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A novel tanning agent for pickle-less chrome-free tannage

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Abstract

Many alternative chrome free tanning systems have been proposed owing to chrome pollution problems, but few have been widely applied. One of the main reasons for the failure of chrome-free tanning system was that tanning should be done at pickle pH of 2.5-3.0, so considerable neutral salts must be used which result in a net increase in total dissolved solids (TDS) in tannery wastewater. So pickle–less tanning is becoming more and more important due to environmental problems. In this study, a new tanning agent was applied in pickle-less tannage. This tanning agent possesses low reactivity in the acidic conditions, but has good tanning ability in the alkaline conditions. An attempt has been done to tan goatskins using SPR after bating and pickling to pH 2.5-3.0 has also been performed as a control. The results show the shrinkage temperature of experimental leathers is 88°C higher than that of control leather. The experimental leathers possess good physical properties

1. Introduction

Nowadays, chrome tanning is the most preferred tannage in leather industries; it makes the leathers with excellent physical and organoleptic properties. But, chrome tanning has its own disadvantages. Firstly, the Cr (III) existing in leather might be transformed into Cr (VI) in some extreme conditions, and as we know, Cr(VI) has been proven to be toxic in nature.[1] Meanwhile, chrome pollution may occur through discharge of waste water and chrome-containing solid wastes. With respect to the disposal of these wastes, there are tightening regulations in most countries, and it is increasingly difficult for leather industry to comply with the emerging regulations.[2] So many researches in leather sector have concentrated on work to explore chrome-free tannage to substitute for chrome tannage.

A suitable tannage as an alternative to chrome tanning should possess following characters: imparting high hydrothermal stability, processing white or pale colored and lightfast leather, and having low environmental impact.[3] As the worldwide environment problems become more and more serious, to explore clean technology of leather manufacture become more and more important. Now with respect to the disposal of neutral salts such as sodium chloride, there are tightening regulations in most countries. In the processing of skins turned into the finished leathers, a pickling process is performed before tanning, which can change the charge of collagen fibers, benefiting the penetration of tanning agents and preventing the rapid combination of the collagen with tanning agents, because many tanning agents such as chromium salts, formaldehyde, glutaraldehyde and so on, can react with

carboxyl or amino groups on side chains of collagen in acid conditions(around pH4.0) to produce effective cross-links between collagen fibers. In conventional pickling process, sodium chloride is previously added to prevent the swelling of the collagen of skins in the acid conditions.

The pickling process has been applied for many years. Although the salt and acid are effective, they cause a serious environmental problem. The salt occupies about 35 percent of total dissolved solids (TDS) in the effluents[4, 5]. In addition the acid can turn into the neutral salt by basification; it also increases the TDS in the tannery effluent[4, 5]. The effluent can not be used for irrigation, which may retard growth of crops and destroy soil structure. Furthermore the improper operation in pickling process would lead to loose grain.

Therefore, the aim of this study is to examine the application of chrome-free tanning agent SPR in the pickle-less tannage. Tanning agent SPR has been synthesized and patented, whose main composition is a kind of amphoteric high molecular compound containing considerable amino and carboxyl groups and a few of aldehyde groups, whose molecular weight is about 2000~3000.

2. Materials and method

2.1. Materials and instruments

All chemicals used for leather processing were of commercial grade. SPR tanning agent was synthesized in the laboratory scale. Goatskin bated pelts were made by ourselves. UV-250PC ultraviolet spectrophotometer was purchased from Japanese Daojin Instrument Company. WGZ-200 ratio turbidimeter was purchased from Shanghai Precision & Scientific Instrument CO., LTD, China.

2.2. Biodegradability evaluation of SPR tanning agent

The general experimental methods and the principles for biodegradability evaluation of chemicals were as in the literature[6].

2.3. Effect of tanning conditions on tanning property of SPR

Based on the properties of SPR, the tanning properties were tested according to different tanning pH, different tanning temperature and different offer of SPR tanning agent.

2.3.1. Effect of tanning pH and temperature

The pH of bated pelts was adjusted to5.5, 6.0, 6.5, 7.0, 7.5 and 8.0, respectively. 3% SPR was used (based on the weight of limed pelt) for tanning. The tanning process was carried out at room temperature (25~30^{o}C) in a drum of diameter 50cm. After rolling for 2 hours, the shrinkage temperature of leather was measured. Then the tanning temperature was elevated to 35^{o}C, the shrinkage temperature of leather was measured after rolling for 2 hours. Finally, the tanning temperature was elevated to 40^{o}C; the shrinkage temperature of leather was measured after rolling for 2 hours.

2.3.2. Effect of tanning time

100% water and 3% SPR tanning agent were added into the drum after the bated pelt was washed. After rolling for 2h at room temperature, the tanning liquor was adjusted to pH 8.0 using sodium bicarbonate solution in 1 hour. After rolling for 1 hours, the tanning temperature was elevated to 40°C, and the shrinkage temperature was measured every 1 hour.

2.3.3. Effect of SPR offer

100% water was added into the drum after the bated pelt was washed. The offer of SPR used for tanning were 2, 4, 6, 8, 10 and 12% (based on weight of limed pelt), respectively. After rolling for 2 hours, the tanning pH was adjusted to 8.0 and then temperature was elevated to 40°C, the shrinkage temperature of leather was measured after tanning for 3h.

2.4.1. Control and experimental tanning Using SPR

2.4.1. Control tanning process

The tanning experiments were carried out on bated goatskin. Four pieces of bated goatskin were taken for the control process.

2.4.2. Experimental and tanning process (pickle-less tanning)

The tanning experiments were carried out on bated goatskin. Four pieces of bated goatskin were taken for experimental process.

Table I Control tanning process of bated goatskin using SPR

Process	Chemicals	%	Duration	Remarks
Pickling	Water	60		Room temperature
	Sodium chloride	7.0	20min	
	Acid formate	0.8	30min	
	Sulfuric acid	0.5	15min×3+60min	
Tanning	SPR	4	120min	
	Sodium carbonate	0.8	20min×3	
	Sodium bicarbonate	0.6	20min×3+60min	pH 8.0
			180min	40°C, Ts 85 °C

Table II Experimental tanning process of bated goatskin using SPR

Process	Chemicals	%	Duration	Remarks
Tanning	Water	50		Room temperature
	SPR	4	120min	
	Sodium bicarbonate	0.6	20min×3+60min	pH 8.0
			180min	40°C, Ts 88°C

2.5. Shrinkage temperature determination

The shrinkage temperature of tanned leather, a measure of hydrothermal stability of leather, was measured using Theis shrinkage meter. The values reported are an average of three measurements.

2.6. Uptake of dye and fat-liquoring agent measurement

The experimental and control crusts were subjected to standard dyeing and fat-liquoring processes, respectively. The dyestuff was a common commercially available black dye, added at 2% based on the weight of tanned crust. The fat-liquoring agent is MK (TFL company), added at 18% on the weight of tanned crust. The spent liquors from both control and experimental processing were collected and analyzed for % uptake of dye and fat-liquoring agent. After proper dilution, the uptake of dye was investigated using a spectrophotometer, and the uptake of fat-liquoring agent was investigated using a ratio turbidimeter.

2.7. Physical properties of leather

The mechanical properties of leather were measured by an LJ-500tensile strength tester and bursting strength testing machine, and the detailed testing methods were as in the literature[7].

3. Results and discussion

3.1. Biodegradability of SPR tanning agent

During the past few decades, the awareness of environmental problems has increased considerably, so a kind of excellent leather chemical product not only possesses good properties, but also has little environmental impact. The main composition of SPR tanning agent is a kind of high molecular compound containing a few of aldehyde groups. As shown in Table III, the extent of biodegradation of SPR is high even if its concentration is as high as 1-2.5g/L. But the BOD_5value can not be measured when the concentration of SPR is equal to 5g/L. In spite of that, SPR is easy to be biodegrade by tannery activated sludge, which implies that SPR should possesse little environmental impact.

Table III BOD_5/COD values of SPR tanning agent

Concentration (g/L)	1	2	2.5	5
BOD_5/COD values	0.541	0.357	0.370	-

- BOD_5 cannot be detected

3.2. Effect of tanning conditions on tanning property of SPR

3.2.1. Effect of Tanning pH and Temperature

The shrinkage temperatures of leathers tanned by SPR at different pHs and different temperature are listed in Figure 1. Obviously, both increased tanning pH and elevated tanning temperature benefit the increase of the shrinkage temperature. At room temperature, the shrinkage temperature of leather increases with the increase of pH, and the maximum shrinkage temperature is obtained at pH 8.0. A few of aldehyde groups existing in the high molecular of SPR can react with amino groups of collagen side chains to form covalent cross-links between collagen fibers in tanning process, and thus increase

shrinkage temperature of leather. More amino groups exist in the form of uncharged state (-NH_2) in a high pH range, which favors the nucleophilic reaction of amino groups with SPR. Therefore, a higher shrinkage temperature is obtained at higher pH. However, the maximum shrinkage temperature is only 76°C, and when the pH is 7.0, the shrinkage temperature is 68°C, which indicates that SPR tanning agent has not produced tanning properties obviously. From Figure 1, it is obviously that the shrinkage temperature increased with the increasing tanning temperature. When the temperature was elevated to 40°C, the maximum shrinkage temperature increases to 86°C from 76°C, which indicates the tanning temperature affect the reactivity of SPR. At room temperature, SPR possesses low reactivity with amino groups of collagen in the range of pH 6.0-8.0, so SPR can penetrates all cross section of pelts. After penetration, in order to promote the reactivity of SPR, the tanning pH was adjusted to 8.0 and the tanning temperature was elevated to 40°C.

3.2.2. Effect of tanning temperature and time

The shrinkage temperatures of leathers tanned by SPR for different times at pH8.0 and 40°C are shown in Figure 2. The highest shrinkage temperature around 87°C is achieved in the third hour of tanning after the tanning temperature was elevated to 40°C. After tanning for 3 hours, the shrinkage temperature has no change. So the optimal tanning time is 3 hours.

3.2.3. Effect of SPR offer

The shrinkage temperatures of leathers tanned by different offers of SPR under 40°C at pH 8.0 are given in Figure 3. It can be seen that the shrinkage temperature of leather increases with increasing offer of SPR. However, when the offer is beyond 2%, there is no significant increase in the shrinkage temperature. But the fullness of tanned leather is not perfect. Hence, based on an overall consideration of fullness, shrinkage temperature and cost of tanned leather, the optimal offer of SPR for tanning is 4%.

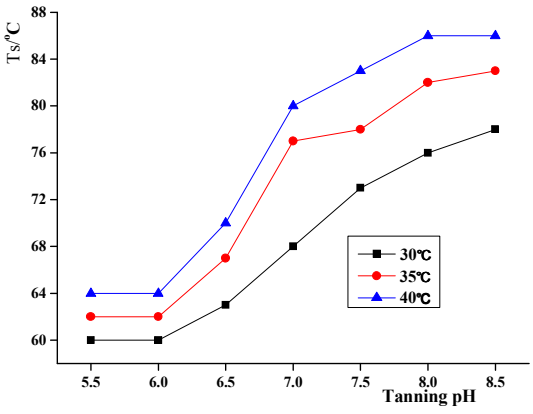

Figure 1. Effect of tanning pH and temperature on shrinkage temperature of leather

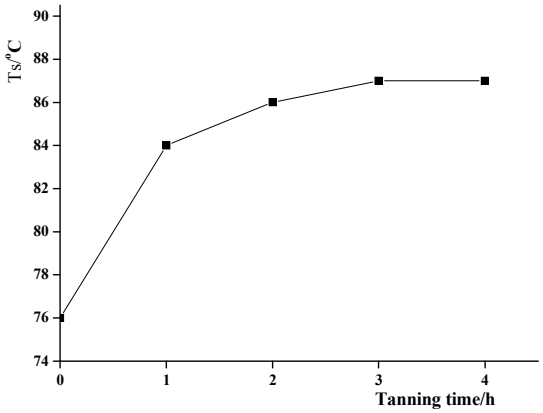

Figure 2. Effect of tanning time on shrinkage temperature of leather

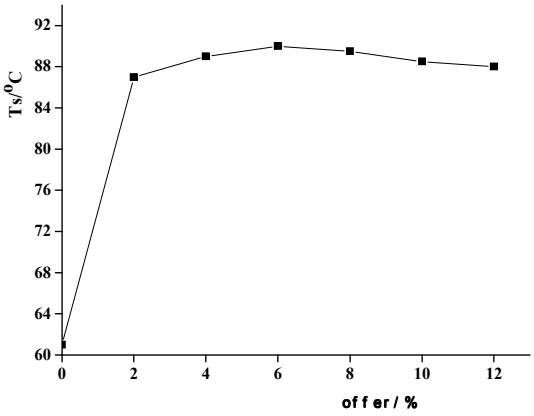

Figure 3. Effect of SPR offer on shrinkage temperature of leather

3.3. Bulk properties of tanned leathers

It is well known that the conclusions of hand and visual evaluation method are subjective, which varies from person to person. However it could be taken as reliable. The assessment values of tanned leathers are shown in Figure 4. It can be seen that the fullness, grain smoothness and grain tightness of experimental leather are superior to those of control leather. The reason may be that the collagen fibers of the pelts without pickling are hydrolyzed slighter than that of the pickled pelts. As such, the control leather softer slightly than that of the experimental leather. In a word, the general properties of the experimental leather are superior, and the pickle-less tanning method employing chrome-free tanning agent SPR is feasible and quite easy in practice.

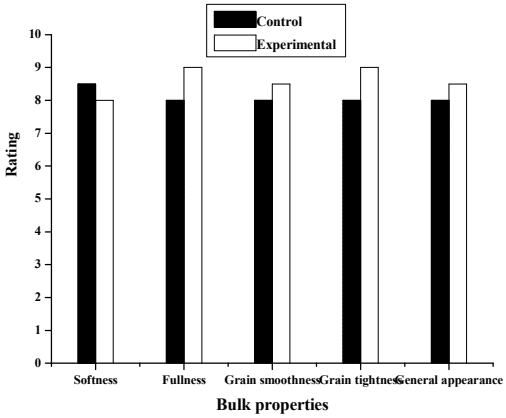

Figure 4 Organoleptic properties of the control and experimental leathers

3.4. Uptake of dyestuff and fat-liquoring agent measurement

The results about uptake of dyestuff and fat-liquoring agent are listed in Table IV. It is obvious that both experimental and control crusts tanned with SPR exhibit the excellent affinity to dyestuff and fat-liquoring agent. This is because that SPR is a kind of high molecular containing considerable amounts of amino groups which have positive charge; so much positive charge exists in the crust tanned by SPR. Meanwhile, both dyestuff and fat-liquoring agent exhibit negative charge. Unlike charges attract each other, so the crust tanned by SPR exhibits high absorption ratio to dyestuff and fat-liquoring agent, and there is no difference between the experimental and control crusts. From figure 5, we can see that the post tanning liquors from two tanning methods are clear, because most re-tanning agents also exhibit negative charge nearly.

Table IV Uptake of dyestuff and fatliquoring agent

Uptake/%	Dyestuff	Fatliquoring agent
Control	99.9	97.8
Experiment	99.8	98.0

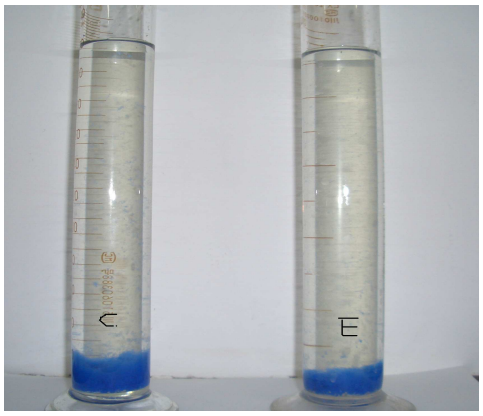

Figure 5 Samples of post tanning liquor (C, control; E, experimental)

3.5. Physical properties of leathers

The results of physical properties of leathers are listed in Table V. Using pickle-less tanning method (experiment), the tensile strength and tear strength are superior to that of control, furthermore, the elongation is shorter. These phenomena imply that the leather tanned by SPR in the pickle-less tannage can be filled with higher tightness, which attributes to slighter hydrolysis of collagen fibers.

Table V **Physical properties of finished leathers of two tanning methods**

Tanning method	Tensile strength/MPa	Elongation /%	Tear strength /N/mm
Control	9.8	45	48
Experiment	11.4	35	54

4. Conclusions

The SPR tanning agent in this study presents satisfactory property in pickle-less chrome-free tannage. The optimal tanning conditions were that penetration under room temperature for 2 hours then adjusting the pH to 8.0 and elevating the tanning temperature to 40°C, reacting for 3 hours. A shrinkage temperature of leather around 88°C is readily achieved when the offer of SPR is 4%. Using pickle-less chrome-free tannage, the tanned leather possesses better fullness, grain smoothness and grain tightness. In post tanning process, both the leather from the two tanning methods possess excellent absorption ratio for re-tanning agent, dyestuff and fat-liquoring agent. The physical properties of finished leather from pick-less tannage are superior to that of control. This pickle-less chrome-free tannage not only less environmental pollution of neutral salts but also eliminates the chrome pollution. Beyond that, SPR is easy to be biodegrade by tannery activated sludge and possesses little environmental impact. Therefore, SPR tanning agent seems to be a widely accepted product by tanneries.

5. References

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