A Novel Nano-SiO_2 Tannage for Making Chrome-Free Leather

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Abstract: A novel pickle less combination tannage based on nano-SiO_2 and oxazolidine as a substitute for chrome tanning has been developed. The size and distribution of nano-SiO_2 in protein, the hydrothermal stability, the mechanical properties and the antifungal effect of final leather as well as the evaluation of eco-friendly characteristics of combination tannage were investigated. Scanning Electric Microscope (SEM) analysis indicates that the distribution of nano-SiO_2 in protein is even when the SiO_2 concentration is lower than 5 wt% (on bated pelt weight), and the size of SiO_2 particles can be controlled to a range from 60 to 150 nm. But when the SiO_2 concentration is higher than 7 wt%, most of particles conglomerate together and the size of the SiO_2 particles is larger than 400 nm. Differential Scanning Calorimeter (DSC) study shows that the shrinkage temperature of final leather which is related to the content of nano-SiO_2 is more than 95℃. Compared to the chrome tannage, leather tanned with oxazolidine-nano-SiO_2 demonstrates a higher resistance to mould than conventional wet blue. The later incubated for 3 days began to grow mildew, whilst the oxazolidine-nano-SiO_2 tanned leather which was incubated for 6 days had no mildew, showing fine antifungal effect. Environmental impact assessment shows that the developed process exhibits significant reduction in total solids (TS) and better biodegradability of organic compound in the effluent when compared to chrome tanning.

Key words: oxazolidine; nano-SiO_2; combination tannage; pickle less; environmental impact

1 Introduction

With the enhancement of environment consciousness and the change of consumption concept, the world market is eager for clean leather technology. These also drive researchers to explore eco-friendly products and processes for an alternative chrome tanning system. It has been reported that silicon dioxide and sodium silicate are used for manufacturing wet-white leathers. Silica based tanning produces white leathers hence, the concept of wet-white tanning as a potential alternative to wet blue tanning is appealing. Silica tannage also produces leathers with softness and fluffiness because of the gelling nature of silica.[1]However, the drawbacks associated with the solo tanning with silica are the lack of desired shrinkage temperature and strength properties in the leathers.[2]

Nano-particles, due to their small size, abundance of un-paired atoms and high combination ability with polymer substrates, [3] provide a possibility for application in tanning. If a precursor containing nano-particles (such as nano-SiO_2) is introduced into fibers of hide, this precursor will *in-situ* produce nano-SiO_2 under a special triggering condition such as radiation, heat, hydrolysis or gas reaction etc, then a protein-SiO_2 organic-inorganic nano-hybrid with a strong interaction between the organic and inorganic phases will result due to the high surface activity and high surface energy of nano-particles. The collagen fiber, which has played the role of controlling the nano-particle size and inhibiting their

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agglutination, act as organic phase; nano-SiO_2 distributed evenly in the collagen fiber acts as inorganic phase.[4-6] The introduction of nano-particles can not only efficiently enhance the mechanical properties, thermal and hydrothermal stability of leather, but also impart unexpected functional features such as UV-resistance, fungi-resistance and anti- microbial.[7] As a result, the mechanical properties and hydrothermal stability of collagen treated with nano-SiO_2 will be obviously enhanced due to the strong bonding between the organic and inorganic phases. [5] This procedure is superior to Silica tannage and expected to yield a novel substitute process for conventional chromium tannage in leather-making.

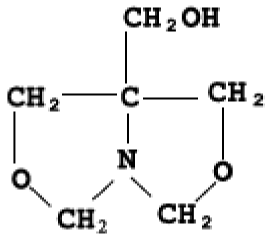
On the other hand, oxazolidine, with functional oxazolidine-ring acting as a new cross-linking agent can increase the shrinkage temperature of leather.[8]Oxazolidines are heterocyclic derivatives obtained by a reaction of amino-hydroxy compounds with aldehydes. The application of oxazolidine as a pre-tanning agent before nano-SiO_2 tannage is desired to contribute the collagen fiber higher stabilization, such as a higher shrinkage temperature and a greater resistance to chemical attack of leather. At the same time, oxazolidine with cationic charges can provide a suitable condition for the following nano-SiO_2 tanning, which results in desirable permeation rate for nano-tanning agent.[9]

In this work, the development of a novel combination tannage based on a nano-SiO_2 and oxazolidine has been attempted as an alternative chrome-free tannage. The tanning conditions of the new combination system, physical-chemical characteristics of leathers and the environment impact of this tannage are presented.

2 Experimental

2.1 Materials

Conventionally processed bated goatskins were taken for the tanning trials. All chemicals used for leather processing were of commercial grade. The nano-SiO_2 tanning agent was prepared as in the literature,[10] it consists of nano-precursors（tetraethoxy silane, TEOS) and dispersion carrier（modified animal or vegetable oil）. The oxazolidine was prepared as in the literature[8] and the structure is as follow.



2.2 Optimization of oxazolidine for pre-tanning

The goatskins were processed to a bated stage by conventional method. Bated goatskins were firstly treated with 2% of sodium bicarbonate to a pH 4.0. Subsequently, different content of oxazolidine were offered namely 1.0 wt%, 1.5 wt%, 2.0 wt%, 2.5 wt% (based on bated pelt weight) and the drum was run for 2hrs. Then 2 wt% formic acid was used to adjust the pH to be 3.5. The drum was run for another 1 hour.

2.3 Oxazolidine –nano -SiO_2 combination tanning

Before nano-SiO_2 tanning, the pre-tanned goatskins were squeezed and shaved. Then different content of nano-SiO_2 tanning agent namely 3wt%, 5wt% and 7wt% was offered and the drum was run for 3-4hrs. After complete penetration of nano-tanning agent, the mixture of 1wt% sulfuric acid and 1wt% formic acid diluted with 150 wt% water were added to decrease the pH to be 2.5 in 1.5 hrs. Then stop the drum over night. Next day a basification was carried out by the addition of 2wt% sodium formate and 2wt% sodium bicarbonate (1:10 dilution) in four instalments at an interval of 15min. Finally, the drum was run for another 2hrs and the pH was checked to be 5.0-5.5. [11]

2.4 Conventional chrome tanning and post tanning process

Chrome tanned leathers were obtained according conventional method.

Leathers tanned with chrome and oxazolidine-nano-SiO_2 were shaved to a uniform thickness of 0.8mm respectively. The post tanning formulation, including neutralization, re-tanning and fatliquoring, is given in Table 1.

Tab1. Post tanning formulation for both combination tannned and chrome tanned leathers

Process	Chemicals	Quantity	Duration	Remarks
Neutralization*	Water	100%		
	Sodium formate	1%		
	Sodium bicarbonate	1.25%	3×10min+30min	Check pH 6.0-6.2
Washing	Water	100%	10min	
Retanning	Water	100%		
	Relugan D (BASF)	3%	30min	
	Relugan DLE (BASF)	2%	30min	
Fatliquoring	Lipoderm liqor SLW(BASF)	4%		
	Lipoderm liqor SAF(BASF)	3%		
	CORIPOL MK (TFL)	3%	45min	
Fixing	Formic Acid	2%	3×10min+45min	Pile overnight

*For combination tannned leathers, neutralization was not carried out as the pH was already 5.0

2.5 Differential scanning calorimetry studies

The hydrothermal denature temperature of combination tanning leather was studied by using a Differential Scanning Calorimeter (German NETZSCH DSC-200). The leather samples were first air dried at ambient temperature, and then moistened with water for 24hrs and excess water was removed by pressing the samples lightly in between laboratory tissue paper. The moisture content was determined between 60 and 70% for the samples.[12] Then the samples were sealed in a DSC cell and heated at a constant rate of 5℃/min. The peak temperatures on DSC curve were defined as shrinkage temperature(℃).

2.6 Mechanical properties test of leather samples

Mechanical properties such as tensile strength, elongation, tear strength and grain crack strength were measured according to standard procedures.[13] Each value reported was an average of four (2 along the backbone, 2 across the backbone) measurements.

2.7 Color measurement

Reflectance measurements were made for oxazolidine-nano-SiO_2 combination tanned leathers using X-RiteColor 8200 Series spectrophotometer. The L, a, b and c values were calculated. 'L' indicates the lightness, 'a' represents red and green axis, where 'a' ＞0 means red and 'a'＜0 means green. 'b' represents yellow and blue axis, where 'b' ＞0 means yellow and 'b'＜0 means blue. 'c' represents chromacity.

2.8 Scanning Electron Microscopic analysis

Samples from experimental leathers were cut from the official sampling position. A JEOL JSM-5900LV series Scanning Electron Microscope (SEM) was used for observing the size and distribution of nano-SiO_2. The micrographs of nano-SiO_2 on the grain surface and in the cross -section were obtained by operating the SEM at low vacuum with an accelerating voltage of 20KV in different lower and higher magnification levels.

2.9The antifungal effect of leather tanned with oxazolidine –nano -SiO_2

The bacterial stains－Aspergillus niger, Aspergillus flavus and Paecilomyces Bainier were selected to test the antifungal effect of the samples (chrome-tanned and oxazolidine-nano–SiO_2 combination tanned leathers). The cell density of the culture was determined by a standard plate count method. The cultures were diluted with sterilized water to give cell density of 100-200 cfu/mL. The samples were placed on the plates with appropriate Czapek medium firstly, then 0.1mL cultures was patched on each sample. Finally, the samples were incubated at 28℃ for 6 days.

2.10 Analysis of spent tan liquor

Spent tan liquor from experimental processing was collected and analyzed for biological oxygen demand (BOD), chemical oxygen demand (COD) with German Lovibond instrument. Total solids (TS, dried at 103-105℃ for 1 hr) according to the standard procedures.[14] The values reported are average of 3experiments along with their standard deviations.

3 Results and discussion

3.1 Optimization of oxazolidine offer

Because nano-precursors（tetraethoxy silane, TEOS) are prone to be hydrolysis before its complete penetration, so the skin needs to be squeezed (to remove most of water) and shaved before nano-SiO_2 tanning.[7] Oxazolidine was used as a pre-tanning agent, in one hand, to improve the mechanical properties of bated skin so as to facilitate the squeezing and shaving; on the other hand, to change their surface charge so as to facilitate the penetration of nano-precursor before hydrolysis.

The offer of oxazolidine was optimized mostly based on the shrinkage temperature (T_S) of the leather and the subsequent penetration time of nano-SiO_2 tanning agent. The offer of oxazolidine varied from 1.0wt%-2.5wt%, the shrinkage temperature and the penetration time of nano-SiO_2 tanning agent are presented in Table 2. It can be seen that there is an increase in T_S on increasing the amount of oxazolidine, but higher offer of oxazolidine will prolong the penetration time of nano-SiO_2 tanning agent. Hence, 2.0% oxazolidine was chosen for further experiments.

Tab 2. Effect of oxazolidine content on Ts of leather and the penetration time of nano-precursor

oxazolidine offer (%)	*T_S (℃)	penetration time of nano-SiO_2 tanning agent (hrs)
1.0	75	4-5
1.5	77	4-5
2.0	80	3-4
2.5	82	5-6

* Peak temperature on DSC curve.

3.2 The hydrothermal stability of nano-SiO_2 and oxazolidine combination tanned leather

The hydrothermal denature temperatures of collagen in presence and in absence of nano-SiO_2 were studied using DSC analysis. The position, width, height and symmetry of the thermogram peak provide information about the thermal denature of collagen over a defined temperature range. The shrinkage temperature of collagen is normally related to the onset temperature of its peak in a DSC pattern and can be used as a measure of the hydrothermal stability of collagens subjected to different treatments.[12-13] An increase in the shrinkage temperature is usually an indication of an increase in the stability of wet collagen. The DSC patterns of skin powder treated with oxazolidine (2wt%) and oxazolidine (2wt%) combination with 3wt%，5wt%，7wt% nano-SiO_2 are shown in Fig.1.

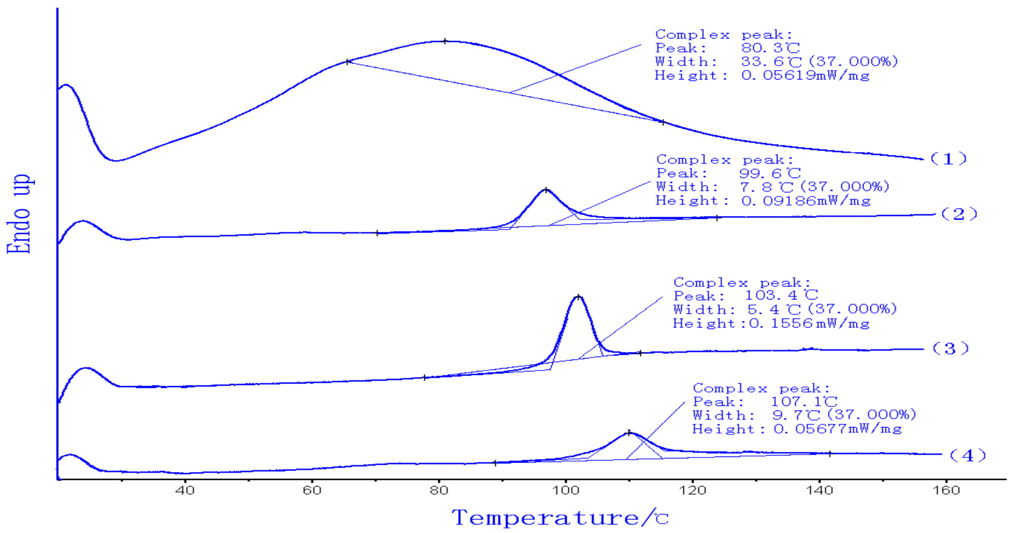


Fig.1- DSC profiles of skin treated with : (1)oxazolidine (2wt%); (2)oxazolidine (2wt%) and nano-SiO_2 (3wt%); (3) oxazolidine (2wt%) and nano-SiO_2 (5wt%); (4)oxazolidine (2wt%) and nano-SiO_2 (7wt%).

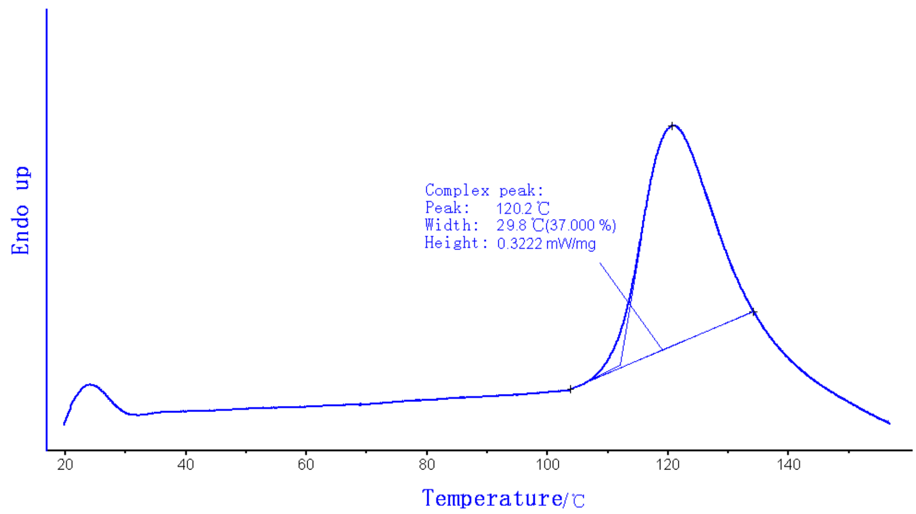


Fig.2- DSC profile of chrome (1.2 wt%Cr_2O_3) tanned skin powder

As already known, the shrinkage temperature of chrome tanned leather is approx 120-130℃, and a sharp endothermic peak can be observed on DSC curve, figure 2 is a typical DSC curve of chrome tanned leather. But for hide treated with 2 wt% oxazolidine, no obvious endothermic peak on DCS curve can be observed instead of a width peak occurs (Fig1 (1)), which means that the tanning effect of oxazolidine is so limited that it can not contribute the hide high hydrothermal stability. Fortunately, hide treated with 2 wt% oxazolidine then followed 3wt%, 5wt% and 7wt% nano-SiO_2, the endothermic peaks are similar to chrome tanned leather and become narrow and sharp, moreover, the shrinkage temperatures of final leather reach 99.6℃，103.4℃ and 107.1℃, respectively (Fig.1). Obviously，the combination tannage can efficiently improve the hydrothermal stability of leathers and the tanning effect of nano-SiO_2 is superior to oxazolidine.

3.3 Mechanical properties of leather tanned with oxazolidine- nano-SiO_2

Tensile, tear and grain crack strength tests were carried out along and across the backbone line for leather combination tanned with oxazolidine (2 wt%) and nano-SiO_2 (5 wt%). The mean values corresponding to each experiment are given in Table 3. It can be seen that the physical strength values are all superior to the stipulated standards of chrome-free leather and close to the chrome tanned leather.

Tab3. Physical Strength of crust leathers tanned with chromium and oxazolidine –nano -SiO2

Tanning system	[1]Tensile strength （MPa）	[1] Extension at Break (%)	[2]Tear strength (N/mm)	[2]Burst strength (Kg/cm^2)
Combination tanning	14.7	83.2	49.6	12.2
Chrome tanning	15.9	78.8	52.5	13.4
Stipulated standards (in China)	＞6.5	25-60	＞18	-

1 Average of 4 samples (two along the backbone and two across the backbone)

2 Average of 2 measurements

3.4 Color measurement results

The color of oxazolidine (2wt %) and nano-SiO_2 (5wt%) combination tanned leather was determined by spectrophotometer. The 'L', 'a', 'b' and 'c' values, the parameters used to assess color are shown in Table 4.

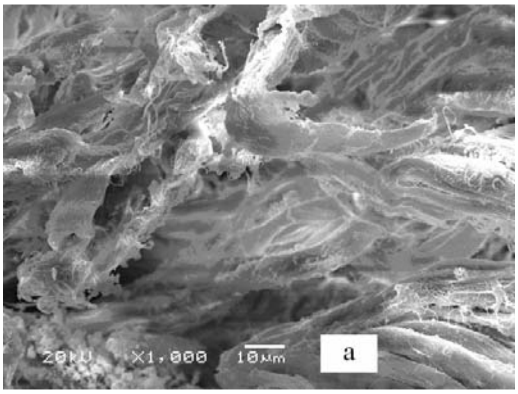
Tab 4. Color measurement of nano-SiO2 and oxazolidine combination tanned leather

L	a	b	c
93.71	0.75	7.13	7.17

'L' represents whiteness, which on a scale of 0-100, 100 means pure white, in this case the value of 'L' has been found to be 93.71.This indicates that the color obtained is lighter in shade. The 'c' value indicates that the color obtained has less intensity. Thus the color measurement indicates that the leathers made using this new combination system are suitable for making pastel shades.

3.5 The influence of nano-SiO_2 content on the size and distribution of SiO_2 in protein

Scanning Electron Microscopy was employed to study the fiber structure and the size and distribution of SiO_2 in protein. The cross section structures of both crust leathers tanned with chrome and combination tannage with a magnification of 1000 are given in Fig.3 (a、b). Although the fiber structures of both samples are similar, the former shows a more opened structure and the later is tighter.



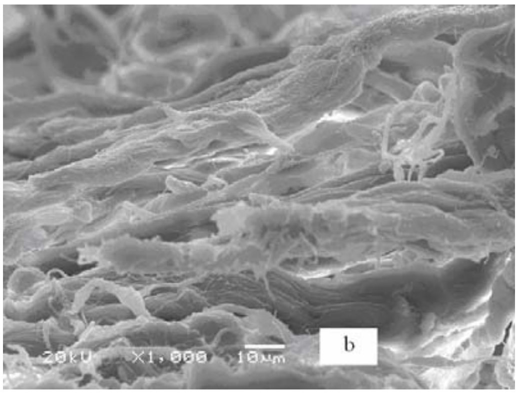


Fig.3 – Scanning Electron Micrograph showing the cross section (×1,000) of (a) chrome tanned leather and (b) oxazolidine (2wt%) and nano-SiO_2 (5wt%) combination tanned leather

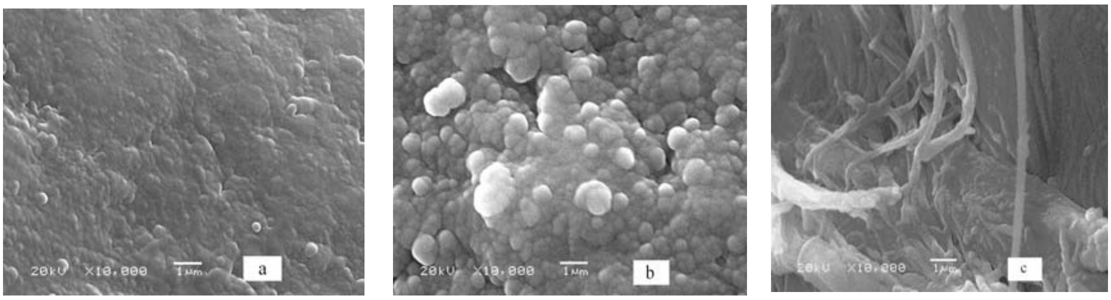
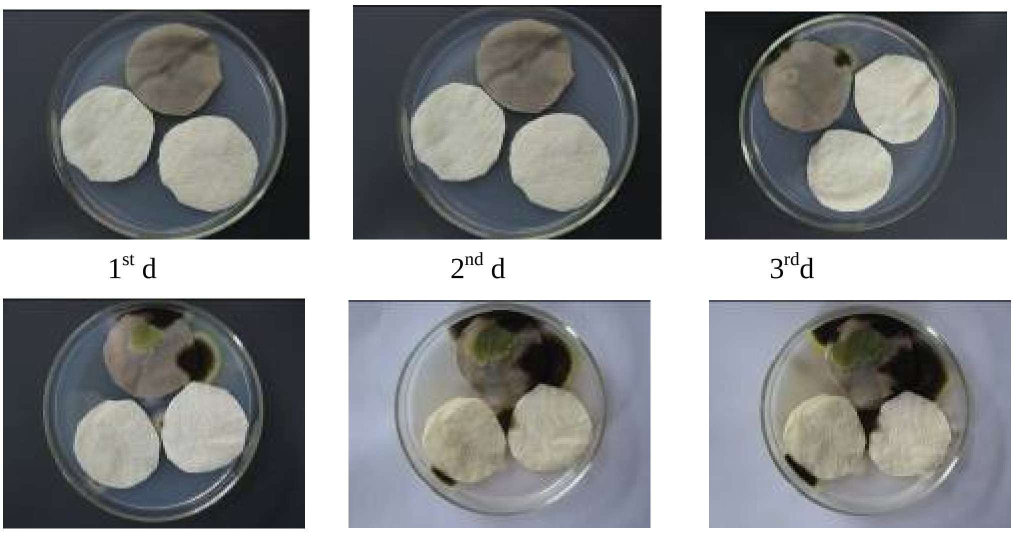


Fig.4– Scanning Electron Micrograph showing the grain surface (×10,000) of leather treated with (a) oxazolidine (2wt%) and nano-SiO_2 (5wt%); (b) oxazolidine (2wt%) and nano-SiO_2 (7wt%); (c)the cross section of oxazolidine (2wt%) and nano-SiO_2 (3wt%) combination tanned leather

The SEM micrographs of the grain surface of leathers tanned with oxazolidine (2wt%) combination with 5wt％ and 7wt％ nano-SiO_2 are given in Fig.4 (a、b). It is found that for the leather tanned with 5wt% nano-SiO_2 the size scale of SiO_2 on the grain is approx 200-400nm, whilst when the nano-SiO_2 content is higher than 7wt%, excessive SiO_2 particles agglutinated both on the surface of leather and the spaces of collagen fibers, as a result, the distribution of SiO_2 on the surface of leather is not even, the size scale of party nano-SiO_2 particles is higher than 500nm (Fig.4b). Fig.4c is the cross section morphology of leather tanned with 3wt% nano-SiO_2, it can be seen that all collagen fibers are surrounding by the inorganic particles, the size scale of SiO_2 is approx 60-150nm. Obviously, the size scale of SiO_2 particles in final leather is closely dependent on the SiO_2 content.[7]

3.6 The antifungal effect of the oxazolidine and nano-SiO_2 combination tanned leather

A dual plate assay was used to determine qualitatively the antifungal ability of samples modified with different methods to various fungal. Fig.5 are the growth states of Aspergillus niger, Aspergillus flavus and Paecilomyces Bainier on the surface of leather tanned with oxazolidine -nano -SiO_2 (two pieces, white color) and chrome (one piece, grey color).



1st d 2nd d 3rd d

4th d 5th d 6th d

Fig.5 Photograph of the antifungal effect of nano-SiO_2 tanned and chrome tanned leathers

It can be seen that the oxazolidine –nano -SiO_2 combination tanned leathers which were incubated for 6 days had no mildew, while the chrome tanned leather which was incubated for 3 days began to grow mildew. This is very useful for biomaterials or leather-making. Hides with have been treated with nano-SiO_2 demonstrates a higher resistance to mould than conventional wet blue. [15] Provided that the hides are further processed within a week, there is no need for treatment with a bactericide or a fungicide.

When shaving it is important to remember that the hides will significantly increase in thickness during subsequent tannage. This means that the chosen shaving thickness should be some 20% below the required final thickness. The generated shavings are chrome-free and can be composted or used in the production of foodstuffs and possibly also as a raw material for the pharmaceutical industry.[9]

3.7 Environment benefit

The impact of pickle less oxazolidine-nano-SiO_2 combination tanning system on the environment was assessed by the spent tan liquor analysis for TS, BOD_5 (BOD 5 days later) and COD. It can be seen from Table 5 that the COD value in combination tannage is higher than in chrome tanning due to the application of oxazolidine. While the TS load value for combination tanning process is lower than that of the chrome tanning process. And the residues of nano-SiO_2 tannage in the effluent would become the part of soil.

It is known that the pickling process increases the total dissolvable solid（TDS）of the effluent. Nano-SiO_2 tannage is performed on bated pelt without pickling, so the pollution of neutral salt is significantly decreased in this new combination system. Moreover, dispersion carrier (modified oil) is a good softness agent, that is to say, tanning and fatliquoring are carried out at the same time. Thus plenty of environmental pollution caused by conventional pickling and fatliquring process is avoided.

Tab.5 Spent tan liquor analysis of oxazolidine and nano-SiO_2 combination tanning

Tanning system	COD(ppm) value	TS(ppm)	BOD_5 /COD
Combination tannage *	3580±20	31,380 ±150	0.73
Chrome tannage (1.2 wt%Cr_2O_3)	3120±15	55,960±180	0.28

*Combination tannage : 2wt% oxazolidine and 5wt% nano-SiO_2

The biodegradability of the organic compound is commonly evaluated by the value of BOD_5 /COD. It also can be quantitative to utilize the value of BOD_5 /COD for assessment of the biodegradability. The value is higher; the biodegradation of organic compound is easier[16-17]. The relationship between BOD_5 /COD value and the biodegradability of the organic compound are shown in Table 6.

Tab.6 The relationship between BOD5 /COD value and the biodegradability of the organic compound

BOD_5 /COD	>0.45	0.3~0.45	0.2~0.3	<0.2
Biodegradability	easier	easy	difficult	more difficult

In comparison with chrome tannage, the BOD_5 /COD value is greater for combination tannnage (0.73) than for chrome tannage (0.28), which demonstrates that the effluent of combination tanning process is easier biodegradation than that of chrome tanning process.

4 Conclusions

A new pickle less combination tannage based on oxazolidine and nano-SiO_2 has been developed. It has been found that the introduction of nano-particles can improve the hydrothermal stability of leathers. The shrinkage temperature of final leathers treated with 3 wt% and 5 wt% nano-SiO_2 can reach 99.6℃ and 103.4℃ respectively. The mechanical properties of resultant leather tanned with this new combination system are similar to chrome tanned leather and superior to the standard of chrome-free leather. Hides with have been treated with oxazolidine -nano- SiO_2 demonstrates a higher resistance to mould than conventional wet blue. From an environment impact assessment, it has been found that the TS values are much less than that of chrome tanning system and the effluent of combination tanning process is easier biodegradation than that of chrome tanning process.

Acknowledgments

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References

[1] Fathima, N.N, Rao, J.R. and Nair, B.U.; Augmentation of sheep derived properties in goatskins for garment manufacture: Role of chromium- silica tanning agent. JSLTC 87,227, 2003.

[2] Fathima, N.N, Kumar, T.P and Kumar, D.R., Rao, J.R and Nair, B.U.; Wet white leather processing: A new combination tanning system. JALCA101, 58, 2006.

[3] Fan, H. and Shi, B.; Nano-composite of protein-silica (titanium) organic/inorganic hybrid-a novel concept of leather making. China Leather1, 1, 2002.

[4] Fan, H., Li, L. and Shi, B.; Characteristics of leather tanned with nano-SiO2. JALCA 100,22,2005.

[5] Fan, H., Shi, B. and He, Q.; Tanning characteristics and tanning mechanism of nano-SiO2. JSLTC 88, 139, 2004.

[6] Fan, H., Shi, B. and Li, L.; Nano hybrid of protein/inorganic particles for collagen materials, Functional Materials 1, 231, 2004. Polymer-based nano-composition for leather-tannage and its preparation. CN 02134175.3.

[7] Fan, H., Li, H. and Liu Y.; Nano-SiO2 tannage for producing novel metal-free leather. Proceedings of the 7th Asian international conference of leather science and technology (Section I), 222, 2006.

[8] Luan, S, Liu, Y. and Fan, H.; A novel pretanning agent for high exhaustion chromium tannge. JSLTC 91, 149, 2007.

[9] Li, H., Zhou R. and Fan H., The UV shielding, antimicrobial and antifungal effect of novel nano-SiO2/collagen materials. Proceedings of the 7th Asian International Conference of Leather Science and Technology (Section Ⅱ), 1077,2006.

[10] Fan, H., Li, L. and Shi, B.; Polymer-based nano-composition for leather-tannage and its preparation. ZL: 02134175.3, 20, 10, 2002.

[11] Lu, Y., Fan, H. and Li, H.; Study on the Tanning Method of Nano-SiO2 and Its Technics BalanceⅠ. China Leather1, 5, 2008.

[12] Choudhury, S.D., DasGupta, S., Norris, G.E.; Unravelling the mechanism of the interactions of oxazolidine A and E with collagens in ovine skin. International Journal of Biological Macromolecules 40, 351, 2007.
[13] A.D. Covington, R.A. Hancock, I.A. Ionnidis, J. Soc; Leather Technol. Chem, 73, 1, 1989.
[14] Chandrasekaran, B., Rao, J.R., Prasad, B.G.S. and Nair, B.U.; Management of chromium wastes in tanneries.J.Indian Assoc.Environ.Manag.16,168,1989.
[15] Li, H., Fan, H. and Zhou, R.; Study on the antifungal effect of leather tanned with nano-SiO2. Leather Science and Engineering 5, 12, 2007.
[16] Cao, J., H, C.; A simple method of estimation of the dilution ratio in BOD5 determination. PTCA (PARTTB: Chemical analysis) 37(5), 206, 2001.
[17] Lu, G., Zhao, Y. and T, J.; Press in the biodegradability and structure-biodegradability relationship of organic chemicals. Chemical Bulletin 2, 113, 2002.