

# Preparation and Application of Cr-Fe Tanning Agent Reduced by Chrome Shavings and Iron(II)

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**Abstract:** In order to minimize chromium consumption and chrome recycling in tanning industry, a chromium-iron (Cr-Fe) tanning agent was prepared using chrome shavings in combination with  $\text{Fe}^{2+}$  as reducing agent. By observing the influence of Cr/Fe ratios and basicity on the storage stability and tanning properties of the prepared tanning agents, synthesis methods were selected and improved. In summary, a series of novel organic Cr-Fe tanning agents were prepared i) with the Cr/Fe ratios being 1.5:1 and 2:1, ii) masked by tartrate and citrate and iii) adjusted to different basicity. The aging stability, heat stability and physical-mechanical properties of the crust leather tanned with i) new Cr-Fe tanning agent, ii) a conventional chrome tanning agent and iii) iron sulfate were compared by subjecting to the aging tests, i.e., hot-air ageing, wet-heat ageing, hot-oxygen, DSC analysis and physical-mechanical. Chromium content and nitrogen content in the spent tanning liquor were measured with atomic absorption spectrometry and Kjeldahl determination to compare the developed Cr-Fe tanning agents and the conventional chromitan. In conclusion, the study shows that it is feasible to prepare Cr-Fe tanning agent using chrome shavings and ferrous sulfate as a reductant. The properties of the leather with the new Cr-Fe tanning agents were comparable to the conventional chrome tanned leather. However, the nitrogen content of the spent liquor with the Cr-Fe tanning agents was higher than the conventional chrome-tanning effluent due to the presence of protein intermediates.

**Key words:** chrome shavings; iron; reductant; Cr-Fe tanning agents; heterocomplex; ageing stability

## 1 Introduction

In recent years, iron tannage has once again attracted the attention of researchers. As an eco-friendly tanning agent, iron tannage offers unique advantages, when considering today's environmental requirements. In Platon and Gaidu's work, <sup>1-4</sup> heterocomplexes, like Cr-Fe, Cr-Al-Fe, Cr-Fe-Zr, were prepared, and they were structurally more stable than their homo-complexes. Thanikaivelan and Rao<sup>5</sup> also developed a novel chrome-iron tanning agent that was able to replace commonly used chrome salts. In this work, various organic acids were applied as masking agents to improve the stability of the newly developed products. It was found that the prepared chrom(ium)-iron tanning agent could be used as a chrome saver tannage. As a new technique to producing chrome-free car seat leather, Kleban of Bayer Company<sup>6</sup> used special masking agents to pretreat the pickled hides, basic iron sulphate for tanning and newly-developed syntans for retanning. The leathers would have pleasing aesthetics, good color-fastness and good physical-mechanical properties.

Use of chrome shavings as a reductant to prepare chrome tanning agent has long been known.

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However, the prevailing views upon this approach are negative, because the reaction are very complex giving rise to the formation of many intermediate organics. In spite of this, recently, in Rao's work, <sup>7-8</sup> chrome shavings were used alone, or 1:1 with molasses as chromium reductant. Products obtained in this way were found to have tanning properties similar to the conventional chrome tanning agent, as far as the crust properties and the exhaustion of spent tan liquors were concerned. Rao's work supported the feasibility of using chrome shavings as a reductant.

As a result of earlier work, <sup>9</sup> we found that if properly controlled, the reducing reaction of chrome shavings could be consistent and reproducible. As it is well known, that iron (II) has strong reducibility.

$$\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$$

Further to study of using chrome shavings as reducing agent, iron sulfate was used to replace sodium bisulfite. This would not only reduce the residual Cr (VI), a crucial point relating to the reaction behavior of shavings and the amount of intermediate organic substances obtained, but also introduce nontoxic iron (III) as a tanning agent, thereby minimizing the potential of chromium pollution.

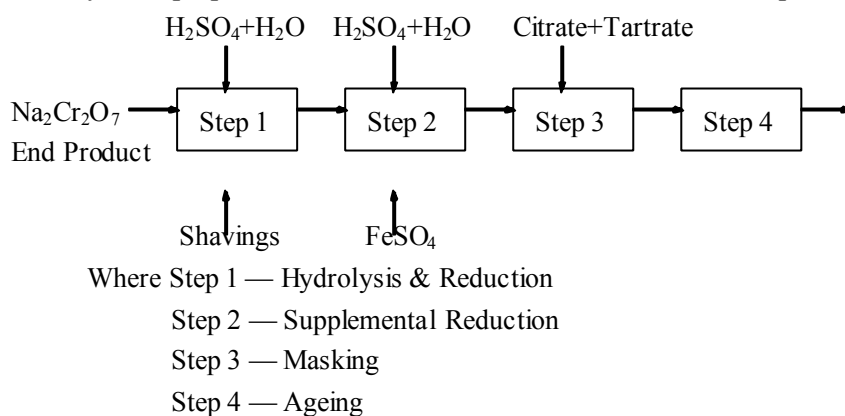
## 2 Experimental

### 2.1 Materials

Cowhide chrome shavings were from a domestic tannery (China). The moisture, volatiles and ash content of chrome shavings were determined using the international standardize methodology. Iron sulphate, Tartrate, Citrate were of analytical reagent grade.

### 2.2 Preparation of Cr-Fe tanning agent

Following the procedure shown in Figure 1, two products with 1.5:1 and 2:1 Cr/Fe ratio and 20% basicity were prepared and named as Product A and Product B respectively.



**Fig. 1 Technical process for preparing Cr-Fe tanning agent**

### 2.3 Tanning trials

The tanning process for Cr-Fe tanning agent was similar to the conventional chrome tannage. Meanwhile, chrome tannage and iron tannage were performed with the same metal oxide offer. 1.6% sodium tartrate and 0.7% sodium citrate were used as the masking agents in the iron tannage.

### 2.4 Analysis of Cr-Fe tanning agent

#### 2.4.1 Determination of Cr-Fe content

Cr-Fe content in the new tanning agents were measured with sodium peroxide.

#### 2.4.2 Determination of basicity

The basicity of the new tanning agents was determined with the oxalate method.

### 2.5 Property tests of curst leathers

All the samples for property tests were cut according to the official requirements.

### **2.5.1 Physical and mechanical properties of crusts**

The physical and mechanical properties of the crust leathers were tested according to the national standards required for leather products.

### **2.5.2 Differential Scanning Calorimetry (DSC) of crusts**

DSC was performed at the rate of 10 °C/min or 5 °C/min.

### **2.5.3 Ageing qualities of crusts**

The ageing tests were carried out as the literature<sup>9</sup>, including (1) hot air ageing; (2) hydrothermal ageing; (3) hot oxygen ageing.

## **2.6 Analysis of the spent tanning liquor**

### **2.6.1 Determination of chromium and iron content**

The chromium content and the iron content in the spent liquor were analyzed with the atomic absorption spectrometry.

### **2.6.2 Determination of total nitrogen content**

To show the influence of the organics in Cr-Fe tanning agent on the spent liquor, total nitrogen content was determined following the Kjeldahl process.

## **3 Results and Discussion**

### **3.1 Optimization for Cr/Fe ratio, basicity and organic ligands**

(1) Selection of Cr/Fe ratio: Cr-Fe tanning agents with Cr/Fe ratio of 1:1, 1.5:1, 2:1, 3:1 and basicity of 20% and 25% were applied to the tanning trials. The results showed that the products of 2:1 or 1.5:1 Cr/Fe ratio were the most desired.

(2) Selection of basicity:

**Tab. 1 Relationship between basicity and storage stability**

Cr : Fe		Basicity			
2 : 1	15%	18%	20%	23% ↓ <sup>a</sup>	25% ↓
1.5 : 1	15%	18%	20%	23% ↓	25% ↓

<sup>a</sup> ↓ means precipitation produced in storage.

From Tab. 1, to avoid precipitating in the storage period, the basicity should not exceed 20%, as the pH at this basicity had lowered to 1.8. And, 20% was selected as the basicity of the products.

(3) Selection of masking agents: Masked by sodium tartrate or citrate, the Cr-Fe tan liquors were analyzed for the precipitation pH and the UV-visible spectroscopy.

The spectroscopy indicated that sodium tartrate had higher influence on the complex structure. On the other hand, the result showed that with the increase of the ligand's amount, the precipitation pH rose, while sodium citrate showed more obvious effect and also cost lower price. So, the two organic ligands were mixed as shown in Tab. 2.

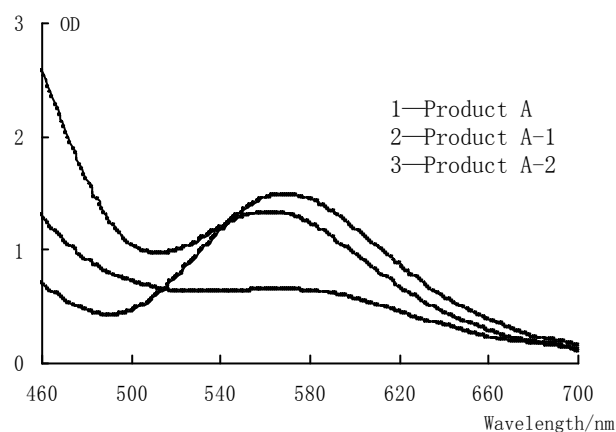
**Tab. 2 Relationship between mixture ratio of masking agents and precipitation pH**

Cr : Fe = 1.5 : 1		Cr : Fe = 2 : 1	
M <sub>2</sub> O <sub>3</sub> :Tartrate:Citrate	Precipitation pH	M <sub>2</sub> O <sub>3</sub> :Tartrate:Citrate	Precipitation pH
1 : 0.6 : 0.1	5.0	1 : 0.4 : 0.1	5.3

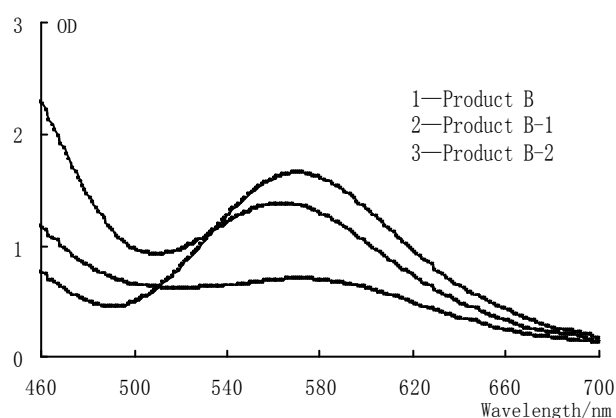
### 3.2 Analysis result of Cr-Fe tanning agents

#### 3.2.1 UV-visible spectroscopy

From Fig. 2, Fig.3 and Tab. 3, first, comparing the absorption curves of Product A & A-1 and Product B & B-1, not only with the peak position and the peak value, but also with the curve shape, obvious changes occurred. Product A or B had sharp peaks, while Product A-1 or B-1 had very flat peaks. This indicated that the organic ligands changed the inner structure of the complex, which also coincided with the pH potentiometric titration analysis. In addition, compared with Product A-1 or B-1, hypsochromic shift happened to the peak of Product A or B with the shift value being 6nm or 10nm. This showed that the organic ligands had formed bridge bonds or cyclic structures with the central ions. Second, comparing the spectral absorption curves of Product A & A-2, Product B & B-2, the peak shifted 9nm or 8nm, which demonstrated that the change of the complex structures was caused not only by the complexation with the organic ligands, but also the formation of a new Cr-Fe heterocomplex.



**Fig. 2 Spectral absorption curves of product A, A-1 & A-2**



**Fig. 3 Spectral absorption curves of product B, B-1 & B-2**

**Tab. 3 Characteristic peaks of different products**

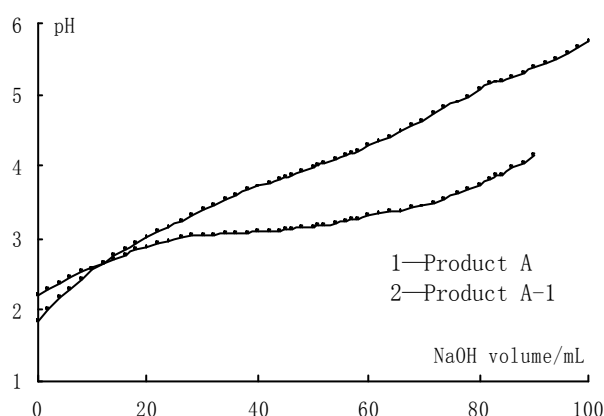
Product	A	A-1	A-2	B	B-1	B-2
Cr : Fe	1.5 : 1	1.5 : 1	no Fe	2 : 1	2 : 1	no Fe
Masked or not	masked	unmasked	masked	masked	unmasked	masked
Wavelength/nm	561	567	570	564	574	572

Absorbance	1.335	0.656	1.489	1.379	0.700	1.651
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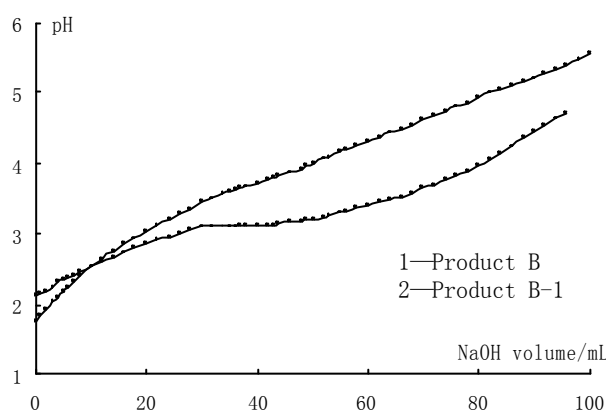
### 3.2.2 pH potentiometric titration

From Fig. 4, Fig. 5 and Tab 4, the titration curve shapes of Product A or B were totally different from Product A-1 or B-1 and the precipitation pH of the former went higher. This indicated that with the addition of the organic ligands, the complex structure had been changed and the alkali resistance had been improved.

To sum up, the pH potentiometric titration showed that the organic ligands had entered the inner sphere of Cr-Fe complexes and thus found the basis to act as bridging ligand to combine Cr and Fe into heterocomplexes.



**Fig. 4 pH potentiometric titration curves of Product A & A-1**



**Fig. 5 pH potentiometric titration curves of Product B & B-1**

**Tab. 4 Comparison of the pH potentiometric titration results**

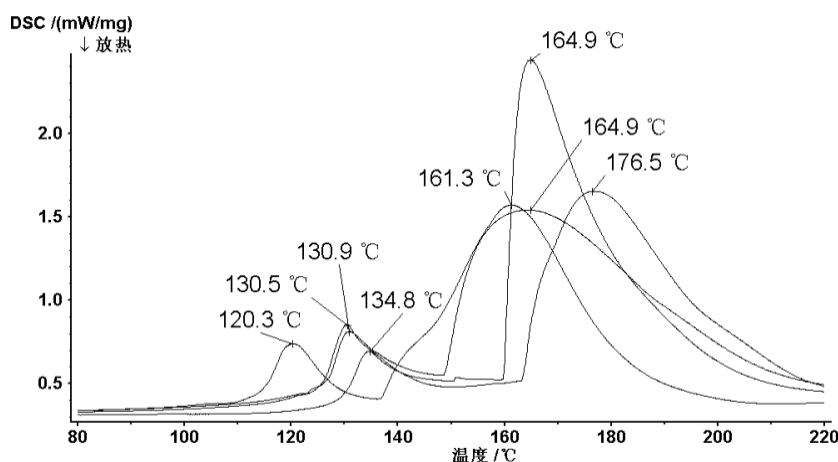
Product	Initial pH value	At the precipitation point	
		pH value	Consumed alkali volume /mL
A	1.85	5.26	86
A-1	2.20	3.68	78
B	1.75	5.28	92
B-1	2.11	4.14	84

### 3.3 Result of crust property tests

From Tab. 5, compared with chrome tanned leather, leathers tanned by Product A or B showed better properties except for a slightly lower water vapor permeability but the air permeability was excellent. Therefore, as far as the crust properties were concerned, the requirement for chrome less tannage had been fulfilled together with a good hygienic quality.

**Tab. 5 Physical and mechanical properties of crust leathers**

Leather tanned by	Tensile strength/ N/mm <sup>2</sup>	Elongation under specified load/%	Break elongation / %	Tear strength/ N/mm	Break load /kg	Break high /mm	Water vapor permeability/ mg/(10cm <sup>2</sup> ·24h)	Air permeability/ mL/(cm <sup>2</sup> ·h)	Substance increase/%
Chromium	15.4	17	40	67.9	10	9.8	271.2	7.26	25.4
Iron	12.3	15	35	52.2	3	9.4	258.1	15.70	32.3
Product A	24.2	18	41	83.3	18	11.6	245.9	67.25	33.3
Product B	21.4	14	41	84.6	21	12.0	230.5	50.57	42.3



**Fig. 6 Differential scanning calorimetric plot at the rate of 10°C/min**

**Tab. 6 DSC analyses of crust leathers(at the rate of 10°C/min)**

Leather tanned by	Chromium	Iron	Product A	Product B
First peak	134.8	120.3	130.5	130.9
Second peak	176.5	161.3	164.9	164.9

As shown in Fig. 6 and Tab. 6, the first peak indicated the bonds between the collagen fibers were weakened or broken; the second peak indicated the fibers were totally disintegrated.

From Tab. 6, at the same heating rate, the sequences from high temperature to low temperature at the first peak, which indicated the heat stability of the crusts, were as follows: Chrome tanned leather > Crust B ≈ Crust A > Iron tanned leather. Meanwhile, to the temperature difference at the first peak comparing with chrome tanned leather, only 4°C showed for Crust A or B, while 10°C-14°C for iron tanned leather.

Therefore, despite reduced chrome amount, the heat stability of Crust A or B could still match the chrome tanned leather.

**Tab. 7 Ageing qualities of crust leathers <sup>a</sup>**

Index	Leather tanned by	Original	After air aging	Dry heat stability	After hydrothermal aging	Hydrothermal stability	After oxygen aging	Hot oxygen stability
Tensile strength/ N/mm <sup>2</sup>	Chromium	16.7	18.0	107.8%	12.2	73.1%	13.0	84.2%
	Iron	13.4	18.7	139.6%	cracked	cracked	9.3	75.6%
	Product A	17.3	18.2	105.2%	12.0	69.4%	19.2	79.4%
	Product B	20.8	20.3	97.6%	15.2	73.1%	24.4	114.1%
Break elongation/ %	Chromium	48	42	88%	48	100%	35	73%
	Iron	36	43	119%	cracked	cracked	34	94%
	Product A	49	49	100%	48	98%	54	110%
	Product B	42	43	102%	40	95%	37	88%
Tear strength/ N/mm	Chromium	67.9	64.5	95.0%	61.1	90.0%	47.5	70.0%
	Iron	52.2	67.2	128.7%	cracked	cracked	35.6	68.2%
	Product A	83.3	90.2	108.3%	81.2	97.5%	85.4	102.5%
	Product B	84.6	80.1	94.7%	73.2	86.5%	86.0	101.7%
Ts <sup>b</sup> /°C	Chromium	114	103	-11 °C	115	+1 °C	106	-8 °C
	Iron	96	89	-7 °C	cracked	cracked	84	-12 °C
	Product A	108	103	-5 °C	106	-2 °C	98	-10 °C
	Product B	105	97	-8 °C	105	0	97	-8 °C
Softness <sup>c</sup> / mm	Chromium	4.5	3.6	80%	3.8	84%	3.9	87%
	Iron	4.9	4.2	86%	cracked	cracked	3.9	80%
	Product A	4.2	3.4	81%	3.2	76%	3.7	88%
	Product B	3.5	3.4	97%	3.2	91%	3.2	91%

<sup>a</sup> Ageing stability= $P_2/P_1 \times 100\%$ , where  $P_1$  and  $P_2$  refer to the property before and after ageing;

<sup>b</sup> The shrinkage temperatures were measured in glycerin bath.

<sup>c</sup> The softness was measured by the ST-300 Leather Softness Measuring Instrument.

From Tab. 7, after hot air ageing, the properties of Crust A and B did not change much. According to the research of Hummel and Germann on the correlation between natural and artificial ageing, hot air ageing under such conditions was equal to the effect of around one-year natural ageing. Hence, leathers tanned by Product A or B would still be in good condition after one year's storage. To hydrothermal ageing, iron tanned leather couldn't stand such long-time steaming and cracked; while the property of Crust A and B also weakened, the changing degree was close to the chrome tanned leather. To hot oxygen ageing, the tear strength of Crust A and B was nearly unchanged while obvious decline occurred to the chrome tanned and iron tanned leather, and the stability in other properties of Crust A and B were comparable to the chrome tanned leather. Yet comparing Crust A and Crust B, the latter showed stronger hot oxygen fastness.

To sum up, compared with the chrome tanned and iron tanned leather, Crust A and B had greatly improved the poor ageing qualities of iron tanned leather. The age stability could be comparable with chrome tanned leather and even stronger under hot oxygen ageing conditions.

### **3.4 Spent tan liquor analysis**

From Tab. 8, the chrome exhaustion of the prepared products only achieved the conventional level of 1g/L approx. The total nitrogen content was higher than the chrome-tan waste liquor, owing to the existence of the protein intermediates.

**Tab. 8 Analyses of the spent tanning liquors**

Liquor source	Cr <sub>2</sub> O <sub>3</sub> /g/L	Fe <sub>2</sub> O <sub>3</sub> /g/L	Total nitrogen/mg/L
Chromium	Not tested	/	164.3
Product A	0.76	0.88	373.9
Product B	1.19	0.65	467.6

#### 4 Conclusions

(1) It is feasible to prepare Cr-Fe tanning agent using chrome shavings as the main reductant and iron (II) sulphate as the supplemental reductant.

(2) The formation of the Cr-Fe heterocomplexes is bridged by the organic ligands, which makes it possible to replace partial chrome with iron without losing the leather qualities.

(3) With the same metal oxide offer, the Cr-Fe tanned leathers are comparable to the chrome tanned leather in the physical and mechanical properties and ageing stability. But the total nitrogen content of the spent tan liquor is higher than conventional chrome-tan waste, owing to the existence of the protein intermediates.

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