Study on the Removing and Preventive of Cr (VI) in Chrome Leather

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Abstract: Several kinds of reducing agents, tannins and antioxidants were used in retanning process as additives for decreasing the formation of Cr(VI) in chrome leather. The application of compound additive agent, which was mixed up with the optimized reducing agent, tannin and antioxidant, was measured. The result showed that the reducing agents had great effect on removing Cr(Ⅵ) in chrome leather, and tannins and antioxidants had great effect on preventing Cr(Ⅵ) formation in chrome leather under the heating and illumination conditions. The complex agent can reduce the Cr (Ⅵ) used as additives in retanning process of chrome leather, and the Cr (Ⅵ) content in crust leather was lower than 2mg/kg under the heating and illumination condition.

Key words: chrome leather; hexavalent chromium; antioxidant; reducing agent; tannin

There are many researches on the reason of Cr (VI) formation and the method of Cr (VI) prevention in chrome leather at home and abroad. However, the problem is still not completely solved. How to eliminate Cr (VI) in chrome leather, How to prevent the Cr (VI) formation in chrome leather in the use and storage, which are still a hot spot in leather researches.

Several kinds of reducing agents, tannins and antioxidants are used in retanning process as additives to decrease the Cr (VI) formation in chrome leather. The compound additive agent is mixed up with the optimization reducing agent, tannin and antioxidant and its application was measured also.

1 Experiment

1.1 The principal experiment reagent

Hydroquinone (analytical pure); anhydrous sodium sulfite (analytical pure); sodium thiosulfate (analytical pure); gallic acid (analytical pure); bayberry tannin extract (industrial product); black wattle extract (industrial product); tara extract (industrial product); the vegetable tannin extract (laboratory-made).

1.2 The principal experiment instrument

Temperature control experiment drum; DHG—9075A type electric heating drying oven; SHZ—82 type Temperature oscillators; 722N type visible spectrophotometer.

1.3 Cr (VI) measurment

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The content of Cr (VI) in the finished leather was tested adopting the measures of IUC-18 announced by chemical analysis committee of international chrome leather technologist and chemist association federation committee.

1.4 The process of leather production

Goat wet blue→degreasing→chrome retanning→neutralizing→retanning→dyeing→fat liquoring→fixing, using technological process of goatskin garment leather to treat blue leather. The fat-liquoring was used by synthetic fatliquoring, sulfited fish oil and compound fat-liquoring agent.

1.5 Experiment Contents

1.5.1 The prevention and treatment of different reductants to Cr（Ⅵ）on chrome leather

Using the process of goatskin garment leather manufacture in 1.3, 2.5% dosage (take wet blue as basis weight）of sodium thiosulfate, sodium sulfite and sodium bisulfite was added in retanning process. Then the crust leather was treated with natural drying， heating or lighting separately. In the end the content of Cr(Ⅵ) was measured and the quality and impression of crust leather was evaluated.

1.5.2 Study on the prevention and treatment effects of different tannin extract on Cr（Ⅵ）in chrome leather

Using the process of goatskin garment leather manufacture in 1.3, 2.5% dosage (take wet blue as basis weight）of bayberry extract, mimosa extract and tara extract was added in retanning process. Then the crust leather was treated with natural drying， heating or lighting separately. In the end the content of Cr(Ⅵ) was measured and the quality and impression of crust leather was evaluated.

1.5.3 Study on the prevention and treatment effects of different antioxidant on Cr（Ⅵ）in chrome leather

Using the process of goatskin garment leather manufacture in 1.3, 2.5% dosage (take wet blue as basis weight）of bayberry extract, mimosa extract and tara extract was added in retanning process. Then the crust leather was treated with natural drying， heating or lighting separately. In the end the content of Cr(Ⅵ) was measured and the quality and impression of crust leather was evaluated.

1.5.4 Study on the prevention and treatment effects of compound additive on Cr（Ⅵ）in chrome leather

Based on the results from measurement 1.5.1 to 1.5.3, a kind of compound additive was mixed by the dispersants with optimized reductants, tannins, antioxidants. Using the process of goatskin garment leather manufacture in 1.3, 0.5%, 1.0%, 1.5%, 2.0% and 2.5% dosage (take wet blue as basis weight）of compound additive was added in retanning process. Then the crust leather was treated with natural drying， heating or lighting separately. In the end the content of Cr(Ⅵ) was measured and the quality and impression of crust leather was evaluated.

2 Results and Discussion

2.1 The prevention and treatment of different reductants to Cr（VI）on chrome leather

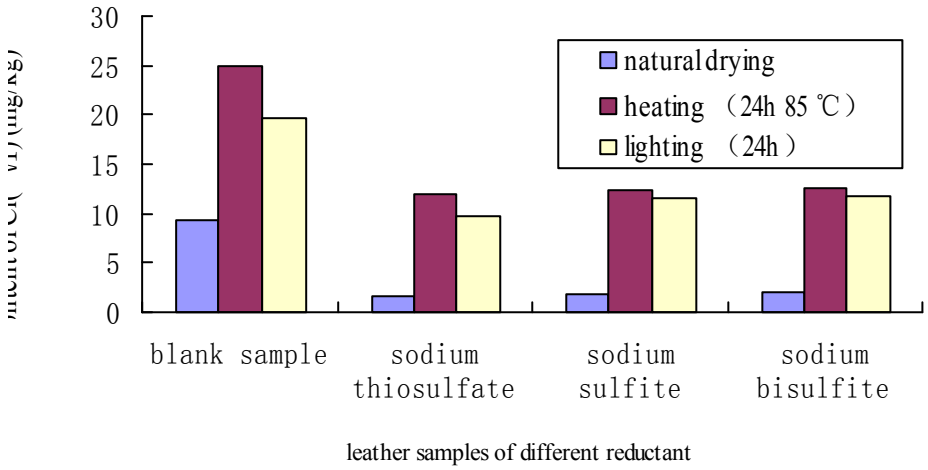

Fig.1 The prevention effective of different reductants to Cr(VI) on chrome leather

The results were shown in Fig.1. The content of Cr(VI) in blank sample was much higher than the sample treated by different reductants and the content of Cr(VI) increased obviously after heating or lighting also. The content of Cr(VI) in chrome leather decreased significantly when the sample was retanning by different kinds of reductants, and also the samples after heating or lighting. It indicated that the content of Cr(VI) in chrome leather could be reduced into Cr(III), and the $Na_2S_2O_3$ was best in the application effect of reductants.

The content of Cr(VI) in chrome leather could not be reduced completely with a single reductant in the paper measurement. And it was more than 2mg/kg which was higher than correlative standard. So the chrome leather with single reductant could not eliminated Cr(VI) completely, and could not inhibition Cr(VI) formation during heating or lighting also.

2.2The prevention and treatment of different tannins to Cr（VI）on chrome leather

The results were shown in Fig.2:

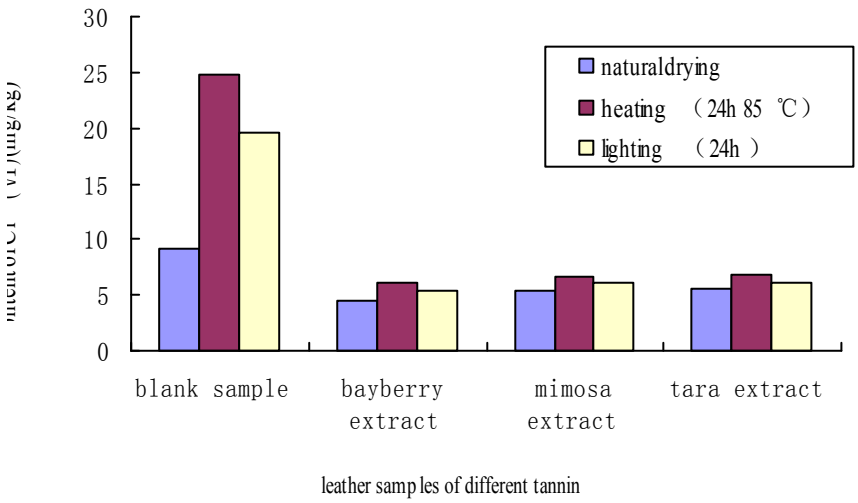

Fig.2 The prevention effective of tannins to Cr(Ⅵ) in chrome leather

In the Fig.2, the result showed that the content of Cr(Ⅵ) in blank sample was much higher than the samples treated by different tannins, and the content of Cr(Ⅵ) increased obviously after heating or lighting also. The content of Cr(Ⅵ) in chrome leather decreased significantly when the sample was retanning by different kinds of tannins, and also the samples after heating or lighting. It indicated that the content of Cr(Ⅵ) in chrome leather could be prevented effectively with some kinds of tannins, and the bayberry extract was best in the application effect of tannins. From the quality and impression access of crust leather, the chrome leather with vegetable extract retanning would be feeling hard. And the chrome leather with bayberry extract and mimosa extract retanning had the deep color. So it had certain limitation in direct using tannins to prevent Cr(Ⅵ) in chrome leather.

The content of Cr(Ⅵ) in chrome leather could not be prevented completely with only tannin in the paper measurement. And it was more than 2mg/kg which was higher than correlative standard. So the chrome leather with single tannin retanning could not eliminated Cr(Ⅵ) completely, and could not inhibition Cr(Ⅵ) formation during heating or lighting also.

Compared with Fig.1, reductant could eliminate the Cr(Ⅵ) exist in chrome leather effective, and tannins could prevent the Cr(Ⅵ) formation in chrome leather after heating or lighting effective. The fatliquor in chrome leather contained unsaturated double bond, which made the autoxidation reaction occurred easily and formed peroxy radical. This process could provide favorable condition for Cr(Ⅲ) oxidized into Cr(Ⅵ). But the tannin with phenolic hydroxyl could remove peroxy radical and inhibit the chain reaction of Cr(Ⅲ) oxidized into Cr(Ⅵ). So the content of Cr(Ⅵ) in chrome leather with tannin treating were not increased significantly even after lighting or heating.

2.3 The prevention and treatment effect of different antioxidant to Cr（Ⅵ）on chrome leather

The results were shown in Fig.3.

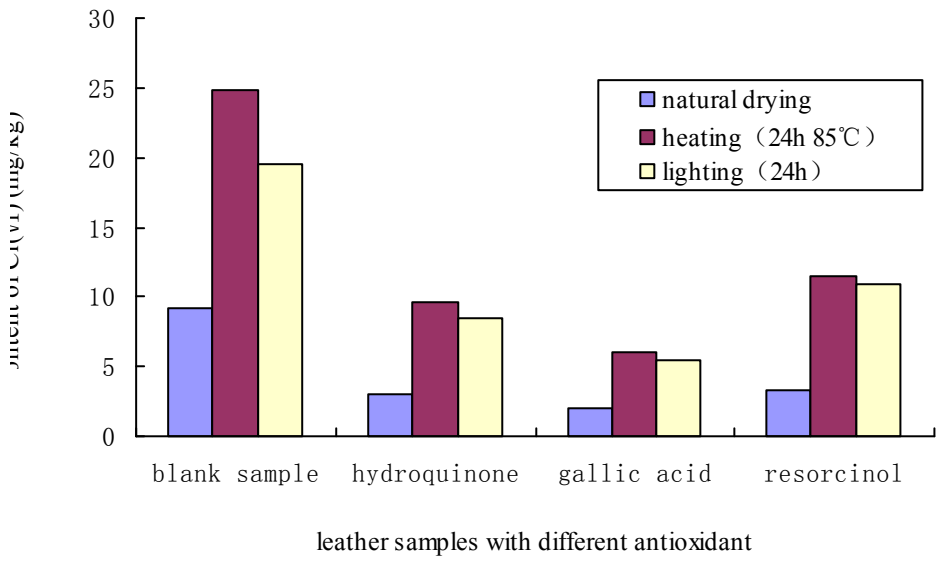

Fig.3 The effective of prevention Cr（Ⅵ）in chrome leather of different antioxidants

In the Fig.3, the result showed that the content of Cr(Ⅵ) in blank sample was much higher than the samples treated by different antioxidants, and the content of Cr(Ⅵ) increased obviously after heating or lighting also. The content of Cr(Ⅵ) in chrome leather decreased significantly when the sample was retanning by different kinds of antioxidants, and also the samples after heating or lighting. It indicated that the content of Cr(Ⅵ) in chrome leather could be prevented effectively with some kinds of antioxidants, and the gallic acid was best in the application effect of antioxidants.

The content of Cr(Ⅵ) in chrome leather could not be prevented completely with a single antioxidant in the paper measurement. And it was more than 2mg/kg which was higher than correlative standard. So the chrome leather with single antioxidant retanning could not eliminated Cr(Ⅵ) completely, and could not inhibition Cr(Ⅵ) formation during heating or lighting also.

Compared with Fig.1, reductant could eliminate the Cr(Ⅵ) exist in chrome leather effective, and tannins could prevent the Cr(Ⅵ) formation in chrome leather after heating or lighting effective. Compared with Fig.2, the prevention mechanism and effect of antioxidant and tannin to Cr(Ⅵ) in chrome leather were similar. From the quality and impression access of crust leather, the color and feeling of goat chrome leather with reductant retanning was same with it without reductant retanning. So the reductant had more advantage in application on Cr(Ⅵ) prevention.

2.4 The prevention and treatment effects of compound additive to Cr(Ⅵ) on chrome leather

The results were shown in Tab.1.

From the Tab.1, the result showed that the compound additive could prevent Cr(Ⅵ) formation effectively in chrome leather. When the content of compound additive reached 2.5%(take wet blue as basis weight), the content of Cr(Ⅵ) in chrome leather was lower than 2mg/kg whenever heating or

lighting, which was under the national standard.

Tab.1 The effect of the different content of compound additive to prevent Cr（Ⅵ）on chrome leather

Content of extract	content of Cr(Ⅵ)/(mg/kg)		
	natural drying	lighting 24h	heating 24h 85℃
0%	9.23	24.86	19.55
0.5%	6.98	22.35	16.32
1.0%	3.45	15.34	13.21
1.5%	2.87	11.02	9.66
2.0%	1.63	3.42	3.05
2.5%	0	1.68	1.52

3 Conclusions

Reducing agents, tannins and antioxidants could prevent and decrease Cr(Ⅵ) formation in chrome leather. The reducing agents had better effect on Cr(Ⅵ) removing in chrome leather, and tannins and antioxidants had the better effect on the prevention of Cr(Ⅲ) oxidized to Cr(Ⅵ) in chrome leather by heating or lighting. It was impossible to get the Cr(Ⅵ) content below national standard by the one of reductants, tannins or antioxidants in chrome leather. The process of Cr(Ⅲ) oxidized to Cr(Ⅵ) in chrome leather could be prevented completely by the retanning with compound accitives from reasonable choosing of reductants, tannins and antioxidants. In the paper, the content of Cr(Ⅵ) in chrome leather was lower than the national standard 2mg/kg whenever heating or lighting, with the retanning of preventive agent, which was complex with the optimization reducing agent， tannin, antioxidant and decentralized agent and 2.5% (take wet blue as basis weight) using.

Acknowledge

This research was supported by National Nature Science Foundation of P.R.China (Item Number: 20676076).

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