Tanning Performance of a Novel Chrome-Free Complex Tanning Agent: Penetration and Distribution

by

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Abstract

Penetration of tanning agent in leather plays an important role in tanning performance and properties of finished leather. A novel complex tanning agent composed of Al–Zr salts and highly-oxidized starch ligand, named TWLZ, was used for chrome-free tanning. The masking effect of highly-oxidized starch reduced the electropositivity of metal complexes, which should help penetration of TWLZ and moderate its fixation during tanning. The effects of tanning agent dosage, basification method and pretreatment method on the distribution of TWLZ in leather were investigated. Using 8% TWLZ and basifying with magnesium oxide benefited the penetration and distribution of TWLZ throughout the cross-section of leather. Pretreatment with an amphoteric organic tanning agent could regulate the charge state of the hide, balance the penetration and fixation of TWLZ, and thus show uniform distribution and satisfactory tanning performance. This work will guide the establishment of TWLZ chrome-free tanning system.

Introduction

Reducing chrome input in leather production is the current consensus and an inevitable trend to achieve the sustainable development of the leather industry.[1-3] Therefore, numerous chrome-free tanning technologies have been developed as possible alternatives to the prevailing chrome tanning.[4-6] Among these technologies, non-chrome mineral tanning, such as aluminum and zirconium tannage, are still considered a promising substitute to chrome tanning.[7,8] This is because the tanned leather shows a similar dehydrated state and charge property (high isoelectric point) to wet blue and matches well with the current post-tanning processes.[9] However, traditional aluminum tanning gives leather with good softness, but poor stability to heating and washing.[10] Zirconium salts have good filling properties, however its strong binding ability with skin collagen will make leather firm and rigid.[11] One of the main reasons is attributed to the high hydrolysis and olation ability of Al/Zr salts,[10,11] thereby leading to the deposition and overload of Al/Zr salts on the surface of leather.[12,13] Therefore, an essential issue involved in the application of non-chrome mineral tanning agents is to resolve the conflict between penetration and fixation and achieve a uniform distribution of the tanning agent.

A useful approach to moderate fixation and promote penetration of Al/Zr salts is the introduction of a masking agent (ligand) into the metal complex.[14] The use of some micromolecular organic acids, such as lactic acid and citric acid, is familiar to tanners.[15,16] Unfortunately, the upgrade on distribution uniformity of metal salts was not significant according to previous work.[13] We recently developed a novel chrome-free complex tanning agent where a highly oxidized starch ligand was introduced into an Al–Zr bimetal complex and resulted in excellent tanning performance.[9,17] This ligand is supposed to show good masking performance due to its multiple carboxyl groups and relatively large molecular size, and thus may favor the penetration and distribution of Al–Zr complexes. This tanning agent containing Al–Zr salts and the starch ligand was named as TWLZ. In this study, the charge property of TWLZ was determined to elucidate the mechanism of penetration and fixation of TWLZ in leather. Furthermore, the effects of tanning agent dosage, basification method and pretreatment method on TWLZ distribution were investigated to formulate an optimal recipe for uniform distribution of TWLZ. Our aim was to develop a practical tanning technology and provide a basis for the industrial application of TWLZ in a chrome-free tanning system.

Experimental

Materials

Pickled cattle hide was purchased from a local tannery. A powdery chrome-free complex tanning agent named TWLZ was prepared by mixing $Al_2(SO_4)_3{\cdot}18H_2O$ (60 wt%), $Zr(SO_4)_2{\cdot}4H_2O$ (25 wt%), and highly-oxidized starch (15 wt%) according to our previous work.[17] A blend of $Al_2(SO_4)_3{\cdot}18H_2O$ (70.6 wt%) and $Zr(SO_4)_2{\cdot}4H_2O$ (29.4 wt%) was also prepared for determining the charge property of metal complexes. The only difference between this blend and TWLZ was that the highly-oxidized starch ligand was not included in this blend. Three types of pretreatment agents used before tanning, i.e. anionic fatliquoring agent (AFA), cationic fatliquoring agent (CFA), and amphoteric organic tanning agent (TWS), were provided by Tingjiang New Materials Co., Ltd. (Sichuan, China).

Charge property of metal complexes in TWLZ

The contents of cationic, anionic and electroneutral metal complexes in the TWLZ solution were determined using a

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precipitation method[18] to reveal the charge state of the TWLZ tanning agent in the initial stage of tanning. Twenty ml of 1.5 g/L TWLZ solution was mixed with 1 ml anionic precipitant (Sodium diisobutyl naphthalenesulfonate, a type of anionic surfactant, Xinrunde Chemical Co. Ltd., Hubei, China). This blend was centrifuged for 5 min at a speed of 5000 r/min and washed by distilled water to obtain the precipitate. The precipitate was digested with hydrogen peroxide and nitric acid using a microwave device (Multiwave PRO, Anton Paar, Austria), and its Al and Zr contents were determined by ICP-OES (Optima 8000, PerkinElmer, USA). The sum of Al and Zr contents was defined as the cationic metal complexes content. Similarly, 20 mL of 1.5 g/L TWLZ solution was mixed with 0.05 ml cationic precipitant (a type of cationic polyamine resin, Jogel Industrial Co., Ltd., Shanghai, China) to form a precipitate. Centrifugation, digestion and ICP-OES analysis were followed to obtain the anionic metal complexes content. Al and Zr contents of the TWLZ solution were determined by ICP-OES after direct digestion, and their sum was defined as the total metal complexes content. The cationic metal complexes percentage and anionic metal complexes percentage of TWLZ can be calculated according to formulas (1) and (2). The remaining part was considered as the electroneutral metal complexes percentage.

$$\text{Anionic metal complexes percentage (\%)} = \frac{\text{Anionic metal complexes content}}{\text{Total metal complexes content}} \times 100 \quad (1)$$

$$\text{Cationic metal complexes percentage (\%)} = \frac{\text{Cationic metal complexes content}}{\text{Total metal complexes content}} \times 100 \quad (2)$$

In addition, a blend of $Al_2(SO_4)_3 \cdot 18H_2O$ and $Zr(SO_4)_2 \cdot 4H_2O$ mentioned in Materials was also used for determining the charge property of metal complexes following the same procedures.

Determination of zeta potential of pretreatment agents

CFA emulsion (2 g/L), AFA emulsion (0.5 g/L) and TWS solution (20 g/L) were prepared for Zeta potential determination. The pH of emulsion/solution was adjusted from 2.5 to 6.5 using 0.1 mol/L HCl solution or 0.5 mol/L NaOH solution. The zeta potentials of the samples at different pH values were measured by a particle size & zeta potential analyzer (NanoBrook Omni, Brookhaven, USA).

Effect of TWLZ dosage on distribution of TWLZ in leather

Three pieces of pickled cattle hide (30 cm × 30 cm, from symmetrical parts along the backbone) were tanned using 6%, 8% and 10% TWLZ (based on limed weight, the same below), respectively. The tanning process is shown in Table I. The duration of tanning with TWLZ before basification was defined as a penetration stage. Samples (2 cm × 2 cm) were taken at the end of TWLZ penetration and tanning, and were split into grain layer, middle layer and flesh layer by a freezing microtome to determine the layered contents of the tanning agent. The shrinkage temperature of tanned leather was measured at the end of tanning.

Effect of basification method on distribution of TWLZ in leather

Three pieces of pickled cattle hide (30 cm × 30 cm, from symmetrical parts along the backbone) were tanned with 8% TWLZ separately. The tanning process was based on Table I except that basification operations were conducted differently (see Table II). The final basification pH was controlled at pH 4.0 for all the groups. Samples were taken at the end of basification and tanning to determine the layered contents of the tanning agent.

Effect of pretreatment on distribution of TWLZ in leather

Four pieces of pickled cattle hide (30 cm × 30 cm, from symmetrical parts along the backbone) were tanned according to the recipe shown in Table III. Pretreatment using 2% pretreatment agent (CFA, AFA

Table I
Tanning process

Process	Material	Temperature (°C)	Dosage (%)	Time (min)	Remarks
Tanning	Water		100		
	Sodium chloride		7	15	Drain 20%
	TWLZ		6/8/10	300	Sample and stop overnight. Next day run for 30 min. pH < 2.0
	Magnesium oxide		0.3×3	30×3	
	Sodium bicarbonate		0.5×3	15×3	
	Water	40	200	120	Stop overnight. Next day run for 30 min and sample. pH = 4.0

Table II

Basification operations

Method	Basification operations
Mixed basification	0.3% magnesium oxide was added 3 times at intervals of 30 min. Then 0.5% sodium bicarbonate was added 3 times at intervals of 20 min. Afterwards, the drum kept running for 90 min.
Sodium bicarbonate basification	0.5% sodium bicarbonate was added 3 times at intervals of 15 min, followed by addition of 0.3% sodium bicarbonate for 6 times at intervals of 20 min. Then the drum kept running for 75 min.
Magnesium oxide basification	1.1% magnesium oxide was added, and the drum kept running for 240 min.

Table III

Tanning process with pretreatment

Process	Material	Temperature (°C)	Dosage (%)	Time (min)	Remarks
Pretreatment	Water		100		
	Sodium chloride		7	15	Drain 20%
	Pretreatment agent		2	60	
Tanning	TWLZ		8	300	pH < 2.0
	Magnesium oxide		1.1	240	
	Water	40	200	120	Stop overnight. Next day run for 30 min and sample. pH = 4.0

or TWS) was conducted before TWLZ tanning for 60 min. One piece of hide was directly tanned by 8% TWLZ without pretreatment as the control. The other operations of the control group were the same as Table III. The tanned leathers were sampled for determination of layered contents of tanning agent and isoelectric point.

Determination of tanning agent contents in layered leather

The thickness of leather sample was measured by a thickness gauge. Then the sample was split into three layers with equal thickness, which were grain layer, middle layer and flesh layer, by a freezing microtome (CM1950, Leica, Germany). The split samples were dried to constant weight and digested for determining Al and Zr contents by ICP-OES. The tanning agent contents (the sum of Al_2O_3 and ZrO_2, based on the weight of dry leather) in the three layers were calculated to evaluate the distribution of tanning agent in leather. Measurements were made in triplicate, and the results were presented as the means ± standard deviation. Additionally, the distribution index of tanning agent was calculated as formula (3) according to previous work:[13,16]

$$\text{Distribution index (\%)} = \frac{2 \times M}{G + F} \times 100 \qquad (3)$$

where G is the tanning agent content in grain layer, M is the tanning agent content in middle layer, and F is the tanning agent content in flesh layer.

Determination of isoelectric point (pI) of leather

The pI of pickled hide/tanned leather was determined according to literature.[19] In brief, a leather sample was dried and ground into fine fibers using a grinding mill (ZM 200, Retsch, Germany). Then 10 g of the ground sample was dispersed in 400 ml of water to measure the zeta potentials at different pH values by a zeta potential analyzer (Mütek SZP-10, BTG, Germany). The pI of leather, which was the pH value at the zero point of zeta potential, was found from the pH-zeta potential curve.

Results and Discussion

Charge properties of tanning agent, pickled hide and tanned leather

Electrostatic interactions between chemicals and leather are considered one of the driving forces for the mass transfer of chemicals in leather.[9,20,21] Moreover, the coordination reaction between tanning metal ions and carboxyl anions on collagen is related to the charge state of the pickled hide.[19] Thus, the penetration, fixation and distribution of tanning agents in leather should be influenced by the charge properties of both tanning agent and pickled hide. The blend of Al–Zr salts is strongly electropositive in aqueous solutions (Figure 1a) since it is easy to undergo hydrolysis and olation to form cationic complexes.[10,11] This will lead to rapid surface bonding and an uneven

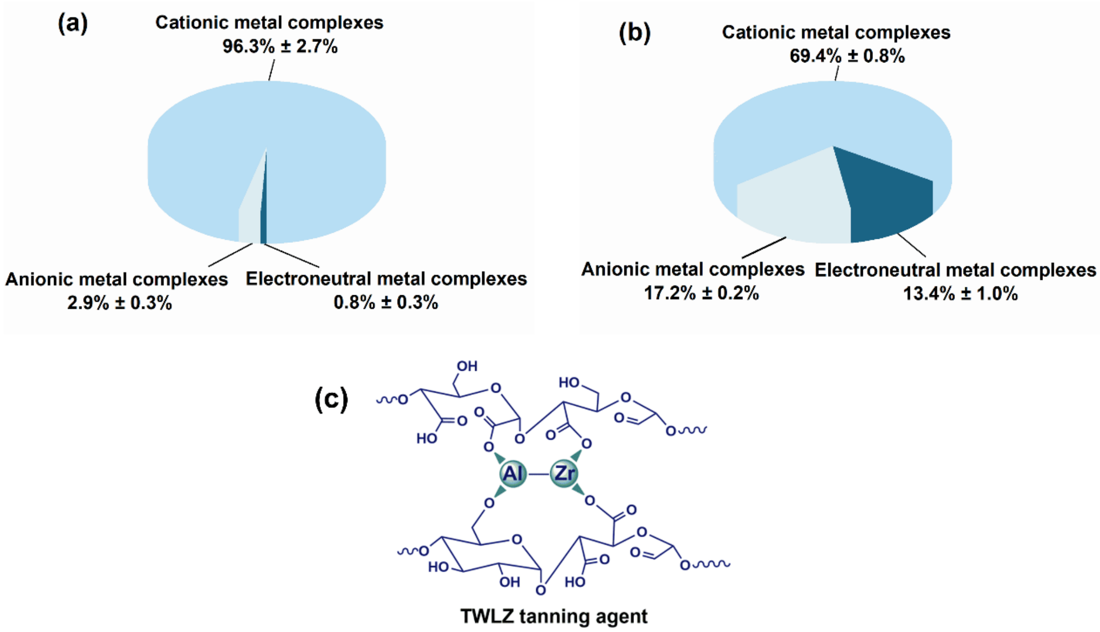

Figure 1. The proportion of metal complexes with different charge states in **(a)** $Al_2(SO_4)_3$–$Zr(SO_4)_2$ blend and **(b)** TWLZ; **(c)** structural schematic diagram of TWLZ.

distribution of Al–Zr salts in leather[13] because its carboxyl anion in collagen attracts cationic metal complexes by electrostatic force and then coordinates with metal ions. Figure 1b shows that cationic metal complexes accounted for only 69.4% of all the components in the TWLZ tanning agent (a blend of aluminum sulfate, zirconium sulfate and highly-oxidized starch), and the proportions of anionic metal complexes and electroneutral metal complexes grew to 17.2% and 13.4%, respectively, compared with the blend of Al–Zr salts. This result should be attributed to the introduction of a highly-oxidized starch, a macromolecular ligand with multiple carboxyl groups, into the metal complexes.[7] The masking effect of the ligand reduced the electropositivity and reactivity of metal complexes (Figure 1c) and should benefit the penetration of metal complexes. Meanwhile, the pI of pickled hide was 5.5 (Figure 2), suggesting that the pickled hide was electropositive, and the ionization of carboxyl groups was restricted in the initial stage of tanning (pH < 2.0). This result was also beneficial to the uniform penetration of metal complexes. As the tanning float pH rose during basification, the electropositivity of metal complexes was enhanced. The carboxyl groups on collagen were gradually ionized to carboxyl anions and participated in the coordination, and thereby resulted in the bonding and crosslinking of cationic metal complexes in leather. This reaction can also be demonstrated by the fact that the pI of tanned leather increased to 7.1 after tanning (Figure 2).

Effect of TWLZ dosage on distribution of TWLZ in leather

Pickled hide was tanned with 6%, 8% and 10% TWLZ tanning agent, respectively. The tanned leather was split into three layers, i.e. grain, middle and flesh layers, for the determination of tanning agent content. The distribution of the tanning agent in leather after penetration and tanning is shown in Figure 3. A penetration stage

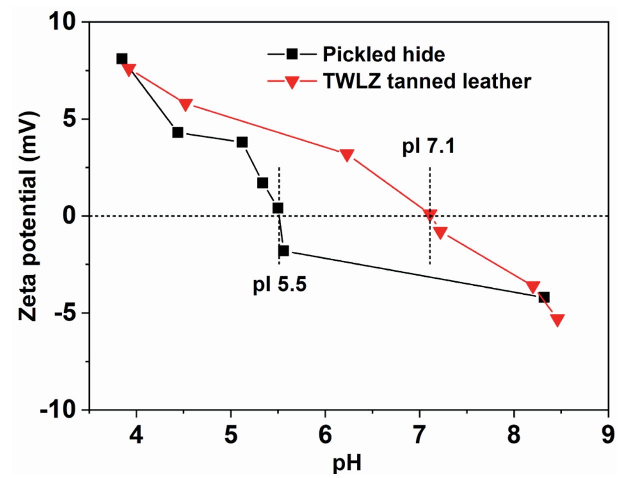

Figure 2. Zeta potentials of pickled hide and TWLZ tanned leather at different pH values.

was set before basification. Figure 3a shows that TWLZ penetrated into the middle layer at that time, and its distribution uniformity was enhanced with the increase of dosage. This result can be attributed to one of the main driving forces of diffusion, namely the concentration gradient. Basification, increasing float length and raising temperature were conducted afterwards to promote the bonding and fixation of Al–Zr complexes in leather. The tanning agent contents in leather after tanning (Figure 3b) were all higher than those after penetration (Figure 3a) and showed a gradual growth with the increase of TWLZ dosage. This resulted in the enhancement of tanning effects as the shrinkage temperatures of tanned leather were 76.2°C, 81.0°C and 83.1°C when using 6%, 8%, and 10% TWLZ. The distribution uniformity of TWLZ can be evaluated by the standard deviation (SD) of tanning agent contents

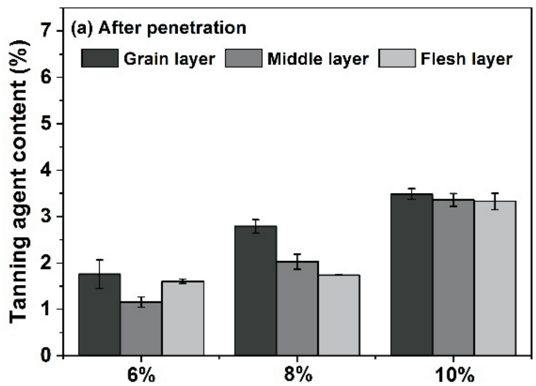

Figure 3. Effect of TWLZ dosage on distribution of TWLZ in leather (**a** after penetration; **b** after tanning)

in grain, middle and flesh layer of the tanned leather. When TWLZ dosage was 8%, the SD of tanning agent contents in the layered leather was lower than the other groups, suggesting more uniform distribution of tanning agent in leather. Further increasing the TWLZ dosage led to the deposition of Al–Zr complexes on grain surface.

Effect of basification method on distribution of TWLZ in Leather

Basification was conducted during the mineral tanning process to get good exhaustion of the metal salts. Inappropriate basification may result in an uneven distribution of the tanning agent, precipitation on leather surface and unsatisfactory properties of finished leather. Here, the effect of basification method on the distribution of TWLZ was investigated. Figure 4 illustrates that basification with magnesium oxide showed higher tanning agent content and a more uniform distribution (lower SD) after tanning compared with the other two basification methods. Magnesium oxide with a low solubility was slowly consumed throughout the tanning process, thereby leading to a continuous pH rise and gradual fixation of tanning agent. Thus, the penetration and binding of TWLZ in leather was more sufficient than the other groups. Sodium bicarbonate basification and mixed basification are batch-type basification. The pH rise fluctuated and showed a zigzag upward trend, particularly at the later stage of tanning. Thus, an uneven distribution of tanning agent was obtained for sodium bicarbonate basification and mixed basification (Figure 4b).

Effect of pretreatment on distribution of TWLZ in leather

In order to improve the penetration, distribution and exhaustion of tanning agents, pretreatment with fatliquors or pretanning agents is commonly carried out before tanning. Here we chose three agents with different charge types for pretreatment. Figure 5 shows that AFA was in an electronegative state in the pH range of 2.5 to 6.5. CFA maintained an electropositive state in the pH range of 2.5 to 6.5. TWS possessed a zwitterionic property with a pI of 4.57. Different pretreatments resulted in quite different tanning performances (Figure 6 and Table IV). As for the distribution uniformity, TWS group performed better in terms of a lower SD of tanning agent contents in layered leather (Figure 6) and a higher distribution index of tanning agent (Table IV) compared with the other groups. On the other hand, AFA group showed the highest SD and the lowest distribution index, indicating an uneven distribution of tanning agent in leather. These results can be explained by the charge state of chemicals/leather and the electrostatic interaction between them. CFA and TWS were electropositive during pretreatment and initial tanning stage ($pH < 3$). They easily penetrated into the positively

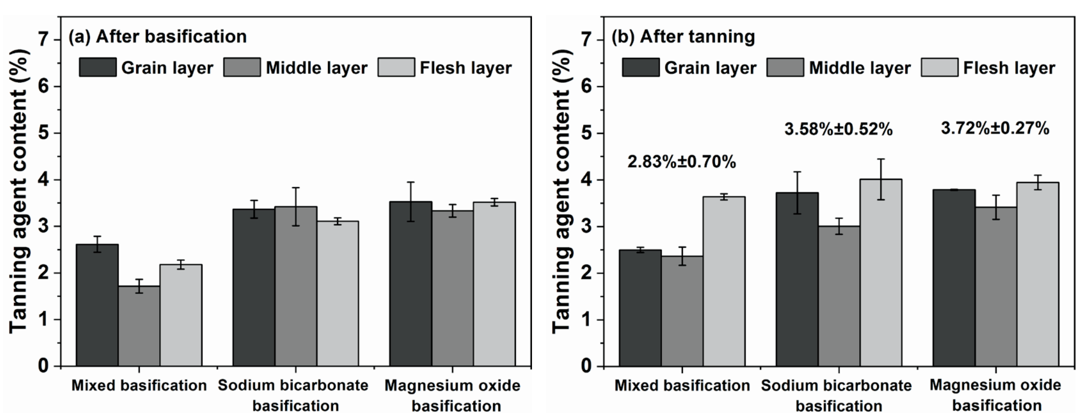

Figure 4. Effect of basification method on distribution of TWLZ in leather (**a** after basification; **b** after tanning)

charged hide by electrostatic repulsion and bound with collagen carboxyl anions, which can be demonstrated by the pI growth of pretreated hide (Figure 7). Therefore, the following coordination of cationic complexes of TWLZ with collagen carboxyl anions was temporarily retarded, and TWLZ tended to penetrate into the core of leather and distribute evenly. In the opposite case, the introduction of anionic AFA reduced the electropositivity of hide (see the pI in Figure 7) and led to excessive surface fixation and uneven distribution of TWLZ.

In addition, CFA group exhibited the lowest total content of tanning agent (3.69%, see Figure 6). This is because of the competitive binding of CFA and TWLZ to leather at the later stage of tanning as they were both cationic chemicals. TWS group showed the highest total content of TWLZ as well as the T_s of leather. The reason should be attributed to the fact that the electropositivity of TWS turned down sharply (Figure 5) as the pH rose during basification, thereby promoting the fixation of TWLZ at the later stage of tanning. As a result, pretreatment with amphoteric agent TWS is beneficial to TWLZ tanning system in consideration of both penetration and fixation of tanning agent.

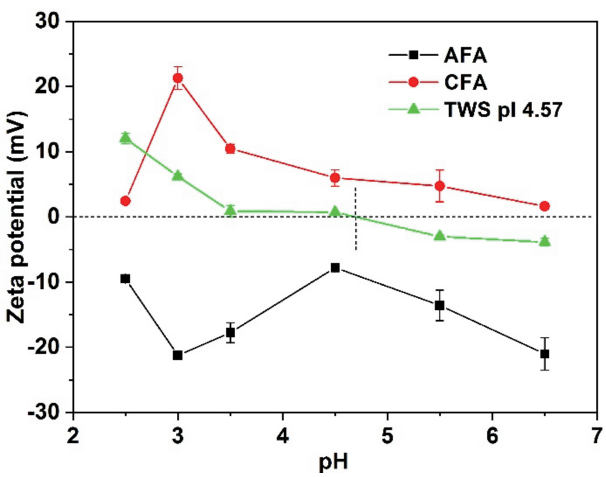

Figure 5. Effect of pH on zeta potential of pretreatment agent.

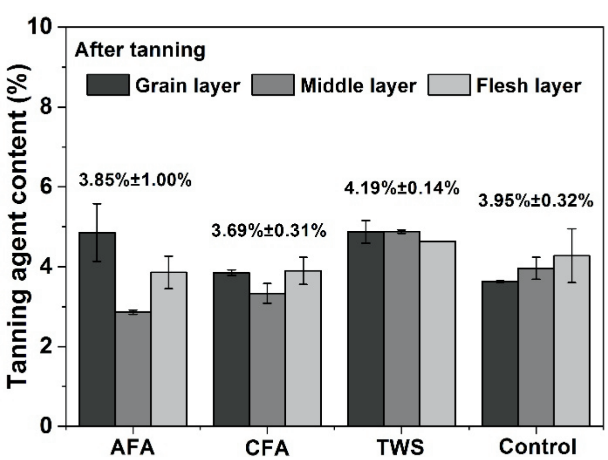

Figure 6. Effect of pretreatment on distribution of TWLZ in leather.

Table IV

Properties of TWLZ tanned leather using different pretreatment methods

Group	T_s (°C)	Distribution index of tanning agent (%)
AFA	79.8 ± 0.2	66.3 ± 8.6
CFA	80.2 ± 0.3	86.2 ± 4.6
TWS	81.9 ± 1.0	102.7 ± 3.1
Control	80.0 ± 0.3	100.6 ± 8.8

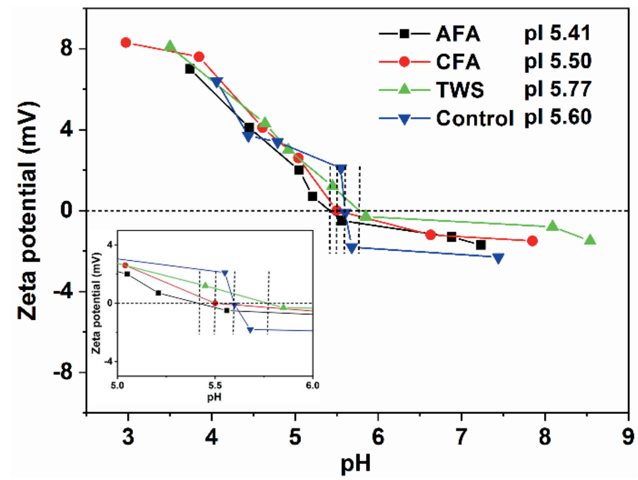

Figure 7. pIs of pretreated hide before tanning.

Conclusions

A complex tanning agent composed of Al–Zr salts and highly-oxidized starch named TWLZ can evenly distribute in the cross-section of leather because the highly-oxidized starch ligand effectively masked the metal ions and reduced the electropositivity of complexes. Using 8% TWLZ, basification with magnesium oxide and pretreatment with an amphoteric organic tanning agent benefited the penetration and uniform distribution of TWLZ in leather. This work is expected to provide a basis for the industrial application of TWLZ in chrome-free tanning system.

Acknowledgement

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