying pH was 5.0 for experimental tanning system. Eight pickled skins were used and every two skins were one experiment. 2.0% THPS and 1.0%, 3.0%, 5.0%, 7.0%basic aluminum chloride (basing on the weight of shaved skins) were used to tanning. The procedure was show in TABLE II. The hydrothermal stability of the wet leather was measured.

Physical testing and handle of leather

According to Chinese standard for garment leather (QB/T2709-2005, QB/T2710-2005 and QB/T2711-2005), tensile strength, elongation at break and tear strength were tested. Every value reported was the average of four (two was along the backbone, two was across the backbone) measurements. The softness, fullness, grain smoothness and grain tightness of leather were evaluated by five experienced tanners. The higher leather got points, the better its property.

TABLE I

Process to pickle and tan for wet salted goatskins

Process	%	chemicals	°C	min	pH	Remarks
Pickling	80	Water	Room temperature			
	8.0	Salt		20		Check Baume'degree to 6~6.5
	1.25	Sulfuric acid		2x20+40	2.8~3.0	
Tanning	X	Granofin FCC		120		O/N, next day druming for 30min
	1.0	Feliderm DP				
	1.0	Catalix L		60		
	0.3	Sodium bicarbonate		5x30+60	5.5~5.7	
	2.0	Tanicor KW		60		Drain
Oxidization	150	Water	Room temperature			
	0.7	Room temperature		60		
Washing	200	Water	Room temperature	10		Horse for 24h, check Ts
Shaving to 0.65mm						
Weighting						

Test of Cr^{6+} and formaldehyde content

The samples for the content of Cr^{6+} and formaldehyde were obtained by IUC 18 and CEN ISO/TS 17226: 2003, respectively.

Analysis with scanning electron microscopic (SEM)[7-10]

Leather samples were cut from the official sampling position (IUP 2). The micrographs for cross section were obtained operating the SEM at low vacuum with an accelerating voltage of 25 KV in different lower and higher magnification levels.

Biodegradability of garment leather[11,12]

The THPS-aluminum combination tanning and chrome tanning garment leather were degraded in soil and the degradation rate and SEM was examined. Some holes were dug in ground and their depth was 10~15cm. Leather samples were put into these holes and covered by soil. Degradation rate was determined by weight difference and the surface structure of degradation leather was observed by SEM.

RESULTS AND DISCUSSION

Optimization of the dosage of THPS

The offer of THPS has been optimized based on the Ts, tensile strength, tear strength and organoleptic properties. The dosage of THPS increased from 1.5% to 3.0% and the Ts of tanned leather were presented in Figure 1. With the increase of the dosage of THPS, Ts took on an increase. When the dosage of THPS was more than 2.0%, the increase of the dosage had no effect on Ts of leather. As shown in Figure 2. The leathers tanned by 2.0% THPS represented better grain smoothness, fullness, grain tightness and softness. Considering the Ts, tensile strength, tear strength and organoleptic properties, the optimum dosage of THPS was 2.0%.

Optimization of the dosage of aluminum retanning agent

As shown in TABLE III, along with the increase of the amount of Tanfix AL powder, Ts also continuously increased, but the organoleptic properties of leathers such as grain smoothness and softness became worse which was

TABLE II
The Process of THPS-aluminum tanning for garment leather

Process	%	chemicals	°C	min	pH	Remarks
Pickling	80	Water	Room temperature			
	8.0	Salt		20		Check Baume'degree to 6-6.5
	1.0	Sulfuric acid		2x20+40	3.5	
Tanning	2.0	Granofin FCC		120		O/N, next day drumming for 30min
	1.0	Feliderm DP				
	1.0	Catalix L		60		
	0.3	Sodium bicarbonate		5x30+60	5.5-5.7	Check pH
	2.0	Tanicor KW		60		Drain
oxidization	150	Water	Room temperature			
	0.7	sodium perborate		60		
Washing	200	Water	Room temperature	10		Horse for 24h, check Ts
Shaving to 0.65mm						
weighting						Based on weight
Degreasing	300	Water	40			
	0.5	Degreasing agent				
	0.3	oxalic acid				
	0.2	Feliderm MPP		40	5.5-5.7	Drain
Washing	300	Water	35	10		Drain
Retanning/fatliquoring	100	Water	35			
	1.5	Tergotan S				
	2.0	Derminol SF				
	2.0	Derminol CFS		30		
	2.0	Derma Black AF135		30		
	6.0	Tamicor SCU		30		
	3.0	Tergotan EF		30		
	4.0	Granofin TA		30		
	0.5	Formic acid		15	3.2	
	2.0	Formic acid		10+30	2.9	Drain
Washing	300	Water	35	5		
Retanning	100	Water	35			
	2.0	Catalix L		60		
	x	Tanfix AL Powder		90		
	1.0	Sodium formate		30		
	0.3	Sodium bicarbonate		30	3.8	
	0.3	Sodium bicarbonate		30		Drain
Next day				30	4.0-4.2	Drain
Washing	300	Water		5		
Neutralization	100	Water	35			
	1.0	Ammonium hydrogen carbonate		40	5.5-5.6	Drain
Washing	300	Water	35	5		
Retanning/fatliquoring	100	Water	35			
	2.0	Derminol CFS		10		
	3.0	Tergotan EF		30		
	100	Water(55_)	45			
	3.0	Derminol SF				
	3.0	Derminol CFS				
	3.0	Derminol ALE				
	3.0	Derminol RA				
	1.0	Derminol NLM		60		
	1.5	Formic acid		30	3.8	
	1.0	Derma Black AF-135		20		
	0.5	Formic acid		30	3.5	
	1.5	Dermagen PC		40		Checking Ts
Washing	300	Water	Room temperature	15		Horse, dry

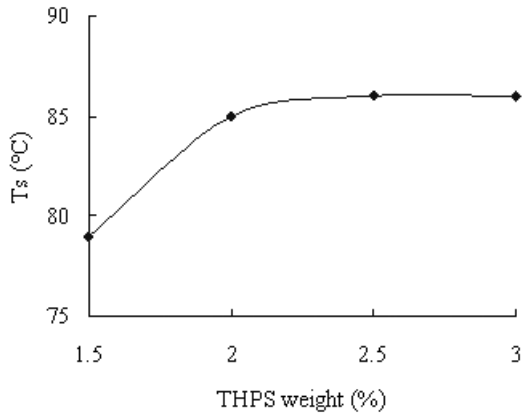


Figure 1: Relation of Ts and the dosage of THPS

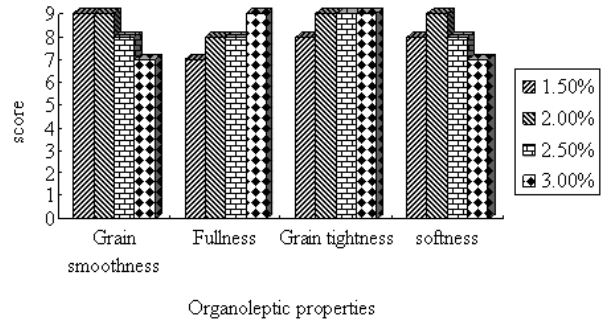


Figure 2: Organoleptic properties of leather tanned by THPS

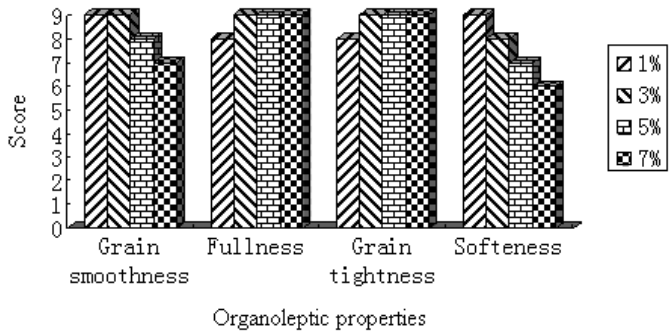


Figure 3: Organoleptic properties of leather tanned with THPS-aluminum

TABLE III

Relation of shrinkage temperature and the dosage of Tanfix AL Powder

The dosage of Granofin FCC (%)	The dosage of Tanfix AL Powder (%)	Ts (°C)
2.0	1.0	85
2.0	3.0	88
2.0	5.0	89
2.0	7.0	91

TABLE IV

Dyeing ability of THPS-aluminum combination tanned leathers

Leather	Color fastness of dry rub	Color fastness to wet rub
Leather tanned by 2.0% THPS	3-4	3
Leather tanned with 2.0% THPS and 3.0% aluminum	4-5	4

described in Figure 3. As shown in TABLE IV, the color fastness to dry/wet rub of leathers tanned by THPS-aluminum was much better than that of tanned by THPS. Hence, based on an overall consideration of grain smoothness, fullness, grain tightness, softness and dyeability, 3.0% Tanfix AL powder was the optimum amount. tanned by 2.0% THPS and 3.0% Tanfix AL powder As represented in Figure 4, there were small fiber bundles in leather tanned by THPS, but for leather tanned by THPS and aluminum, the fiber bundles combined together and looked like flakes. The fiber of THPS-aluminum combination tanned leather was much tighter than that of THPS tanned leather. With the increase of the dosage of Tanfix AL powder, the fiber of leather tanned

Figure 4: The longitudinal cutting section of leather tanned by different methods (X300)

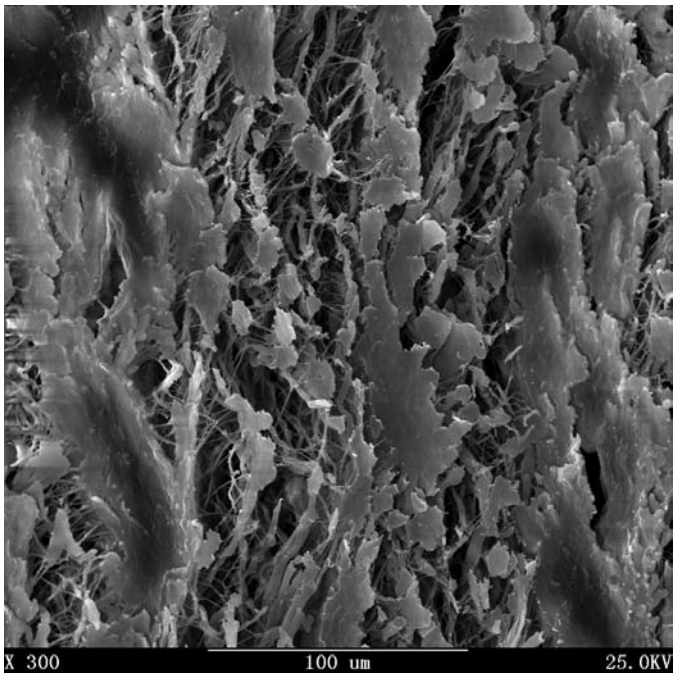


Figure 4a: Leather tanned by 2.0% THPS

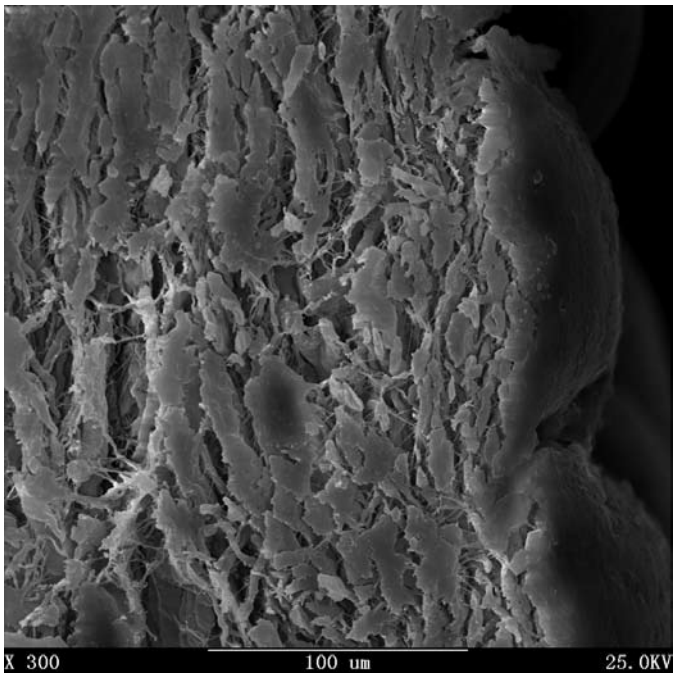


Figure 4b: Leather tanned by 2.0% THPS and 3.0% Tanfix AL Powder

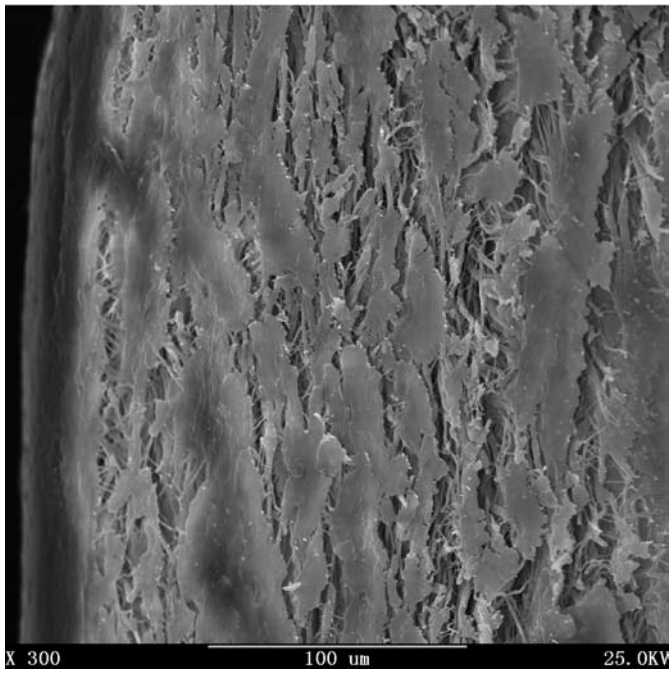


Figure 4c: Leather tanned by 2.0% THPS and 5.0% Tanfix AL Powder

TABLE V

Physic-chemical properties of leathers

Tear force(N)		28.4
Elongation at break (%)		28.5
color fastness to dry/wet rub	dry	4/5
	wet	4
Ts(°C)		91
Formaldehyde(mg/kg)		57.52
Cr^{6+} (mg/kg)		2.15

Figure 5: The grain surface of THPS-aluminum combination tanned leathers (X50)

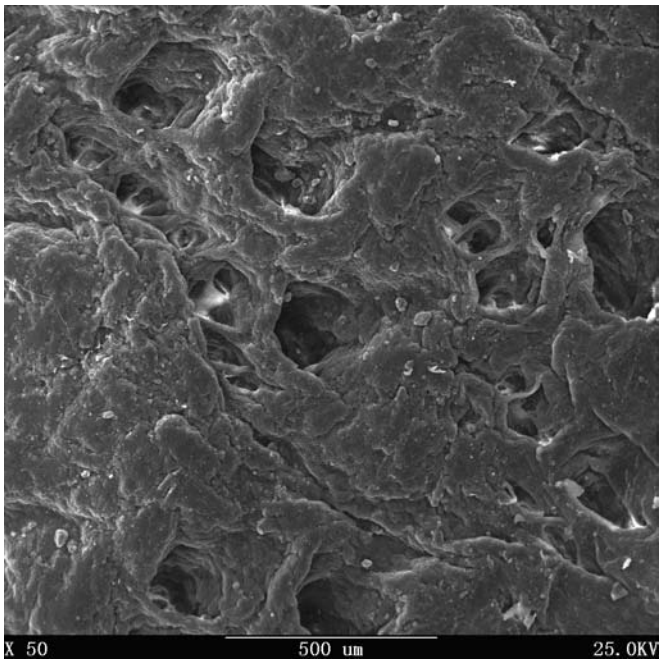


Figure 5a: no degradation leather

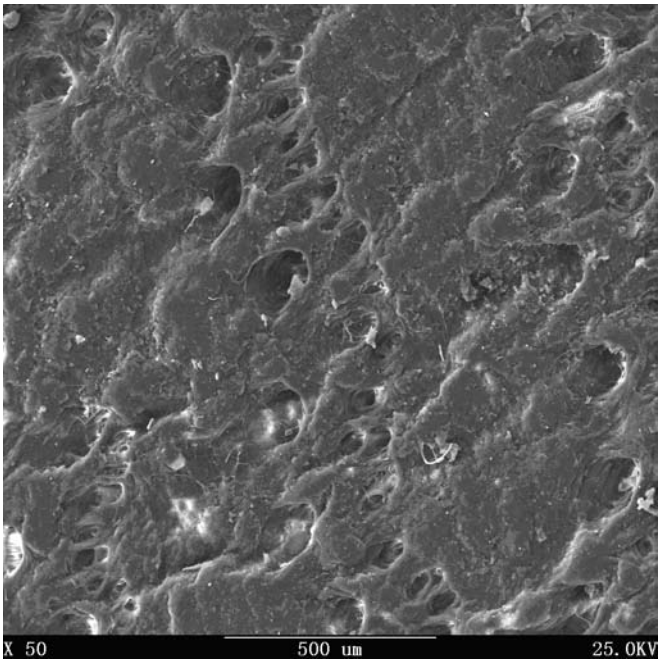


Figure 5b: degradation of leather after 30 days

Figure 6: The grain surface of THPS-aluminum combination tanned leathers (X500)

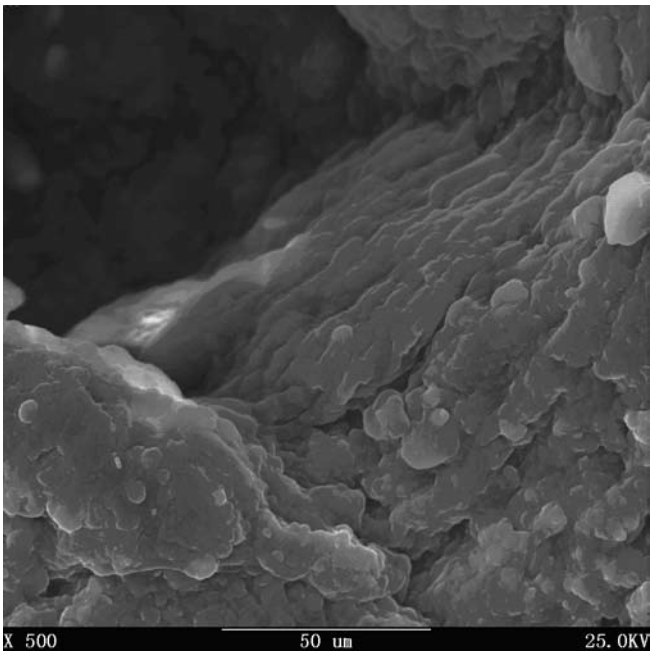


Figure 6a: no degradation leather

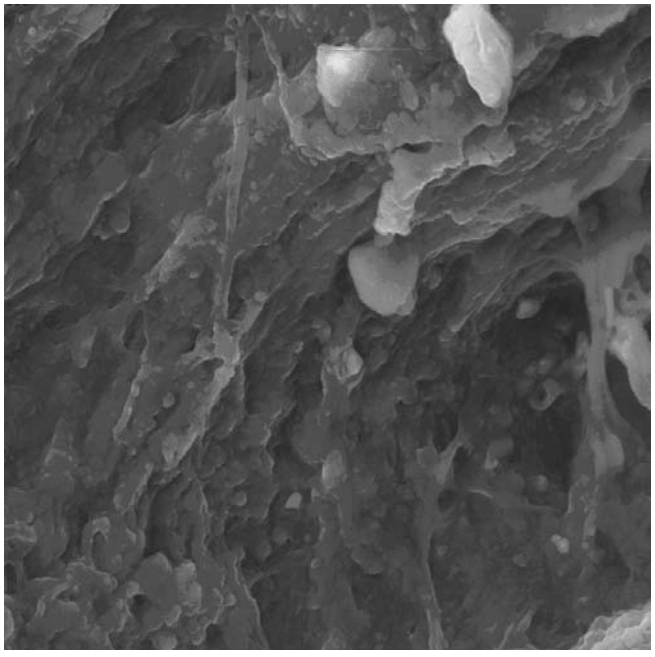


Figure 6b: degradation leather after 30 days

TABLE VI

Relation of degradation rate and days

Time(d)	Degradation rate(%)	
	Chrome tanned leather	THPS-aluminum combination tanned leather
3	1.66	4.42
7	2.01	6.50
14	3.30	9.13
21	5.30	15.47
30	5.65	19.63

by THPS-aluminum became tighter, which proved that with an increase of the dosage of Tanfix AL powder, reactive ability of Tanfix AL powder with collagen fiber became strong. The bulk trial finished in Haining Shangyuan Leather Co., Ltd proved that all indexes of leather satisfied Chinese standard. The results were shown in TABLE V.

Degradation of garment leather

THPS-aluminum combination tanned leathers in degradation experiment were not finished. In TABLE VI, along with the increase of the degradation time, degradation rate continuously increased, but the degradation speed of chrome tanned leather was slower than that of THPS-aluminum combination tanned leather. As represented in Figure 5 and 6, the surface structure of leather which was not degraded was more regular than that of degraded for 30 days. The degradation of THPS-aluminum combination tanned leather was much easier than chrome leather, which was benefit for the sustainable development of leather industry in future.

CONCLUSIONS

In the tanning system of THPS and aluminum combination, when the dosage of THPS and aluminum respectively is 2% and 3%, the organoleptic and physical strength properties of goat garment leather are the best. The bulk trial finished in Haining Shangyuan Leather Co., Ltd proves that all indexes of leather satisfied Chinese standard. Hence, the results suggest that THPS and aluminum tanning system can be used commercially for the manufacture of garment leather. Moreover, 30 days later, the degradation rate of the leathers tanned by THPS-aluminum and chrome are 19.63% and 5.65%, respectively. The SEM images also show that the degradability of leather tanned by THPS-aluminum is better than that of chromed tanned leather.

ACKNOWLEDGMENTS

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REFERENCES

1. Fathima, N. N., Chandrabose, M., Aravindhan, R., etal. Iron-phosphonium combination tanning: towards a win-win approach. *JALCA* **100,** 273, 2005.
2. Zhao Y. T. and Wang X. C. Chinese developments in chrome-free and low-chrome tanning materials. *JSLTC* **91,** 246, 2007.
3. Liu W., Wang W. Q., Zao X. D., etal. Application of organic phosphate tanning technology on sheepskin garment leather. *China Leather* **35,** 7, 2006.
4. Guo W. Y. and Shan Z. H. Exploitation of a kind of phosphonium salt and its lookout of application. *China Leather* **33,** 1, 2004.
5. Dasgupta, S. Chrome free tannages: part I preliminary studies. *JSLTC* **86,**188, 2002.
6. Dasgupta, S. Tanning with tetrakis hydroxymethyl phosphonium sulfate (THPS). Forty-ninth Annual Conference for the Tanners and Leather Technologists, 2004.
7. Fathima, N. N., Aravindhan, R., Rao, J. R., etal. Tannic acid-phosphonium combination: a versatile chrome-free organic tanning. *JALCA* **101,** 161, 2006.
8. Madhan, B., Gunasekaran, S., Naasimman, R., etal. Integrated chrome free upper leather processing-part-II: standardization and evaluation of vegetable-aluminum tanning system. *JALCA* **100,** 373, 2005.
9. Madhan, B., Gunasekaran, S. and Naasimman, R. Integrated chrome free upper leather processing-part-I: selection of tanning system. *JALCA* **100,** 282, 2005.

10. Sundarrajan, A., Madhan, Rao, J. R., etal. Studies on tanning with zirconium oxychloride: part I standardization of tanning process. *JALCA* **98,** 101, 20036.
11. Madhan, B., Aravindhan, R., Ranjithakumar, N., etal. Combination tanning based on tara: an attempt to make chrome-free garment leathers. *JALCA* **102,** 198, 2007.
12. Saravanabhavan, S., Fathima, N. N., Rao, J. R., etal. Combination of white minerals with natural tannings chrome-free tannage for garment leathers. *JSLTC* **88,** 76, 2004.