Preparation of Chrome Liquor Using Chrome Shavings as Reducing Agent

by

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Abstract

Chrome-tanned waste produced in the leather industry would be a heavy burden to the ecological environment if stored without treatment. However, the collagen protein and chrome in leather shavings are both very precious resources and can be recycled. In this study, the high protein containing chrome shavings were utilized for the reduction of chromium(VI) in the preparation of chrome liquor. In the preliminary research, a practical synthesis method using chrome shavings as reducing agent was developed. To investigate the factors influencing the reaction process such as the quantity of sulfuric acid and shavings, reduction time and temperature, etc., various experiments were carried out including orthogonal tests, homogeneous tests, and single-factor tests. Data processing methods were adopted including range analysis, variance analysis, and regression analysis. Mathematical models were built to reflect the relationship of the quantity of sulfuric acid, shavings, and the reduction time to the basicity of chrome liquor and the percent reduction of sodium dichromate by shavings.

Introduction

Processing of leather and leather products will generate a large quantity of chrome containing solid waste, including chrome shavings, which are produced in the splitting and shaving process of wet blue leather. Dried chrome shavings contain 3% - 6% chromium oxide and around 90% collagen protein. However, in leather production, only 30% - 50% of the substances in raw hides and skins are turned into finished leather, the rest converted into solid waste. If they are abandoned, they will cause environmental pollution as well as a waste of natural resources. The annual yield of chrome shavings in China alone comes to more than 300 thousand tons. If these waste materials are recovered and reused, however, they can become valuable to us. Presently, chrome shavings are mostly utilized in the following ways: extracting gelatin or collagen protein;[1-8] making leather addition agents for retanning, filling, fatliquoring;[9-13] producing reclaimed leather;[14,15] used as fertilizer or animal feedstuff;[16,17] preparing surfactants;[18] extracting chrome from burned ashes;[19] etc. Many of these methods also contain a dechroming process where chromium(III) is precipitated as chrome cake or oxidized into chromium(VI) and isolated from the protein fractions.

In this study, chrome shavings are used as reducing agent for preparing chrome liquor, instead of glucose or sulfur dioxide that is applied in the conventional method. The idea is based upon the closed substance cycle concept, that the chrome in shavings again becomes a part of the newly-made chrome tanning agents, the hydrolysates and oxydates of shavings are filled into leather, thereby comprising the tanning superiority of chrome and the filling property of polypeptide into one whole. What comes from leather will finally turn back into leather, it helps reduce the magnitude of waste and pollution.

Before this work, some Chinese researchers had compared wet blue shavings with glucose as a reductant of sodium dichromate in their reaction rates, but detailed preparation method was not reported and the problem of controlling basicity and percent reduction remained unsolved.[20] Recently, Rao *et al*,[21,22] also developed an approach using chrome shavings as a reductant for preparing basic chromium sulfate. In their work, chrome shavings were used either alone or with an equal proportion of molasses for the reduction of chromium(VI). The characteristics of wet blue and the properties of crust leathers tanned with the developed products were comparable to those of conventional chrome tanned leathers, except that the COD of spent liquors was relatively high due to the presence of intermediate organic products. Since 1999, our research group has been engaged in the systematic study of the reutilization of chrome shavings for preparing chrome tanning agent. In this work, through the orthogonal tests, homogeneous tests, single-factor tests, and statistical analysis, the influence of the quantity of sulfuric acid and shavings, reduction time and temperature on the reaction process has been investigated.

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Mathematical models have been built to reflect the relationship of the above factors to the basicity of chrome liquor and the percent reduction of sodium dichromate by shavings. The research findings have been applied for China invention patent (Application No.2004100259050, Date: 3/3/2004).

EXPERIMENTAL

A. Exploration of preparation method

Preliminary method

Prepare a three mouth flask equipped with a reflux condenser, a stirrer and a temperature controlled heat source. Base the quantity of materials on the weight of sodium dichromate. According to different addition orders, the preparation method can be classified into the following four categories:

Method 1: Dissolve sodium dichromate in 150% water and 75% - 90% sulfuric acid in a flask, when the temperature rises to 90°C, add 60% - 75% chrome shavings (dried weight, similarly hereinafter). Keep stirring at 90°C for 2 hours, then add supplemental reductant till no Cr(VI) can be detected.

Method 2: Add 100% water, 10% sulfuric acid and 60% -75% chrome shavings together into a flask, stir it at 90°C for 60 minutes. The hydrolysates are reserved for the next step. Dissolve sodium dichromate in 150% water and 70% - 80% sulfuric acid in another flask, heat it up to 90°C and then add the prepared hydrolysates. Stir it at 90°C for 75 minutes, then add supplemental reductant till no Cr(VI) can be detected.

Method 3: Dilute 75% - 90% sulfuric acid with 100% water, drip the solution into a flask loaded with 60% - 75% chrome shavings at 90°C over a period of 30 minutes, keep stirring for 20 more minutes. Then add sodium dichromate (dissolved in 150% water) and keep stirring at 90°C for 2 hours. Then add supplemental reductant till no Cr(VI) can be detected.

Method 4: Add sodium dichromate, 150% water and 60% - 75% chrome shavings together into a flask, heat it up to 90°C and then add dropwise 75% - 90% sulfuric acid (diluted in 50% water) over a period of 30 minutes. Keep stirring at 90°C for 2 hours and then add supplemental reductant till no Cr(VI) can be detected. (Note: This method is adopted in the following experiments.)

Selection of supplemental reductant

Under appropriate conditions, chrome shavings can reduce sodium dichromate completely, but as the concentration of sodium dichromate and sulfuric acid continues to decrease, at the end of the reaction, to reduce the minute quantity of sodium dichromate, large quantity of chrome shavings will be needed. Chrome tanning agent made in this way contains too many intermediate organics which may exert a strong masking effect on chrome, thereby decreasing its tanning power, or increase the organic content in the spent tanning liquor, as seen in Rao's research.[22] So we consider introducing some other reducing agents stronger than chrome shavings as the reaction approaches balance, to ensure the complete reduction of Cr(VI) without losing the tanning power of chrome and decrease the surplus organics as much as possible. Reducing materials available for this purpose include sodium hydrosulfite, hypo, glucose, sulfur dioxide, etc. Judging from the electrode potential, sodium hydrosulfite has the strongest reductability and undergoes a quantitative reaction with Cr(VI). So we used sodium hydrosulfite as the supplemental reductant and calculate the percent reduction of sodium dichromate by shavings according to the consumption of sodium hydrosulfite.

Method of detecting Cr(VI)

Add a few drops of prepared chrome liquor in acidified water and shake up, then check it with several drops of 10% potassium iodide solution and starch indicator. If the color turns blue, it indicates the existence of Cr(VI); if not, Cr(VI) is proved to be fully reduced.[23]

Determination of chrome content and basicity of chrome liquor

Chrome content is determined by sodium peroxide method. Basicity is determined by oxalate method. The detailed operations are as follows: [24]

Pipette 5 ml chrome liquor into a 100ml volumetric flask and dilute it to 100 ml. Reserve it for the following assays.

Pipette 10ml reserve liquor into a 250ml iodine flask. Add 10 ml water and 2 ml nitric acid, heat and concentrate it to 10ml approx., cool it, add 2 ml of 1:1 sulfuric acid and proceed to heat it until white smokes are given out. Add 10% sodium hydroxide solution to raise the liquor pH up to 5 or so. Then add 2 g sodium peroxide and boil it for 3 - 5 minutes. To promote the decomposition of sodium peroxide, add 5 ml of 5% nickel sulfate solution and continue boiling till no tiny bubbles appear. Cool it down, add hydrochloric acid (1:1) till the precipitates are dissolved and 10 ml more after dissolution. Add 10ml of 10% potassium iodide solution, put on the stopper and allow it to stand in dark place for 5 minutes. Wash the stopper and the sides of the flask with water. Titrate the liberated iodine with 0.1M sodium thiosulfate adding starch TS as the endpoint is approached.

Pipette 10ml reserve liquor, 20 ml of 0.15M sulfuric acid and 50 ml of 2.5% sodium oxalate solution into a 250 ml ground-glass stoppered flask, install a reflux condenser and boil it for 1 hour. Cool it down and wash the sides of the condenser. Add several drops of phenolphthalein indicator

and titrate with 0.2 M sodium hydroxide till the solution appears reddish. Follow the same procedure to perform blank assays without adding chrome liquor.

The formula for calculating Cr_2O_3 content of chrome liquor is:

$$Cr_2O_3\ (g/l) = 152.0 \times V \times N/3$$

and the formula for calculating basicity of chrome liquor is:

$$B\ (\%) = (V_0 - V_1) \times N_1 \times 100/\ (V \times N)$$

Where: V = volume of consumed sodium thiosulfate standard solution in the determination of chrome content, ml

N = concentration of sodium thiosulfate standard solution, mol/l

V_0 = volume of consumed sodium hydroxide standard solution in blank assay, ml

V_1 = volume of consumed sodium hydroxide standard solution in actual assay, ml

N_1 = concentration of sodium hydroxide standard solution, mol/l

152.0 = molecular weight of Cr_2O_3

B. Investigation of the factors influencing basicity and percent reduction

As an important criterion of chrome tanning agent, basicity has a great influence on tanning effect. There are many factors influencing basicity, so it is necessary to find a way of controlling basicity for the preparation. It was reported that the reduction reaction of shavings was too complicated to obtain a regular basicity. To this question, we carried out the following experimental investigations. By fixing the quantity of sodium dichromate and water, the category of chrome shavings, the addition order and the reaction temperature, we investigated the effect of sulfuric acid and shavings quantities and reduction time on basicity and percent reduction. Mathematical models of controlling basicity and percent reduction were built.

Modified preparation method

Add 100 parts sodium dichromate with 200 parts water in a reaction vessel, install a reflux condenser and a temperature control apparatus, then add shavings (containing 65~85 parts organics), heat it up to 90°C in a water bath and drip in increments 65~85 parts sulfuric acid (diluted in 100 parts water) over a period of 30~50 minutes. Keep stirring for 90~180 minutes, then add sodium hydrosulfite till no Cr(VI) can be detected. Determine the chrome content and basicity of the prepared chrome liquor, and calculate the percent reduction of sodium dichromate by shavings according to the consumption of sodium hydrosulfite.

Orthogonal tests

The orthogonal design is a method for multifactorial experiment. It selects typical points from the full scale tests to perform the experiment. These selected points have the nature of homogeneity, orthogonality and overall comparability. Through orthogonal tests, the significance of the investigated factors on the outputs can be revealed. The orthogonal table is represented as $Ln(q^m)$, where n refers to the number of tests, q refers to the number of levels, m refers to the number of columns.

In this experiment, three factors were investigated: sulfuric acid quantity, organic quantity and reduction time, for each factor three values(namely three levels) were selected within the set range. Therefore, $L_9\ (3^4)$ was selected to perform the experiment as shown in Table VIII.

TABLE I
Factors and Levels of Orthogonal Tests

Factors	Sulfuric acid quantity(%)	Organic quantity(%)	Reduction time(min)
1	65	65	90
2	75	75	135
3	85	85	180

Single-factor tests

Fix the organic quantity and reduction time, then perform the single-factor tests investigating the influence of sulfuric acid quantity as shown in Table I.

Homogeneous tests

The homogeneous design is also a method for multifactorial experiment. Compared with orthogonal test, the homogeneous test has more uniformly distributing test points, providing more options to the triers. It is a robust experimental design, especially suitable for mathematical modeling. The

TABLE II
Factors and Levels of Homogeneous Tests

Levels	1	2	3	4	5	6	7	8
Sulfuric acid quantity (%)	70	72	74	76	78	80	82	84
Organic quantity (%)	50	55	60	65	70	75	80	85
Reduction time (min)	90	100	110	120	130	140	150	160

homogeneous table is represented as $U_n(q^m)$, where n refers to the number of tests, q refers to the number of levels, m refers to the number of factors. In this experiment, eight levels were selected for each of the three factors. U_8 (8^3) was selected to perform the experiment. See Table II.

C. Composition analysis of chrome liquor

Separated by cation and anion exchange resins respectively, the cationic, neutral and anionic chrome complexes were determined and calculated. The separated liquids were analyzed by ultraviolet-visible spectroscopy.

D. Tanning tests

Apply the prepared chrome liquor to the tannage of pickled cattle and goat skins, then measure the shrinkage temperature and substance increase of the wet blues.

Results and Discussion

A. Optimization of preparation method

Exploratory research shows that in Method 1, as the concentration of sulfuric acid keeps decreasing with the reaction going on, the later-added chrome shavings cannot be hydrolyzed effectively. Moreover, the addition of solid materials in the reaction process is not a convenient operation in practice. While Method 2 and Method 3 overcome the disadvantage of adding solid materials, they are both in the pattern of hydrolysis first and then redox. When the redox reaction occurs, the concentration of sulfuric acid has decreased, thus slowing down the reaction. Method 4 combines the hydrolysis and redox reaction in one step, the reaction is easy to control, the operation is simple, and more important, the results show good repeatability. Therefore, Method 4 is selected for further investigation into the method's stability and its influencing factors.

B. Results of investigation with the selected method

Results are shown in Table III. No. 1 to 5 show that when the quantity of chrome shavings ranges from 75% to 100%, it has little influence on basicity. However, when the quantity of shavings is too small, the basicity is low. This may be explained as little consumption of sulfuric acid in the hydrolysis process. A too large quantity of shavings will also lower basicity for the reason that an increase of organic acids produced in the hydrolysis of shavings may change the structure of chrome complex. Percent reduction of sodium dichromate rises with more shavings used. Results from No. 6 to 13 show that as the quantity of sulfuric acid increases, it obviously lowers the basicity and improves the percent reduction. Comparing the results from No. 10 to 13 with those from No. 1 to 9, it can be seen that as the experimental scale becomes larger, the results turn out more satisfying, reflecting a stronger regularity and higher percent reduction. Results from No. 14 to 19 present good repeatability, and the larger the scale, the more stable the reaction.

The above experiments demonstrate the feasibility of using shavings as reducing agent for preparing chrome tanning agent. Standards like basicity can be controlled accurately. Tanning tests applied on cattle hides show a similar effect to conventional chrome tanning agent. The wet blue leathers are characterized by a uniform blue color, a fine grain, an improved fullness and a shrinkage temperature higher than 95°C.

C. Effect of sulfuric acid and shavings quantities and reduction time on basicity and percent reduction

Based upon the exploratory experiment, further improvement was made to the preparation method. To control the dosage more accurately, the quantity of chrome shavings was calculated according to its organic content, and the amount of water was also adjusted.

Orthogonal tests

Results of the orthogonal tests are shown in Tables IV, V, VI, and VII. Analysis in Table V indicates that the quantity of sulfuric acid(Factor A) has the greatest influence on basicity while the organic quantity(Factor B) and the reduction time(Factor C) show an influence much smaller within the range of selected levels. According to the influence degree on percent reduction, the primary and secondary orders of the three factors are: sulfuric acid quantity > reduction time > organic quantity. Range analysis achieves the same results as the exploratory experiment.

The ANOVA in Table VI shows that the influence of sulfuric acid quantity on basicity is of high significance, reduction time has little influence, and organic quantity has no influence on basicity within the range of selected levels. Therefore, by fixing the organic quantity and reduction time to an appropriate value, basicity adjustment can be achieved by means of adjusting the quantity of sulfuric acid.

The ANOVA in Table VII shows that sulfuric acid quantity is also of high significance on percent reduction. Within the range of selected levels, organic quantity has a relatively significant influence and reduction time has a significant influence on percent reduction.

TABLE III
Effect of the Quantity of H_2SO_4 and Shavings on Basicity and Percent Reduction

No.	$Na_2Cr_2O_7$ (g)	Shavings (g, T.D.)	H_2SO_4 (g)	$NaHSO_3$ (g)	Basicity (%)	Percent reduction (%)
1	20	10	17.7	9.0	22.6	56.7
2	20	15	17.7	7.2	32.2	63.4
3	20	18	17.7	6.5	34.7	68.8
4	20	20	17.7	6.0	32.3	71.2
5	20	25	17.7	4.7	20.0	77.4
6	20	20	15.0	7.5	48.5	63.9
7	20	20	16.0	7.6	45.8	63.5
8	20	20	20.0	5.0	23.3	76.0
9	20	20	22.5	4.7	9.3	77.4
10	100	75	78.0	18.0	33.7	82.7
11	100	75	78.5	17.8	32.2	82.9
12	100	75	80.0	17.2	31.2	83.5
13	100	75	84.5	15.0	25.6	85.6
14	100	75	78.0	18.0	33.3	82.7
15	100	75	78.0	18.1	33.5	82.6
16	100	75	78.0	18.0	34.2	82.7
17	50	44	44.0	15.5	32.0	70.2
18	50	44	44.0	16.0	31.0	68.8
19	50	44	44.0	16.5	31.0	68.3

TABLE IV
Design and Results of Orthogonal Tests

No.	"A" H_2SO_4 quantity, %	"B" Organic quantity, %	"C" Reduction time(min)	Percent reduction	Basicity %	Substance increase, %	Ts°
1	65	65	90	65.5	45.5	/	/
2	65	75	135	72.6	46.2	/	/
3	65	85	180	77.0	45.0	/	/
4	75	65	135	75.5	38.3	47.9	94
5	75	75	180	85.4	37.5	31.5	93
6	75	85	90	77.3	38.8	42.7	96
7	85	65	180	87.8	29.4	32.0	98
8	85	75	90	82.6	29.0	42.3	99
9	85	85	135	88.2	31.0	38.8	98

Note: 1.Tanning was applied on goatskins with 1.8% Cr_2O_3 on pickled skin weight;
2. Sample No. 1 - 3 were excluded from tanning tests because they produced precipitates when diluted.

TABLE V
Results of Range Analysis

	Basicity Analysis				Percent Reduction Analysis		
	"A" H_2SO_4 quantity	"B" Organic quantity	"C" Reduction time		"A" H_2SO_4 quantity	"B" Organic quantity	"C" Reduction time
K1	45.6	37.7	37.8	K1	71.7	76.3	75.1
K2	38.2	37.6	38.5	K2	79.4	80.2	78.8
K3	29.8	38.3	37.3	K3	86.2	80.8	83.4
Range	15.8	0.7	1.2	Range	14.5	4.5	8.3

Note: Range = Kmax - Kmin.

TABLE VI
Results of Variance Analysis on Basicity

Variance source	Sum of square of deviations	Degrees of Freedom	Variance	F value	Significance
A	374.96	2	187.48	436	highly significant
B	0.86	2	0.43	1	insignificant
C	2.18	2	1.09	2.53	little significant
e	0.86	2	0.43		
E = e + B	1.72	4	0.43		

Note: e reflects the influence of random factors. As B has as little influence as e on basicity, it is also regarded as random error and incorporated with e as the residual error.

TABLE VII
Results of Variance Analysis on Percent Reduction

Variance source	Sum of square of deviations	Freedom	Variance	F value	Significance
A	315.78	2	157.89	114.83	highly significant
B	36.73	2	18.36	13.36	relatively significant
C	103.04	2	51.50	37.46	significant
e	2.75	2	1.38		

Results of single-factor tests on sulfuric acid quantity

According to the analyses of orthogonal tests, the quantity of sulfuric acid plays a dominant role in basicity control when the organic quantity ranges between 65% ~85% and reduction time between 90~180 minutes. Therefore, by fixing the organic quantity and reduction time, the reaction can be effectively controlled by means of adjusting the quantity of sulfuric acid. Single-factor tests were carried out to make a further investigation (see Table VIII). The relationship of sulfuric acid quantity to basicity and percent reduction is shown in Figure 1 & 2.

Figure 1 shows a linear relationship between sulfuric acid quantity and basicity. The mathematical model of Fig.1 is: Basicity (%) = -0.787X + 97.7, where X refers to H_2SO_4 quantity on dichromate weight; Figure 2 also shows a linear relationship between sulfuric acid quantity and percent reduction, but the latter tends to increase more rapidly as the acid quantity goes higher than 90%. This can be explained for the reason that as the sulfuric acid quantity increases to a certain degree, the intermediate oligopeptides may be enhanced to resume their reducibility, leading to the discontinuity of the redox reaction. The mathematical model of Fig.2 is: Percent Reduction (%) = 0.276X + 54.5 (X: 65%~90%); Percent Reduction (%) = 0.623X + 29.1 (X>90%). Comparing the shrinkage temperatures of the leathers tanned by chrome liquors of different basicities (Table VIII), it can be seen that their tanning effects are basically the same as conventional chrome tanning agent. Basicity of approximately 33% has a better tanning effect than the others, and a too high basicity will result in a decreased Ts due to the disadvantage for penetration.

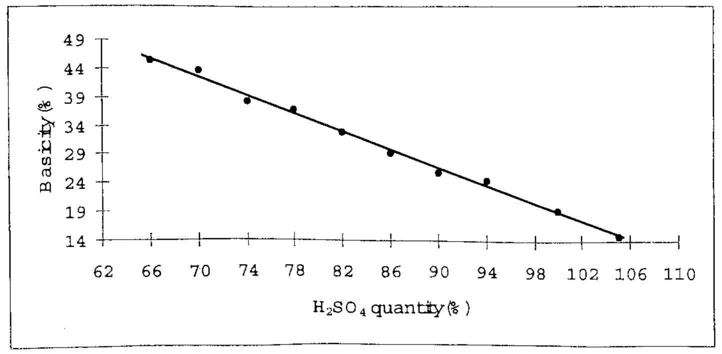

Figure 1. - Relationship between sulfuric acid quantity and basicity

Results of homogeneous tes

The regression analysis of the results in Table IX develops the following mathematical models:

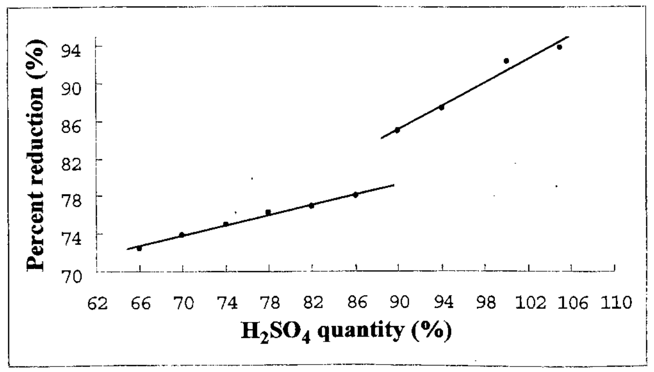

Figure 2. - Relationship between sulfuric acid quantity and percent reduction

TABLE VIII
Results of Single-factor Tests on Sulfuric Acid Quantity

No.	1	2	3	4	5	6	7	8	9	10
H_2SO_4 quantity %	66	70	74	78	82	86	90	94	100	105
Basicity %	45.5	43.7	38.5	37.0	33.1	29.4	26.1	24.6	19.4	14.9
Percent Reduction %	72.5	73.8	75.0	76.3	76.9	78.1	85.0	87.5	92.5	93.9
Ts °	97	n.t.	98	n.t.	114	108	102	n.t.	100	n.t.

Note: 1.Tanning was applied on goatskins with 1.8% Cr_2O_3 on pickled skin weight.
2. "n.t." refers to "not tested".

TABLE IX
Design and Results of Homogeneous Tests

No.	H_2SO_4 quantity %	Organic quantity %	Reduction time (min)	Percent reduction	Basicity %
1	70	60	120	70.5	40.7
2	72	80	150	85.7	40.1
3	74	70	90	74.4	36.0
4	76	50	140	68.7	31.0
5	78	85	110	81.2	34.0
6	80	65	160	81.8	33.2
7	82	55	100	76.2	29.4
8	84	75	130	86.9	31.5

TABLE X
Comparison of Experimental Values and Theoretical Values

No.	1	2	3	4	5	6	7	8	9
E.V. of basicity %	45.5	46.2	45.0	38.3	37.5	38.8	29.4	29.0	31.0
T.V. of basicity %	42.5	44.5	46.4	35.9	37.8	37.4	29.3	28.8	30.8
E.V. of percent reduction %	65.5	72.6	77.0	75.5	85.4	77.3	87.8	82.6	88.2
T.V. of percent reduction %	66.6	75.0	83.4	76.8	85.2	81.1	87.1	82.9	91.2

Basicity (%) = 83.0 - 0.734X + 0.118Y;
Percent Reduction(%) = -8.62 + 0.607X + 0.421Y + 0.0931Z

Where X = H_2SO_4 quantity, %
Y = organic quantity, %
Z = reduction time, min

Here the mathematical models have the same form as those of single-factor tests, both of which show a linear relationship between the factors and outputs. Significance test has proved that models from the two methods are both of high significance. Here the models are used to estimate the basicity and percent reduction of orthogonal tests in Table IV, the experimental values (abbreviated as E.V.) and theoretical values (abbreviated as T.V.) are listed in Table X.

The meaning and scientific explanation of each parameter in the mathematical models are under further study.

D. Composition of chrome liquors and the basic technical standards

Analyzed by using ion exchange method and ultraviolet-visible spectroscopy, the prepared chrome liquors are found to contain a major quantity of cationic and neutral chrome complexes, while anionic ratio is relatively small, generally less than 10%. The ratio of cationic and neutral chrome complexes varies with different factors in preparation. See Table XI.

The basic technical standards are:
Basicity: 25% - 45%
Cr_2O_3: 100 - 200g/l
Appearance: dark blue-green fluid

Table XI
Composition of Chrome Liquors

Type of Complex	Cationic	Neutral	Anionic
Basicity 33%	40%	55%	5%
Basicity 38%	22%	73%	5%

Conclusions

1. The present study indicates that it is feasible to use chrome shavings as a reducing agent for preparing chrome tanning agent. The reaction is stable and shows good regularity and repeatability.
2. The quantity of sulfuric acid is the major factor influencing the basicity of chrome liquor and the percent reduction of sodium dichromate by shavings. Since the shavings quantity and reduction time have relatively small influence on basicity and percent reduction, the reaction and the basicity of chrome liquor can be controlled by adjusting the quantity of sulfuric acid.
3. The relationship of sulfuric acid quantity to basicity and percent reduction proves to be linear. This definite relationship has an important meaning in guiding the production and controlling the basicity of chrome liquor.
4. The chrome tanning agent prepared by using shavings as reducing agent contains a major quantity of cationic and neutral chrome complexes with a relatively small anionic ratio. Chrome tanning agent prepared in this way provides a tanning effect essentially the same as that of conventional chrome tanning agent.

References

1. Taylor, M. M., Diefendorf, E. J., Thompson, C. J. *et al*; *JALCA* **88**, 358, 1993.
2. Taylor, M. M., Cabeza, L. F., Dimaio, G. L. *et al*; *JALCA* **93**, 61, 1998.
3. Cabeza, L. F., Taylor, M. M., Dimaio, G. L. *et al*; *JALCA* **93**, 83, 1998.
4. Cabeza, L. F., Taylor, M. M., Brown, E. M. *et al*; *JALCA* **94**, 268, 1999.
5. Kolomaznik, K., Mladek, M., Langmaier, F. *et al*; *JALCA* **95**, 55, 2000.
6. Taylor, M. M., Cabeza, L. F., Marmer, W. N. *et al*; *JALCA* **95**, 243, 2000.
7. Fu, Lihong, Zhang, Mingrang, Qu, Jianjian *et al*; *China Leather* **31**, 43, 2002.
8. Tahiri, S., Bouhria, M., Albizane, A. *et al*; *JALCA* **99**, 16, 2004.
9. Cantera, C. S., De G. M., and Sofia, A.; *JSLTC* **81**, 183, 1997.
10. Cantera, C., Goya, L. and Mingo, R.; *JSLTC* **84**, 29, 2000.
11. Wang, Hongru, Wei, Xianglin, and Wu, Xianji; *China Leather* **30**, 8, 2001.
12. Wang, Kunyu, Pan, Zhijuan, and Zhou, Wanjian; *China Leather* **31**, 13, 2002.
13. Cantera, C., Martegani, J., Esterelles, G. *et al*; *JSLTC* **86**, 195, 2002.
14. Chengdu University of Science and Technology, Northwest Institute of Light Industry; The Chemistry and Technology of Leather Manufacture, Light Industry Press, Beijing, 1996; p.610.
15. Benjamin, A. A. and Joseph, K.; U.S. patent, 6264879, (2001).
16. Brown, E. M., Taylor, M. M. and Marmer, W. N.; *JALCA* **91**, 270, 1996.
17. Shao, Zeen, Xie, Shouling, and Li, Shiying; *China Leather* **30**, 36, 2001.
18. Chengdu University of Science and Technology, Northwest Institute of Light Industry; The Chemistry and Technology of Leather Manufacture, Light Industry Press, Beijing, 1996; p.608.
19. Imai, T. and Okamura, H.; *JALCA* **86**, 281, 1991.
20. Fu, Lihong and Zhang, Mingrang; *China Leather* **30**, 16, 2001.
21. Rao, J. R., Thanikaivelan, P., Screeram, K. J. *et al*; *Env. Sci. Technol.* **36**, 1372, 2002.
22. Rao, J. R., Thanikaivelan, P., Screeram, K. J. *et al*; *JALCA* **99**, 170, 2004.
23. Chengdu University of Science and Technology, Northwest Institute of Light Industry; The Chemistry and Technology of Leather Manufacture, Light Industry Press, Beijing, 1996; p.211.
24. Northwest Institute of Light Industry; Physical and Chemical Analysis of Leather, Light Industry Press, Beijing, 1988.