High Exhaustion Chrome Tanning Process Aided by Sodium Silicate

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Abstract: Due to low uptake of chromium (III) in the traditional chrome tanning, huge amount of chromium in the tanning effluent is not only harmful to human beings but to animals. Furthermore, wastes containing chromium produced in leather manufacturing, such as trimmings and shavings, are seriously hazardous. To relieve pollutions from the traditional chrome tanning, an experiment was developed based on a two-step procedure, i.e., pickled goat skins were pretreated with sodium silicate in acidic and basic fields and then tanned with chromium salts. Conventional chrome tanning process was as control. The results indicate that performances of skins pretreated in basic field were apparently better than those in acidic field, shrinkage temperature (Ts) of skins treated with 7.5% sodium silicate for 3 hours attained 68 ℃. Skins stabilized with silicate could be adapted to shaving readily; most important is that it would not produce wastes containing chromium. Moreover, by the combination of silicates with collagen fibers, the content of chromium (III) ion in the tanning effluents decreased to 960 ppm to get the absorbility of chromium as 91%; Ts of skins tanned with 5% chromium salts attained 104 ℃ (above-mentioned offer as pickled weight basis). Results from scanning electron microscope (SEM) and physic-mechanical properties show that performances of the experimental leathers were on par with the controls. But Ts of the experimental crust leather was slightly higher than the control. The environmental improvements of this process consist in preliminary tanning of the skin so that it may be shaved to obtain chromium free wastes; besides, reduction of chromium content of the tanning effluents will be acquired.

Key words: chrome tanning; cleaner production; high exhaustion; sodium silicate

1 Introduction

The many advantages offered by chrome tanning justify its widespread use for production of almost all types of leather. However, traditional chromium(Ⅲ) tanning process is constantly under threat from the pressure of legislation and ever-tightening restrictions has resulted in tanners coming under pressure to minimize chromium-containing effluents discharge and chromium-containing trimmings, shavings, buffings etc. Research interest has thus centered on the development of high exhaustion chromium tannage. Many available methods, such as chrome combination tannage, [1, 2] auxiliary agents used in chrome tanning, [3, 4] collagenous fibers modified, [5] etc., have already been documented. Methods of disposal of chromium-containing wastes mainly include recycling, buring, incinerating and shaving. Recycling and reuse can not only reduce the chromium involving pollution, but utilize resources mostly to manufacture high-valuable products. Methods of wet-white can be able to produce tannery wastes without chrome, such as shavings, trimmings and buffings, etc., which will be so easy to recycle and reuse that can decrease chromium loading. But the extent of dechroming is difficult to control then it will do harm to following operations, as a result, it is of great significance to acquire a green and eco-friendly method to treat chrome-containing solid waste.

Over the past several decades, the plentiful and low cost silicon materials, such as montmorillonites and palygorskites, have received widespread attention and numerous applications. Owing to their special

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structure and eco-friendly properties, new applications have gradually been acquired of inorganic silicates to leather tanning [6] and liming process. [7, 8] Munz et al. have successfully developed methods to apply sodium silicates as liming substitute in the unhairing operation and to stabilize calf pelts for shaving without pre-tannage. In addition, the application of these silicates improves the exhaustion of later added auxiliaries, especially of chrome tannins. D'Aquino et al. have detailedly investigated a two-step tanning process in which a soluble sodium silicate is used as stabilized agent in acidic and basic fields for pickled calf skins and chromium salts are successively utilized to complete the tanning process on a semi-industrial scale. Results obtained are parallel to above-mentioned one, which are capable of allowing a better fixation of chromium salts and increasing absorbility of chromium. More attentions about almost the same Ts of pickled calf skins pretreated by silicates in acidic and basic fields are paid to, accordingly, tanning process at acid pH was chosen to treat skins for an industrial application which can reduce processing time and consumption of chemical products. However, author do not agree with aforementioned conclusion on the basis of properties of silicates in literature [7] referred to.

So in this study we designed an experiments based on a two-step procedure in which pickled goat skin were pretreated by sodium silicate in acidic and basic fields and then tanned with chromium salts and wanted to know effects of sodium silicate on thermostability of pickled goat skin and subsequent chrome tanning.

2 Experimental

2.1 Materials and Apparatus

The following apparatus and reagents were used in the experiment.

GSD-350 Type drums (300mm×160mm), TS2000-S Type multi-functional stress test machine, lastometer, shrinkage temperature tester, KYKY1008 Type scanning electron microscope (SEM). Basic chromium sulphate salts (BCS) were supplied by Tingjiang Science & Technology Corporation Limited (Chengdu, China), and all other chemicals were of analytical grade, such as sodium silicate (containing 20% silicon dioxide), potassium dichromate, sodium peroxide and sodium hydroxide.

2.2 Methods

2.2.1 Optimization of pretreating process of sodium silicate

Goat skin was processed to pickling operation using traditional pretanning process[9]. Adjacent rectangles (200mm X 150mm) skin sheets were cut from the center of a single side, weighed and was noted. As this experiment mainly discussed effects of sodium silicate on thermostability of pickled goat skin, pretreating process was designed as followings in acidic and basic fields.

Depickling	100%	water 25℃		
	8%	Salts	5min	
	5%	$NaHCO_3$ (diluted with 15 times water)	45min	pH=7
		Drain		
	(100%	water 25℃		
	8%	Salts	50min	
		Drain)		

Silicate Pretreating process:

100%	water 25℃	
a%	Na_2SiO_3 (a=2.5,5,7.5,10,12.5)	
2%	liming auxiliary agents	t h (t=1,2,3,4,5)
1%	Sulfuric acid (diluted with 15 times water)	15min×3

1%	Formic acid (1:15 v/v diluted)	30min pH=3
(0.5%	Sulfuric acid (diluted with 15 times water)	15min×3
0.5%	Formic acid (1:15 v/v diluted)	30min pH=3)

Drain, washed and then Ts of each sheets was analyzed.

Remarks: treating process inside bracket was in acidic field, the other processes are the same.

2.2.2 Optimization of chrome tanning process and control experiment

To obtain the effects of sodium silicate on subsequent chrome tanning, chrome tanning experiments were done to tan skins pretreated by above better process. Chrome tanning process was designed as followings (noted as E).

Chrome tanning process:

100%	water 25℃	
c%	BCS (c=3,4,5,6,7)	120min
1%	HCOONa	30min
1.5%	$NaHCO_3$ (diluted with 15 times water)	15min×3+60min
150%	hot water 40℃	120min pH=4.0

Drain, washed and Ts of each blue wet was determined. Adjacent pickled skin sheets were chosen to be tanned using above chrome tanning process as control experiment (noted as C) and Ts of those were then detected. Aforementioned blue wet leathers were together processed to crust leather using conventional post tanning process. [9]

2.2.3 Analysis of SEM

Samples from the control (C) and experimental (E) sides after chrome tanning were cut from the official sampling position and then dehydrated using acetone and methanol as the standard procedure. [10] The specimens were then coated with gold and a KYKY1008 type scanning electron microscope was used for the analysis. The micrographs for the grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 25 kV with different magnification levels.

2.2.4 Analysis of spent chrome liquor

Chrome liquors collected from both optimized experiment and control processes were analyzed for chromium as per the standard procedures. [10] The percentage of exhaustion of chromium was calculated from the amount of spent liquor collected.

2.2.5 Physical testing and hand evaluation of leathers

Samples for various physical tests from experimental and control crust leathers were obtained as per the standard procedures. [10] Physical properties such as tensile strength, load elongation, %elongation at break, tear strength and grain crack strength were examined as per the standard procedures. [10]

3 Results and discussion

3.1 Optimization of pretreating process of sodium silicate and chrome tanning process

According to designed processes, results of Ts of skins, pretreated by different proportional silicates in acidic and basic fields, are shown in Fig. 1. It is seen that Ts are gradually elevated to 68℃ and 58℃ with additions of silicates in basic and acidic fields, respectively. As is well known that silicate sodium (wasserglass) is easily soluble in water, when a soluble silica monomer, $Si(OH)_4$, is formed at a concentration greater than about 100-200 ppm as SiO_2, that is, greater the solubility of the solid phase of amorphous silica, the monomer polymerizes by condensation to form higher molecular weight species of silicic acid (colloidal particles) that, depending upon the conditions, separate in the form of sol or may aggregate into three-dimensional networks and form gels. [7] The polymerization behavior of silica, as well as the polymerization degree and the size of the colloidal particles, depends on several factors, the most effective being the pH and the presence of salts in solution. In the presence of salts, practically, at every pH value, the colloidal particles evolve towards the gel form, while when salts are absent the colloidal particles assume the state of a stable sol for pH＞7. At pH 1.5-3 the maximum stability of sol occurs, while the minimum sol stability is observed at pH 5-6 when salts are absent and at pH 7 when salts are present. To obtain a good penetration inside skin section, it is necessary that the colloidal silica is present in solution as stable sol of small size particles. Since the presence of salts in the tanning solution is necessary to avoid swelling of the skin, silica gelling is inevitable. It is thus necessary to operate in pH ranges in which the gelling time as longer as possible. Based on the results of literature referred to, [7] in which silicate can cause a pH increase from 7 to 10.5-12 after 3 hours of drumming in basic field, depending on the silicate used and the dosage. By contrast a pH is reduced form 9.0 to 5.0 after 3 hours by using SILICATE 2 in acidic field, even reduced from 9.0 to 6.8 after 1 hour. It is apparently speculated on that the former one do benefit silica's stability to acquire smaller sizes silica sols to penetrate skin section rapidly, but the latter, in theory, can keep silica sols stable only in 1 hour and subsequently the silica polymerize to larger sizes sols or even gels that it can not favor to penetrate skin skin section. That is to say, the actions between the silanol groups, -Si(OH), present on the external surface of the colloidal silica particles, and the polar groups of collagen, will be certainly disadvantageously affected by whether silica penetrate skin section rapidly and thoroughly or not, which in turn have some disfavorable impact on shrinkage temperatures of skin. So there should be some difference under two circumstances, results obtained in this article seem to accord with forementioned conclusions. It is well known that the actions between the silanol groups and the polar groups of collagen would be alike those between vegetable tannins and collagen functional groups, Ts of skins tanned with silicates would no longer be elevated with additions of silicates when hydrogen bonds combination seem to be saturated. As a result, silicate sodium 7.5% and 10% based pickled skins in basic and acidic fields, respectively, are chosen to manage skins.

Results of Ts of skins, pretreated by silicates 10% and 7.5% in acidic and basic fields within different intervals, are shown in Fig. 2. It is shown that Ts of skins are gradually elevated to 68℃ and 58℃ with the time going on in basic and acidic fields, respectively. Ts of skins tend to be invariability after 3 hours of drumming under both two circumstances. It is easy to comprehend that before silica sols react to collagen functional groups, it must penetrate into skins, there is some difference in the size of the silica sols particles between the basic and acidic fields but reactions of penetration and combination tend to be in equilibrium under the two circumstances after 3 hours of drumming. Finally we choose the 3 hours as the processing time.

In view of abovementioned all, process of silicates 7.5% based pickled skins, processing 3 hours in basic field is selected as silicates pretreating process. Similar to the literature referred to, [7] skins can firstly be stabilized by silicates which then are adapted to shaving by obtaining chromium free wastes. Besides, D'Aquino et al. considered that the neutralization at pH 7 before the silicate dosaging was quite onerous either for the higher process times either for the higher energy and chemical products consumption. However, author do not agree with abovementioned points and bring forward to the feasibility that bated skins can be directly managed by silicates to cancel the pickling procedure if only skin collagen fibers be well separated. Researches concerning those will be developed later.

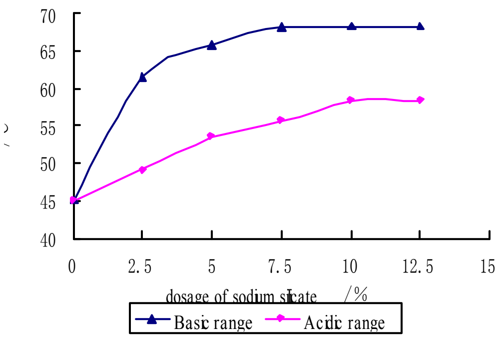

Fig. 1 Effect of dosage of sodium silicate

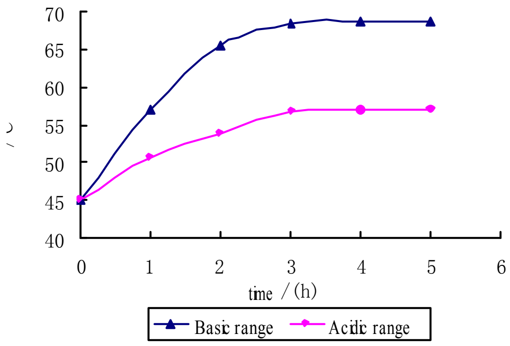

Fig. 2 Effect of silicate pretreating time

Experimental results about the effects of sodium silicate on subsequent chrome tanning (noted as E and C), are seen in Fig. 3. It can be seen that Ts of E wet-blue samples are always a little higher than those of C wet-blue samples. Ts of E samples is 104℃, capable of withstanding boiling test, when dosage of BCS is 5% (offered as pickled skins). Since polymeric silica may interact with chromium salts through chelate-like coordination bonds, thus promoting adsorption of the chromium salt on the silica particles and forming synergism effects to favor the chromium penetration and fixation processes.

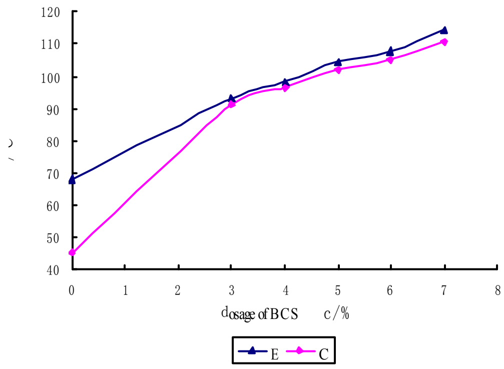

Fig. 3 Contrast of control and experiment tanning

3.2 Analysis of SEM and spent chrome liquor

The scanning electron micrographs of control and experimental samples after chrome tanning showing the grain surfaces and the cross section at a magnification of ×50 are shown in Fig. 4a, Fig. 4b, Fig. 4c and Fig. 4d. It is seen that hair pores of both the samples are visible and clear, experimental sample shows separation of fiber bundles comparable to that of control sample. Owing to irrelevantly operating in samples preparation, a few silica particles are present in the experimental sample but its effect will be very little.

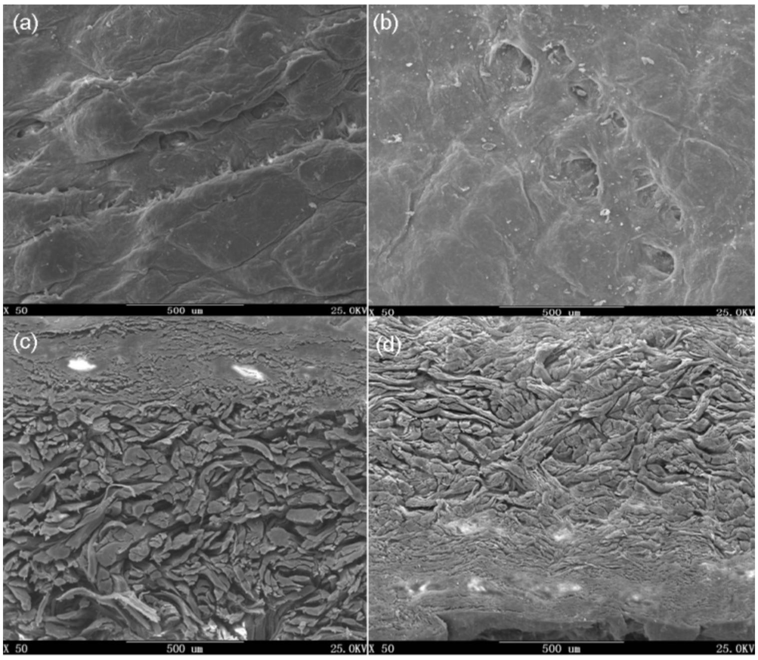

Fig.4 Scanning electron micrographs of control and experimental samples after chrome tanning showing the grain surfaces and the cross section at a magnification of ×50: (a) experimental wet-blue grain surface, (b)control wet-blue grain surface, (c) experimental wet-blue cross section and (d) control wet-blue cross section.

The amount of chromium in spent liquor and the calculated chromium uptake values of control and experimental processes are presented in Tab. 1. Chromium concentration of spent liquor from experimental process is lower than that from control process; the uptake of chromium is greatly increased in the experimental process compared to the control process. This is primarily due to new coordination bonds between silica particles, chromium complex and collagen which form synergism effects to favor the chromium penetration and fixation processes. This is in accordance with the trend observed in Ts of both the experiment and the control samples.

Tab.1 Chromium (III) concentration of spent chrome liquor and uptake of chromium during tanning

Sample	Concentration of Cr^{3+}（ppm）	%Exhaustion
E	960	91
C	2990	72

3.3 Physical testing and hand evaluation of leathers

The strength values of the leathers corresponding to each experiment were given in Tab. 2. Strength properties of the leathers made from the experimental process are comparable to that of control process and all of them meet the Bureau of China Light Industrial Standards specifications. The softness, fullness, grain tightness and grain smoothness of the experimental leathers are comparable with that of conventionally processed leathers. Generally, the appearance and performance of the leathers from integrated process is comparable to the control leathers. Furthermore, Ts of experimental crust leather is slightly higher than that of the control crust leather.

Tab. 2 Physical testing data of control (C) and experimental (E) leathers

Properties	E	C
Tensile strength/(N · mm^{-2})	28.3	25.8
Load elongation/(%)	27	31
Elongation at break/(%)	60	72
Tear strength/（N · mm^{-1}）	48.4	55.3
Grain crack distention/（mm）	15.3	16.4
Ts/（℃）	114	112

4 Conclusions

It can be concluded that the performances of skin pretreated in basic field are apparently better than those in acidic field. Ts of skin treated by 7.5% sodium silicate for 3 hours can attain 68℃ and then which can be adapted to shaving by obtaining chromium free wastes. Moreover, silicates combined with collagen fibers can decrease concentration of chromium (III) ion in tanning effluents to 960 ppm and increase absorbility of chromium to 91% so greatly that Ts of skin tanned with 5% chromium salts can attain 104℃. Results from SEM and physic-mechanical properties show that performances of the experimental leather are on par with the control leather. Ts of the experimental crust leathers are slightly higher than the control crust leather. The environmental improvements of this process consist in preliminary tanning of the skin so that it can be shaved by obtaining chromium free wastes; besides, reduction of chromium content of the tanning effluents will be acquired.

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