PERFORMANCES OF A POLYSILICON BYPRODUCT-SILICON TETRACHLORIDE ON WET BLUE PREPARATION

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Sodium silicate was prepared with a polysilicon byproduct-silicon tetrachloride through hydrolyzation and alkalization. Meanwhile, a new process for wet blue preparation was carried out, including enzyme dehairing, sodium silicate swelling, pickling and semi-chrome tanning. Properties of the wet blue such as mechanical properties, thermal stability and surface color were tested following the standard method. Chrome distribution of the wet blue was investigated with a inductively coupled plasma (ICP). A scanning electron microscope (SEM) and a atomic force microscope (AFM) were also used to illustrate the histological features of the wet blue. Finally, environmental impact of both swelling and tanning process were studied through COD, chrome contention, total solids and turbidity test. The results showed that, the standard requirements for shoe upper leather were met by the wet blue while the dosage of chrome agent was 1.0% (half of the traditional chrome tanning method). Meanwhile, for the wet blue prepared with new method, lighter surface color was presented, less Cr(III) was detected and also equally distributed. More compact fiber bundles were shown on the SEM images. No obvious damages were detected in tropocollagen fiber structures through AFM analysis. Furthermore, compared with the traditional process, COD, total solids and turbidity data of both swelling and tanning effluent provided a lower value. The results could provide a feasible way for silicon tetrachloride recycling, also provide valuable references for clean production of leather industry.

Keywords: silicon tetrachloride; silicon-chrome combination tanning; leather

INTRODUCTION

For recent decades, solar industry has gain a great support from society and has been considered as an important part of clean energy. Production of polysilicon also achieved a considerable scale. It is believed that, about ten tons of silicon tetrachloride will be generated while one ton of polysilicon is produced (Lv *et al.*, 2008). The silicon tetrachloride were highly acidic and corrosive fluid and often causes a serious of environmental problems. Generally, this byproduct can be applied for fumed silica preparation through combustion and hydrolyzation, or for organosilicon manufacture through alcoholysis and hydrolyzation, or even applied in trichlorosilane preparation through Siemens process and reused in polysilicon industry (Barthel *et al.*, 1998). However, it is hard to put the reuse into practice due to the sophisticated requirements of the reactions and the expensive cost of recycling. Therefore, how to deal with this byproduct in a proper way, has became a significant obstacle for the development of solar industry.

Just as with the solar industry, leather chemists are striving for narrowing the problems list which is caused by liming and tanning process. Many cleaner liming and tanning techniques have been developed and widely used so far in leather manufacture. However, there are still some problems for these techniques, such as lime and sulfide cannot be avoided completely, quality of the wet blue was not good as the ones prepared with traditional methods. Such problems always trouble the leather chemists.

In order to solve the problems from both leather and polysilicon industries. A byproduct-silicon tetrachloride obtained from polysilicon industry was used as a raw material. A hydrolyzation and a alkalization process were provided successively. Then, a new wet blue preparation process was carried out. Properties of the wet blue were investigated, environmental impact of this process was also studied. The results will offer a economical way for silicon tetrachloride recycling, also provide valuable evidences for employing sodium silicate into leather industry.

MATERIALS AND METHODS

Preparation of Sodium Silicate

0.5 kg of silicon tetrachloride was slowly added into 2.0kg of water and properly mixed, then hydrolysation reaction was happened following equation (1):

$$SiCl_4+H_2O \rightarrow SiO_2 \cdot xH_2O+HCl \quad (1)$$

After silica gel was formed, it was transferred into an oil bath and heated at 110°C for about 4h. The heating process was stopped until ammonia test showed no hydrochloric gas releasing from the mixture, then silicic acid was prepared.

0.27kg of sodium hydroxide was added into the silicic acid meanwhile stirred at 80°C for 30min, then the alkalization reaction was happened according to equation (2):

$$SiO_2 \cdot xH_2O+NaOH \rightarrow Na_2O \cdot nSiO_2+H_2O \quad (2)$$

Properties of this sodium silicate were tested following the standard methods (Chinese standard: GB/T 4209-2008), and the results showed that in the sodium silicate, content of Na_2O and SiO_2 was 9.77% and 14.28% respectively, modulus was 1.51.

Process for Wet Blue Preparation

Wet salted sheepskins were cut into two sides along the back line. For one side, a enzyme unhairing process(0.25% of 2709 protease, 1.5% of ammonium sulfate, and 0.2% of sodium sulfite, based on salted hide weight), a sodium silicate swelling process (5.0% of sodium silicate, based on unhaired hide weight), a traditional pickling process (pH 2.5), and a semi-chrome tanning process (4.0% chrome tanning agent, based on the pickled hide weight) was carried out successively and taken as sample prepared with new method. The other side was prepared with a traditional leather making process, which was liming (5% of lime), unhairing (3% of lime and 3% of sodium sulphide, based on the wet salted hide), deliming, bating, pickling (pH 2.5) and chrome tanning (8.0% chrome tanning agent) successively and taken as control. Samples for analysis were taken from standard section, meanwhile, effluents from both swelling and chrome tanning process were properly collected.

Analysis of the Wet Blue

Shrinkage temperature, tensile strength and tear strength were tested following the standard method (Chinese standard: QB/T 2713-2005, QB/T 2711-2005), surface color was investigated with a 8200 color master (X-rite, American).

Cr(III) Distribution in the Wet Blue

Even pieces (0.5cm×0.5cm, 0.2cm of thickness) of wet blue were cut from standard section, then the grain side, flesh side and core of the wet blue were separated with a freezing microtome. After a standard wet digestion process, the Cr(III) distribution were investigated with a Optima 2100 ICP-AES instrument (Perkin Elmer, American).

SEM and AFM Analysis

Histology properties of the wet blue were investigated with a JSM-7500F scanning electron microscope (JEOL, Japan) at 5.0kv. Meanwhile, a accessorial energy dispersive spectrometer (EDS) was used to detect the silicon and chrome contention.

Then, the wet blue was sliced from grain side to flesh side with a freezing microtome. Thickness of the slices were 50 um, samples were collected between every 300um. After air dried for 24hs, the character of procollagen was studied with an SPM 9600 atomic force microscope (SHIMADZU, Japan).

Analysis of Spent Liquor

The effluents form both swelling and chrome tanning process were analyzed for CODcr, total solid content and chrome content following standard procedures. Turbidity of the effluents were tested with a WGZ-2000 turbidimeter (scientific equipment co., LTD., China) after diluted for 100 times with distilled water and stilling for 2hrs.

RESULTS AND DISSCUSSIONS

Quality of the Wet Blue

Table 1. Properties of the wet blues

	Shrinkage temperature °C	Tensile strength N/mm^2	Tear strength N/mm	Elongation at break%	Color* L	a	b
New method	105.2±1.5	33.9±1.7	39.5±1.5	35.2±2.0	79.2±0.6	-3.1±0.1	0.5±0.3
Control	113.0±1.0	20.2±1.5	33.6±2.1	32.3±1.8	75.8±1.5	-4.6±0.2	-1.6±0.1
Chinese standard: QB 1873-2004	≥100	≥15	≥35	25-60	-	-	-

* L: "+" indicated a brighter color, "-" indicated a darker color; a: "+" indicated more red, "-" indicated more green; b: "+" indicated more yellow, "-" indicated more blue.

Table 1 indicates that, the mechanical properties and thermal stability of the wet blue presented proper values. Meanwhile quality standard for shoe upper leather were also met. Moreover, compared with the control, better tensile strength and tear strength were obtained by the new method. In addition, because of the reduction of dosage of chrome agent, surface color showed a lighter value. Therefore, in aspect of leather qualities, sodium silicate prepared with silicon tetrachloride can be used in leather industry.

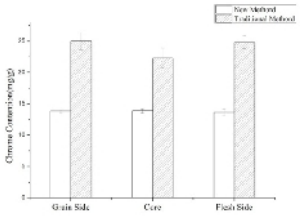

Figure 1. Cr(III) distribution in the wet blue

Figure 1 indicated that, compared with the traditional method, the Cr(III) was more equally distributed in grain side, core and flesh side of the wet blue. Furthermore, due to the reduction of chrome application, chrome contention was obviously less than control.

Histology Properties of the Wet Blue

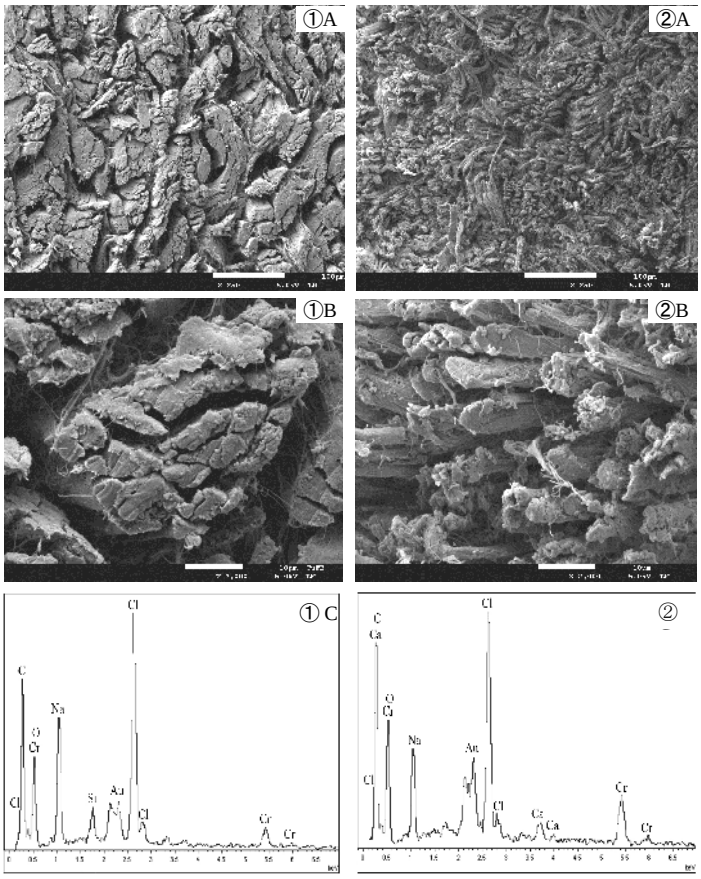

Figure 2. SEM and EDS images of the wet blue (1: wet blue obtained from new method, 2: control A: ×250, B: ×2000, C: EDS spectra)

Figure 2 indicated that, differences between sample and control are obviously existence. For the wet blue obtained from new method, more tightening characters could be discovered. Fiber bundles in sample were heavier and thicker. Meanwhile, lager distances were also shown between these fiber bundles. The sensory property of the wet blue presented a full and compact character. Both silicon and chrome were detected in the wet blue, indicated the sodium silicate was penetrated into the hide through swelling, and still remained after pickling and tanning process.

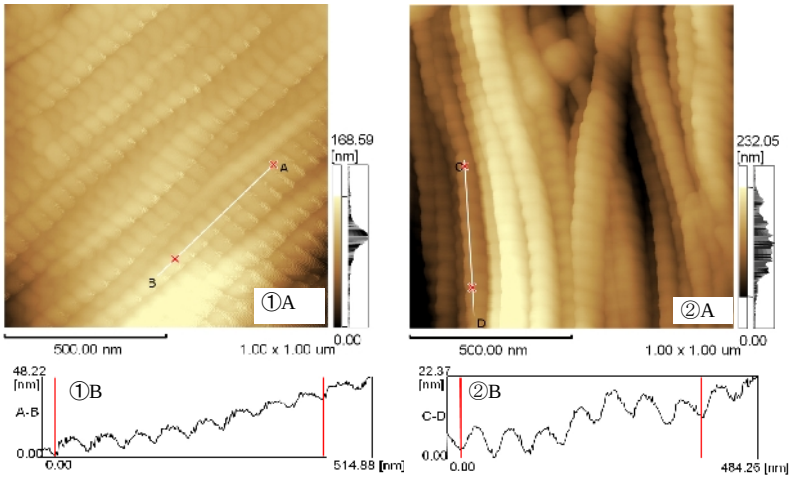

Figure 3. AFM images of the wet blue (1: wet blue obtained from new method, 2: control， A: procollagen images, B， D-period)

Table 2. D-period in each layer in wet blue

	New method (nm)	Control (nm)
First layer (grain side)	56.88±2.31	52.89±0.93
Second layer	56.23±2.34	52.82±1.04
Third layer	52.24±1.05	51.94±0.61
Fourth layer	52.05±0.90	51.18±2.99
Fifth layer (flesh side)	54.76±0.83	55.68±1.03

Based on the Schmitt model, there is a cross striations with 67nm length existed in microfibrils which is also called ‘1/4 stagger’ or ‘D-period’. The cross striations were clearly shown on the AFM images of both sample and control. Furthermore, table 2 shows that, the D-period of microfibrils in each layer of the wet blue were presented a similar value compared with the control. It indicated no obvious collagen structural damages were caused by the new method.

Pollution Load from Swelling and Tanning Process

Table 3. Environmental impact of new method

	Swelling effluent		Chrome tanning effluent	
	New method	Control	New method	Control
Chrome content(mg/L)	--	--	1396±63	3207±91
CODcr(mg/L)	2076±34	2187±62	1634±48	1821±66
TS(mg/L)	2312±44	3068±36	1474±52	2219±94
Turbidity	6.7±0.1	149.7±10.3	3.2±0.6	56.1±7.3

Table 3 shows that compared with traditional leather making process, the environmental influence of the new method were obviously reduced, in terms of lower chemical oxygen demand (CODcr), lower total solid content (TS) and lower turbidity of both swelling and tanning effluents. Reduction of TS and turbidity was contributed to the better solubility of sodium silicate.

But for the tanning effluents, the TS and turbidity difference was mainly due to the tanning effect of silicon agent, which enhanced the mechanical strength of collagen fibers. Therefore, the effluent from tanning process presented a lower TS and turbidity value.

CONCLUSIONS

A polysilicon byproduct-silicon tetrachloride was hydrolyzed and alkalized successfully, and then sodium silicate was properly prepared. A new process for wet blue preparation was carried out. Properties of the wet blue and environmental impact of the new process were also studied. The results showed that, the standard requirements for shoe upper leather were met by the wet blue while the dosage of chrome agent was 4.0% (half of the traditional chrome tanning method). Lighter surface color was also presented. Meanwhile, less Cr(III) were detected and equally distributed in the wet blue. More compact fiber bundles were shown on the SEM images. No obvious damages were detected in tropocollagen fiber structures. Furthermore, compared with the traditional process, COD, total solids and turbidity data of both swelling and tanning effluent provided a lower value. The results could provide a feasible way for silicon tetrachloride recycling. Also provide valuable references for clean production in leather industry.

Acknowledgement

Authors wish to thank to the support from ‘the Fundamental Research Funds for the Central Universities’.

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