PREPARATION AND APPLICATION OF SODIUM SILICATE COMPOUND SWELLING AGENT

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Low modulus sodium silicate was prepared with a polysilicon byproduct-silicon tetrachloride, and used as a swelling agent. Calcium chloride, hydrazine and protease were selected successfully as auxiliaries. Then dosages of the auxiliaries were optimized through the relative weight increase, relative thickness increase, proteoglycan removing and histology study. Based on the auxiliary optimization experiment, a compound swelling agent was prepared and the swelling ability was investigated with a scanning electron microscope and proteoglycan removing test. Finally, the environmental impact of the swelling process was evaluated by total solid of the swelling effluent. The results showed that, when the swelling agent was consisted of 4.0% sodium silicate, 1.0% hydrazine and 0.2% protease, the relative weight increase, relative thickness increase and proteoglycan removing ability reached the highest value, meanwhile fibers were also fully opened. Compared with the traditional liming process, a less total solid value was presented in the swelling effluents. The results could provide a new way for silicon tetrachloride recycling, also provide valuable references for cleaner swelling process.

Keywords: swelling, sodium compound swelling agent, polysilicon

INTRODUCTION

The fiber opening process determines the penetration of chemicals in leather making, also affect the sensory and physical properties of leather. However, some disadvantages of traditional liming are always mentioned by leather chemists, including lower solubility and sludge in liming effluent.

To overcome disadvantages of traditional liming process, many kind of lime-free fiber opening agents was discovered. One of the most famous lime-free swelling agents was sodium silicate. It had been proved that the fiber opening ability of sodium silicate was comparable to that of conventional process. Meanwhile, sodium silicate will not have any negative impact for leather. Compared with the traditional liming process, lower COD, BOD_5 and total solid (TS) data was presented in swelling effluent (Subramani *et al.*, 2008).

In this study, a polysilicon byproduct-silicon tetrachloride was used as a raw material for sodium silicate preparation. Then calcium chloride, hydrazine and protease were selected and optimized successfully as component of silicate compound swelling agent. Fiber opening ability and environmental impact of this compound swelling agent was also studied. The results could provide valuable references for both polysilicon and leather industry.

EXPERIMENTAL

Materials

Wet salted goatskins were selected as raw material. All the chemicals used in leather making process were commercial grade. Silicon tetrachloride was a polysilicon

byproduct collected from Yongxiang polysilicon LLC. The 2709 protease was purchased from Long Kete LLC. Chemicals used for the analysis were all research grade.

Preparation of Sodium Silicate

100g silicon tetrachloride was added into 300g ice water (T≤4°C), and then heated at 120°C to remove the hydrochloric acid. A 10mL water and equal weight sodium hydroxide were added then sodium silicate solution was finally prepared. The properties of this sodium silicate solution were analyzed according to GB/T 4209-2008, the results showed the content of Na_2O and SiO_2 were 12.92% and 15.87% respectively, modulus was 1.27, total dissolved solid was 28.76% and pH was 13.50.

Application of Sodium Silicate and Auxiliaries

Goat skins were soaked conventionally, and soaked skins were unhaired with 1398 neutral protease following a conventional dip and pile method. The unhaired pelts were cut into pieces along the backbone, and then used for the following trials. 4% sodium silicate, X% auxiliary, and 300% water (based on the weight of unhaired pelt) were added into the drum for swelling. The drums were run for 5min per hour in 7 hours then left overnight. The control was prepared following a conventional liming process.

Measurement of Swelling Pelt Weight and Thickness Increase

The relative weight increase was calculated as follows:

$$\frac{w_2 - w_1}{w_1} \times 100\% \tag{1}$$

where w_1 - weight of unhaired pelt, w_2 - weight of swelled pelt.

The relative thickness increase was calculated as follows:

$$\frac{d_2 - d_1}{d_1} \times 100\% \tag{2}$$

where d_1 - thickness of unhaired pelt, d_2 - thickness of swelled pelt.

Scanning Electron Microscope Analysis

The unhaired pelt was cut into two sides along the backbone. One side was prepared with silicate compound swelling agent (4% sodium, 1.0% hydrazine, 0.20% 2709 protease) and then takes as sample. The other side was prepared with a traditional liming process as a control. The samples were then dehydrated with ethyl alcohol and observed with a JSM-5900 scanning electron microscope (Philips Company).

Analysis of Proteoglycans in Waste Liquors

100mL of swelling effluent was filtrated and then analyzed for proteoglycan content with a standard method (Mantle and Allen, 1978).

Analysis of Total Solid Content in Waste Liquors

100mL of swelling effluent was collected and analyzed for total solid (TS) content following the standard procedure (Clesceri *et al.*, 1989).

RESULTS AND DISCUSSION

Optimization of the Kind of Auxiliaries

Table 1. Effect of auxiliaries on the proteoglycan removal

Sample	Sodium silicate-$CaCl_2$	Sodium silicate-hydrazine	Sodium silicate-2709 protease	Sodium silicate	Lime
Proteoglycan removal / (mg/L)	41.67	52.59	55.17	39.12	32.68

The effect of auxiliaries on the proteoglycan removal was shown in Table 1. It indicated that compared with the traditional liming process, sodium silicate swelling agent presented a better proteoglycan removal ability. Furthermore, a significant increase of proteoglycan removal was found while hydrazine and 2709 protease were used as auxiliaries. Furthermore, except the Sodium silicate-$CaCl_2$ group, proteoglycan removal ability was all raised with the addition of auxiliaries. Therefore, hydrazine and protease were selected as auxiliaries of sodium silicate compound swelling agent.

Optimization of the Dosage of Hydrazine

Table 2. Effect of hydrazine dosage on the swelling ability

Dosage of hydrazine / (%)	Relative weight increase / (%)	Relative thickness increase / (%)	Proteoglycan removal / (mg/L)
0.5	58.90	50.44	42.34
1.0	70.26	76.4	56.66
1.5	60.11	60.75	52.39
2.0	64.34	50.58	51.62

Table 2 indicated that the relative weight increase, relative thickness increase and the proteoglycan removal ability were correlated with the dosage of hydrazine. Swelling ability was raised with the dosage increasing until 1.0%. Therefore, 1.0% of hydrazine was selected as auxiliary of sodium silicate compound swelling agent.

Optimization of the Dosage of 2709 Protease

Table 3. Removal of proteoglycan and pelt property of sodium silicate with different dosage of 2709 protease

Dosage of 2709 protease / (%)	Relative weight increase / (%)	Relative thickness increase / (%)	Proteoglycan removal / (mg/L)
0.10	56.33	80.74	49.85
0.15	67.86	78.11	31.59
0.20	70.42	93.33	60.33
0.25	46.15	69.2	49.23

Table 3 indicated the swelling ability of the compound swelling agent was affected by the content of protease. Meanwhile, the highest relative weight increase, relative thickness increase and proteoglycan removal ability was obtained while the content of protease was 0.20%. Therefore, 0.20% of protease was selected as auxiliary of sodium silicate compound swelling agent.

Evaluation of Fiber Opening

Table 4. Proteoglycan removal of pelt

Sample	Lime	Sodium silicate compound swelling agent
Proteoglycan removal/(mg/L)	33.29	57.44

Proteoglycan removal ability of compound swelling agent was shown in table 4. It was evident that the proteoglycan removal ability of compound swelling agent was better than that of control. A better fiber opening ability was obtained with the compound swelling agent (Figure 1).

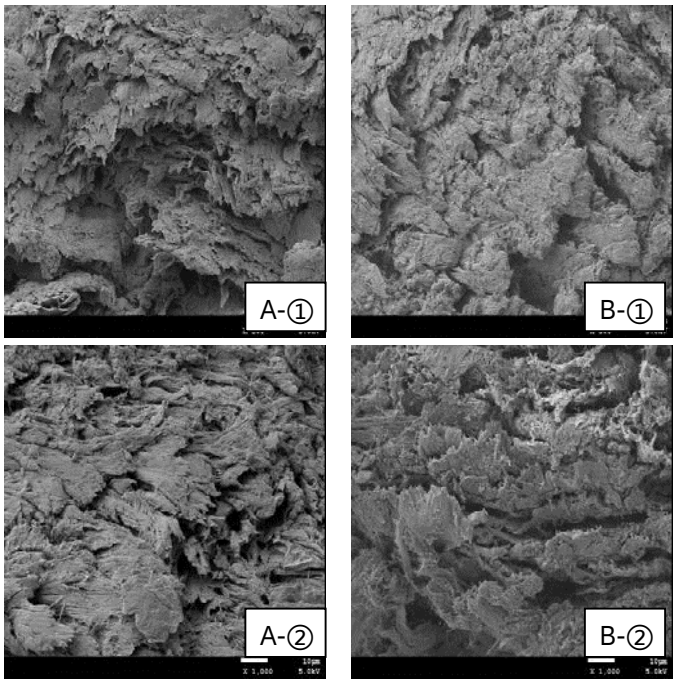

Figure 1. Scanning electron micrographs of swelled pelts (A: sample, B: control; 1:×500, 2:×1000)

Environmental Impact

Table 5. TS in waste fiber opening liquor

Sample	Lime	Sodium silicate compound swelling agent
TS/(g/100mL)	1.5763	1.0547

As shown in Table 5, the TS value of experimental fiber opening process was lower than that of control. The TS loading in experimental fiber opening liquor was decreased by 33% compared with the control process. Lime was the major contributor for TS in the waste liquor in conventional alkali swelling process due to the low solubility of lime. For the experimental fiber opening process, the reduction in TS is mainly due to the elimination of lime. An equivalent spent liquor after fiber opening for experimental and control process was collected and placed for a week. It could be seen clearly that there was a lot of lime residual in control liquor while there was only hair and broken little skin pieces in the experimental liquor. Hence, there was a significant reduction in the TS loading for experimental process.

CONCLUSIONS

A polysilicon byproduct-silicon tetrachloride was used as a raw material for sodium silicate preparation. Meanwhile Calcium chloride, hydrazine and protease were selected as auxiliaries and the content of each auxiliary was optimized. The results showed that, when the swelling agent was consisted of 4.0% sodium silicate, 1.0% hydrazine and 0.2% protease, the relative weight increase, relative thickness increase and proteoglycan removing ability reached the highest value, meanwhile fibers were also fully opened. Compared with the traditional liming process, a less total solid value was presented in the swelling effluents. The results could provide a new way for silicon tetrachloride recycling, also provide valuable reference for cleaner swelling process.

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