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# A non-pickling process for hides and skins using SCM

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## Abstract

During the process of leather manufacture, some chemicals such as salts, acids, lime, etc were discharged as tannery effluent, which would lead to the pollution of environment. Pickling process using sodium chloride, formic acid and sulfuric acid can devote to the tannery effluent. In this study, the synthesized SCM pre-tanning agent was used between the bated and chrome-tanned process in order to obtain a non-pickling process for hides and skins. Investigations indicated that using SCM as pre-tanning agent can get rid of neutral salts and acids, and the chrome exhaustion was higher than 90%. Meanwhile, the performance of leathers was on par with that of leathers conventionally tanned according to physical and tactile evaluation.

## 1. Introduction

Chrome tannage has been used for more than 100 years. Now most of all the tanneries in the world adopt chrome tannage. In the process of hides or skins turned into the chrome-tanned leather, a pickling process is performed before tanning, which can change the charge of collagen matrix ( to minimize the negative charge and maximize the positive charge), benefit the penetration of chrome compound and prevent the rapid combination of the collagen with chromium compound[1]. In conventional pickling process, sodium chloride is previously added into the hides and skins pretreated to prevent the swelling of the collagen in the acidic conditions [2]. Based on the theory of the balance of Donnan, the addition of sodium chloride also increases the ion concentration which results in high osmotic pressure. This enhances the migration of water from the inside of the collagen to the outside, causing a decrease of the ion concentration in the pickling bath so that the swelling of the collagen is avoided[3]. In addition, the addition of acid can passivate the carboxyl groups and make the amino groups exist as amine salts, which cause the fast penetration and slow combination of chrome compound with the collagen.

The pickling process has been applied for many years and serves the chrome tannage. Although the salt and acids are effective, they cause a serious environmental problem as tannery effluent containing high concentrations of salt and acid. The salt occupies about 35% total dissolved solids (TDS) in the effluents [4]. In addition the acids can be turned into the relevant salts by basification, which would increase the TDS in the tannery effluent. The effluent can not be used for irrigation, which may result in dehydration and retarding growth of crops, and affect soil structure [5]. Furthermore the temperature of the pickling process remains at or below 28$^{o}$C conventionally because raw hides and skins have a low shrinkage temperature. Higher temperature would lead to loosing grain or shrinkage

of the hides or skins. Especially in the summer, the pickle process often need to add ice to control the temperature of the bath in order to ensure the quality of the leather. So the pickling process not only need intensive labor and higher cost, but also cause serious environmental problem.

To overcome the problems of the pickle process, some methods have been investigated such as recycle/reuse of pickle liquor, salt free pickling using naphthalene sulfonic acid, pickle-free tanning system using chrome syntan and modified chromium sulfate (BCS) and others[6,7-9]. The purpose of our research is to develop a non-pickling process in chrome tanning system by using a kind of pre-tanning agent named as SCM, which can eliminate the pickling process before chromium tanning with the conventional chrome tanning agent.

## 2. Materials and methods

### 2.1. Materials

All chemicals used for leather processing were of commercial grade. Chromosal B ($Cr_2O_3$ 26%), and Coripol MK were purchased from Bayer Chemicals s.p.a, Germany, TFL Sicence& Technology co.Ltd, Qidao City, Shandong Province, China, respectively. The pre-tanning agent SCM was prepared in the laboratory scale. Goatskin bated pelts were made by ourselves according to conventional technology.

### 2.2. Methods

#### 2.2.1. *Tanning studies with SCM on goatskin*[10]

SCM is synthesized as a chrome-free pre-tanning agent in leather industry, whose main composition is a kind of aliphatic aldehyde without formaldehyde. In order to find the optimal application conditions of SCM, the effect of pH and offer on the tanning properties of SCM were examined.

**Optimization of penetration pH**

Twelve goatskin bated pelts whose area is about 20×20cm$^2$ were pickled or non-pickled according to the need of different penetration pH (2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0). The pelts with different pH were penetrated by 2% SCM (based on the weight of bated pelts), and the float was 100%. The penetration process was carried out under room temperature in the ¢50 stainless steel drum. After rolling for 1 hour, the penetration was checked using Schiff reagent. The emergence of red in the cross section of pelts can show the degree of penetration of SCM. When penetration is completed, the red appears in the cross section of pelts. Simultaneously the shrinkage temperature (Ts) of the pelts in different pH value was determined.

**Optimization of the offer of SCM**

Goatskin bated pelts (pH7.0-7.5) whose area is about 20×20cm$^2$ were tanned under room temperature(~25$^o$C) in the ¢50 stainless steel drum, and the float was 100%. 1%, 2%, 4%, 6%, 8% and 10% SCM (based on the weight of bated pelts) was added into different drum, respectively. Tanning for 1 hour, the shrinkage temperature (Ts) of the tanned leathers was measured.

#### 2.2.2. *Non-pickle process for chromium tanning and conventional chrome tanning*

Based on the tanning properties of SCM, it was introduced starting from bated pelts using the

following steps (offers are on the weight of bated pelts):

| | | | |
|---|---|---|---|
| | Bated pelts | pH 7.0-7.5 | |
| **Pre-tanned** | Float (water, 25°C) | 100% | |
| | SCM | 1- 4% | 60min |
| **Chrome tanning** | Chrome powder | 6% | 120-150min |
| | Sodium formate | 1% | |
| | Sodium bicarbonate | 0.4% | 60min |

Then the latter processes are the same as that of the conventional chrome tanning technology.
As control, the conventional chrome tanning was conducted using traditional pickle process and subsequent tanning with 6% chrome powder.
The bated pelts, pre-tanned crusts were weighted to determine the degree of swelling in float without neutral salts and acid. Ts of the leather both pre-tanned by different amount of SCM and chrome-tanned were measured. Meanwhile, the content of $Cr_2O_3$ in the effluent was examined in different pre-tanning and chrome tanning so as to determine the ratio of absorption of chrome salt.

**2.2.3. Analysis with Scaning electron microscopic (SEM)**
To study the changes in fiber bundles or the complexion of fiber dispersed by different tannges, samples from tanning experiments (including pre-tanning, and chrome tanning) and control crust leathers were cut on the base of the official sampling position[15]. A 200 series scanning electron microscopic (Scan Electric Microscope Japan Electronic co. Ltd) was used for the analysis of fiber weave. The micrographs with different magnification for the cross section of samples were obtained at low vacuum with an accelerating voltage of 20KV. These SEM images were contrasted to show difference and similarity.

**2.2.4. *Dye and fatliquor the crust tanned by non-pickle chrome tanning and control***
The pre-tanned, chrome-tanned crust and the control crust were subjected to standard dyeing and fat-liquoring processes. The dyeing speed was investigated using a spectrometer to measure initial dye absorption and absorption at 30 minutes intervals thereafter. Exactly 1ml of dyeing liquor was diluted to 100ml for these measurements. The dye was a common commercially available black dye, added at 2% based on the weight of tanned crust. A nephelometer was used to measure the absorption of the fatliquor in fatliquoring process. The initial turbidity of the fatliquoring bath was measured on a dilution of 1ml fatliquor bath in 100ml or 50ml. This was repeated every 30 minutes. The fatliquoring agent is MK (TFL company), added at 18% on the weight of tanned crust.

**2.2.5. *Large scale application using non-pickle chrome tanning***
Based on the results of former experiment, 20 pieces of goatskin bated pelts were prepared. A half were pre-tanned by 3% SCM, tanned by 6% chrome powder, and the others were pickled and tanned by conventional method. Then two kinds of crusts tanned by different methods were treated with traditional re-tanning, dyeing, fat-liquoring processes. The tensile strength, elongation and tear strength of the finished leather were measured[11,12].

### 2.2.6. Shrinkage Temperature (Ts) Determination

The shrinkage temperature (Ts) of tanned leather was measured using standard shrinkage meter to show the hydrothermal stability. The shrinkage temperature was measured in water when it was lower than 100ºC, and in glycerol/ water mixture (V/V=3:1) when it was higher than 100ºC. The values reported are an average of three measurements.

## 3. Results and discussion

### 3.1. *Tanning action of SCM*

The results of SCM penetration and Ts of tanned leathers are presented in Table I. Obviously, the pre-tanning agent SCM possesses high penetration rate and can penetrate whole cross of pelts in a wide rang of pH. When the penetration pH is lower than 6.0, SCM has shown no tanning characteristics from Ts listed in Table I. of tanned leathers has no change. When the penetration pH is higher than 6.0, the Ts increases gradually with the increased penetration pH. Even if at high pH, the Ts is lower than 80ºC, which indicates SCM possesses moderate tanning characteristics and do not hinder the penetration of SCM. As a result, SCM can be used to pre-tan bated pelts immediately.

**TABLE I Effect of pH on penetration of SCM and Ts of tanned leathers**

| Penetration pH | Penetration of SCM | Ts/ºC |
|---|---|---|
| 2.5 | Complete | 58 |
| 3.0 | Complete | 58 |
| 3.5 | Complete | 58 |
| 4.0 | Complete | 58 |
| 4.5 | Complete | 58 |
| 5.0 | Complete | 58 |
| 5.5 | Complete | 58 |
| 6.0 | Complete | 60 |
| 6.5 | Complete | 63 |
| 7.0 | Complete | 68 |
| 7.5 | Complete | 73 |
| 8.0 | Complete | 76 |

The effects of the amounts of SCM on Ts from 1% to 10% are listed in Figure 1. Ts increases with the increase of the offer of SCM at the range of zero to 6%. However, Ts does not change obviously when the offer of SCM is over 6%. Because SCM is only used as a kind of pre-tanning agent before chrome tanning, its main function is to disperse collagen fiber and promote the penetration of chrome tanning agent at high pH, the high shrinkage temperature is not the most important thing.

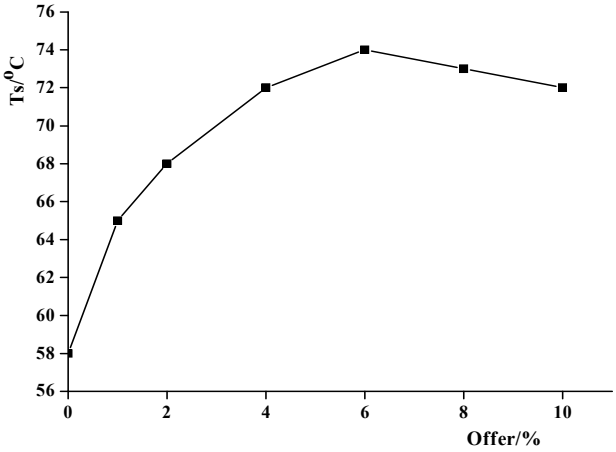



**Figure 1** Effect of SCM offer on the Ts of tanned leathers

3.2.Non-pickle process for Chromium tanning

According to Table II, the shrinkage temperature of SCM-treated pelt increases along with the offer of SCM at a range of 1% to 4%, which indicates that SCM reacts with the collagen and obtain a certain tanning effect. In addition, the weight of the pelts decreased by 4 - 8% through pre-tanning of SCM. It indicates that SCM can prevent the pelts from swelling in float without neutral salts and acids. Therefore SCM can be added into the bated pelts and achieve the effect of tanning the pelts under the condition of non-pickling process.

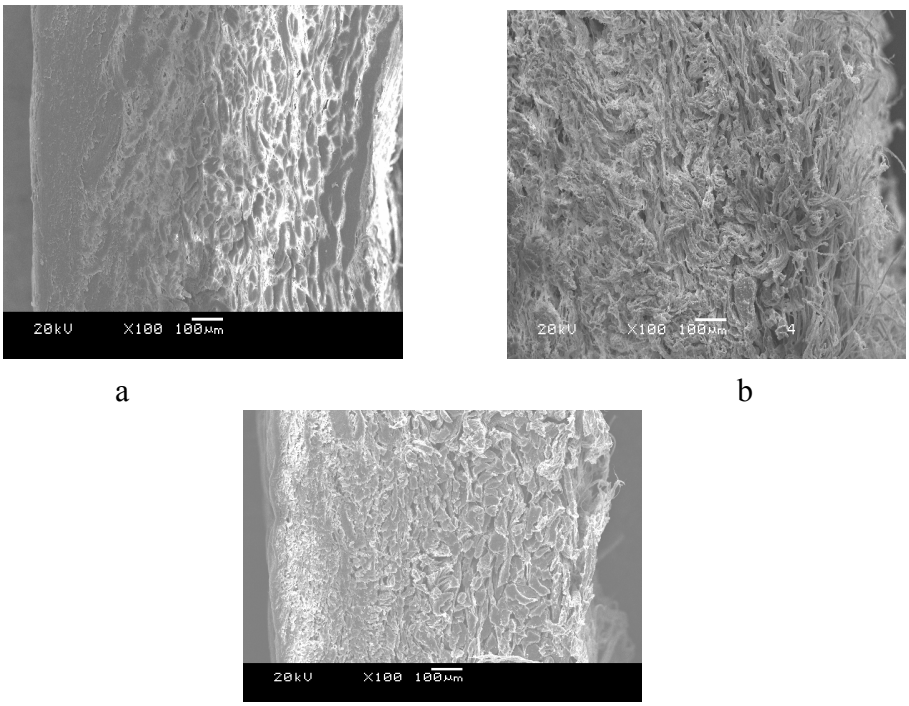
**TABLE II Percent increase in substrate weight as a measure of swelling**

| Regime | $Ts_1$/°C | Increase in weight*/% | $Ts_2$/°C |
|---|---|---|---|
| Traditional pickle | 58 | -35 to -40 | 108 |
| 1% SCM | 67 | -4.0 | 106 |
| 2% SCM | 68 | -7.2 | 109 |
| 3% SCM | 71 | -9.5 | 112 |
| 4% SCM | 72 | -7.8 | 110 |

$Ts_1$/°C: Ts of pickled pelt or pelts pre-tanned by SCM; $Ts_2$/°C: Ts of pelt tanned by chrome powder or pelts pre-tanned by SCM and then tanned by chrome powder

*Percent weight gain or loss before/after picking or pre-tanning

Scanning electron microscopic analysis of SCM, SCM-Chrome tanned leathers and conventional chrome tanned leather were carried out to study the effect of pre-tanning of SCM and Chrome tanning on fiber structure. As presented in Figure 2, the fiber weave of SCM-pretanned leather was dispersed differently and the pore diameter among collagen fibres were changed, which demonstrates that SCM has reacted with the collagen fibre. So the tanning and non-swelling effect of SCM can fix the structure of collage fibres and enlarge bore diameter among collagen fibres, which will be in favor of penetration of chrome tanning agent.




a b c

**Figure 2** Scanning Electron Microscopic photograph (×100 magnification) of the leathers tanned by different tanning agents (a: SCM tanned leathers; b: conventional chrome tanned leathers; c: SCM-Chrome tanned leathers)

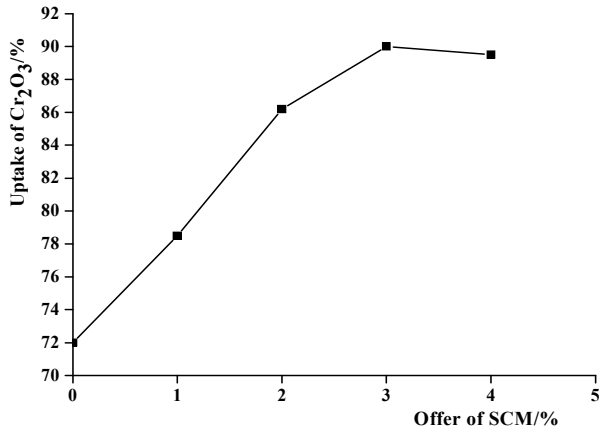



**Figure 3** Effect of SCM offer on the absorption ratio of $Cr_2O_3$

Based on Figure 3, the absorption ratio of $Cr_2O_3$ for pre-tanned pelts are also above that of conventional chrome tanning. Considering the cost and application effect, 2-3% SCM is enough to replace the pickled process.

### 3.3.Comparison of the crust tanned by non-pickle chrome tanning with that tanned by traditional chrome tannin

The results of subsequent dyeing and fat-liquoring process are presented in Figure 4 and Figure 5. The non-pickling process with SCM did not adversely affect the subsequent dyeing and fat-liquoring processes. Chrome tanned crust pre-tanned treated with SCM exhibited the same affinity to fat-liquor and dye as traditional pickled crust did.

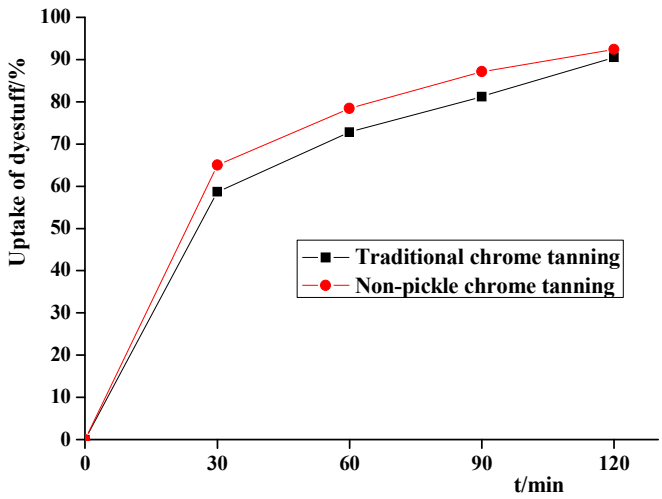



**Figure 4** Uptake of dyestuff under traditional chrome tanning and non-pickle chrome tanning

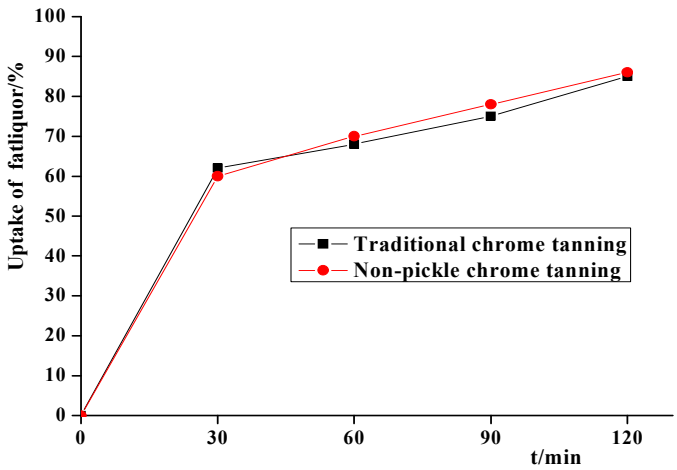



**Figure 5** Uptake of fatliquor under traditional chrome tanning and non-pickle chrome tanning

### 3.4. Results of application of non-pickle chrome tanning

As indicated in Table III, the non-pickling method with SCM provides leather with identical tear strength, elongation to that produced with traditional pickling. The leather produced with SCM has superior tensile strength.

**TABLE III Physical-mechanical properties of tanned leathers**

| Process | Tensile strength /MPa | Elongation /% | Tear strength /N/mm |
|---|---|---|---|
| Traditional techonlogy | 7.8 | 58.2 | 44.0 |
| Non-pickle techonlogy | 10.5 | 58.1 | 46.9 |

## 4. Conclusions

SCM acts as a kind of aliphatic aldehyde, which has certain tanning properties. Ts of the bated pelt tanned by SCM can achieve 76°C when the offer is 6% based on the weight of bated pelt. Importantly, the penetration of SCM in pelts is very easy in a wide range of pH from 2.5 to 8.0. Pre-tanning with 1-4% SCM can prevent the pelts from swelling in float without neutral salts and acids. The tanning and non-swelling effect of SCM can fix the structure of collage fibres and enlarge bore diameter among collagen fibres, which will be in favor of penetration of chrome tanning agent. The shrinkage temperature of pre-tanned, then chrome-tanned crust is on par with the conventional chrome tanned leathers. Meanwhile, the pelts pre-tanned by SCM have higher absorption ratio for chrome tanning agent than that of conventional chrome tanning. Non-pickle chrome tanning technology dose not affect the subsequent dyeing or fat-liquoring process. It imparts tanned leather the identical physical properties to that produced by traditional chrome tanning.

## 5. References

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