

# Study on Application Technics of A Chrome-tanning Assistant of Hyperbranched Polyme with Carboxyl End-group

QIANG Tao-tao\*, WANG Xue-chuan, REN Long-fang YUAN Xu-zhang

(College of Resource & Environment, Shaanxi University of Science & Technology, Xi'an, Shaanxi, P.R. China 710021)

**Abstract:** There are a mass of end groups in hyperbranched polymers. If they complex with chromium (III) ion, they can be used as highly absorptive chrome tanning auxiliaries. Comparing to ordinary highly absorptive chrome tanning auxiliaries, complexing groups in hyperbranched polymers are more, so their effect on absorbing and fixing chromium ion may be better. Meanwhile, it can economize chromium salts, reduce chromium ion pollution to water and protect environment. A hyperbranched polymer with amidogen end-group was synthesized with 3, 5-diaminobenzoic acid by the "one step method", then react with acetaldehyde acid to get a chrome-tanning assistant of hyperbranched polymer named as "HP-I". The chrome-tanning assistant agent was used to tanning sheep garment leather. The optimal technics was obtained. The chrome-tanning assistant agent should be used before adding chrome powder; when adding chrome-tanning assistant agent, pH was 4.0-4.2 after basifying, the optimum dosage of chrome-tanning assistant agent was 2% and chrome powder was only 5%. Under the condition, Ts of leather was equal with traditional chrome tanning.

**Keywords:** hyperbranched polymer; chrome-tanning assistant; application technics; leather

## 1 Introduction

In 1952, Flory<sup>3</sup>, in a statistical analysis of  $AB_m$  polycondensation reactions, demonstrated that these were expected to yield polymers with broad molecular weight distributions. But the non-crystal and non-chain intertwist hyperbranched polymers can't attract researchers' attention. After Y H Kim<sup>4</sup> successfully prepared a hyperbranched polyphenylene in early 1990, researchers began to pay more attention to hyperbranched polymers. Hyperbranched polymers have many particular merits, such as high activity, low viscosity, high solubility, special branched structure and low melt viscosity<sup>5</sup>. Applying foreground of hyperbranched polymers is very wide as tanning and retanning agents, preventive agents of Cr (VI) in leather, highly absorptive chrome tanning auxiliaries, finishing agents and auxiliaries and formaldehyde scavenger in leather industry<sup>6</sup>. A hyperbranched polymer with amidogen end-group was synthesized with 3, 5-diaminobenzoic acid by the "one step method", then react with acetaldehyde acid to get a chrome-tanning assistant of hyperbranched polymer. Moreover, the technics of the chrome-tanning assistant of hyperbranched polymer was optimized.

## 2 Experimental

### 2.1 Main reagent and apparatus

N-methyl pyrrolidone(AR) was provided by Ke Miou Chemicals Research Center in Tianjin; 3, 5-diaminobenzoic acid and 40% acetaldehyde acid are industrial products and supplied by Shengming Chemicals Ltd Company; methylbenzene(AR) was provided by the Sixth Chemicals Factory in Tianjin.

### 2.2 Synthesis of the chrome-tanning assistant of hyperbranched polymer

50g 3, 5-diaminobenzoic acid and 250ml N-methyl pyrrolidone were added into a dry single-mouth flask. After they mixed together, 300ml methylbenzene was added and shaken up. The condensation tube and water separator were linked together, and then reacted at 160°C for 6h. When the reaction was finished, the methylbenzene was

---

\* Corresponding author: professor, Doctoral Advisor, the Dean of College of Resource and Environment, 029-86168257; E-mail: wangxc@sust.edu.cn

extracted and hyperbranched polymer with amidogen end-group was obtained. The second step was the reaction of hyperbranched polymer with amidogen end-group and superfluous acetaldehyde acid. The mol ratio of acetaldehyde acid and academic aminogen was 1.5:1. After mixing them in three-mouth flask and evenly stirring 30min, we adopt pH to 6~7 using sodium hydroxide, after which keep on reacting for 2h.<sup>7</sup> When the reaction was end, superfluous acetaldehyde acid was washed by methylbenzene and N-methyl pyrrolidone was removed with rotary evaporating apparatus. After drying and grinding, the brown powder was chrome-tanning assistant of hyperbranched polymer.

### **2.3 Determination of Cr<sub>2</sub>O<sub>3</sub> content and calculation of chrome tanning agent absorptivity<sup>8</sup>**

The content was measured by acidic potassium permanganate oxidation and diphenylcarbazide coloration. The principle was as follows. After the wastewater was digested, it was oxidated from Cr<sup>3+</sup> to Cr<sup>6+</sup> by potassium permanganate. Excess potassium permanganate was decomposed by sodium nitrate and superfluous sodium nitrate was decomposed by urea. Under acidic solution purple-red complex was obtained by the reaction of Cr<sup>6+</sup> and diphenylcarbazide. Then the purple-red complex was measured by spectrophotometric method. The computational formula was as follows.

$$\text{Chrome absorptivity}/\% = \frac{G - V \times C}{G} \times 100\%$$

G—Cr<sub>2</sub>O<sub>3</sub> content, g; V—tanning bath liquid volume, L; C—Cr<sub>2</sub>O<sub>3</sub> content in bath liquid, g/L.

### **2.4 Determination of Rate of dye-uptake**

Rate of dye-uptake was an important index which was used for evaluating dye property. The bigger of the dye-uptake rate, the higher of the use ratio of dye. In the study the spectrophotometric method was adopted. The computational formula was as follows.

$$\text{Rate of dye-uptake} = \frac{A_0 - A_1}{A_0} \times 100\%$$

A<sub>0</sub>-absorbency of dye liquid before dyeing; A<sub>1</sub>-absorbency of residual dye liquid after dyeing.

Remark: The biggest absorptive wavelength of substantive black G and acidic black ATT respectively were 425nm and 420nm.

## **3 Results and discussion**

### **3.1 Applying technics of HP-I**

There were large numbers of carboxyl in HP-I, so it could be used as high absorptive chrome tanning assistant agent. The combination of high absorptive chrome tanning assistant agent and Cr<sup>3+</sup> could increase chrome absorptivity and Ts, reduce chrome content in wastewater. But if adding sequence was improper, the assistant agent and Cr<sup>3+</sup> would form macromolecule, as a result, it influenced the penetration of chromium salt and physical & mechanical properties of leather. The application result of had significant relationship with technics. Therefore, two technics were designed.

Number 1: pickling sheep skin → depicking (pH=3.0) → standard chrome powder(X%) → assistant HP-I(1%) → basification(pH=4.2).

Number 2: pickling sheep skin → assistant HP-I (1%) → standard chrome powder(X%) → basification (pH=4.2).

The results were shown in Fig.3.

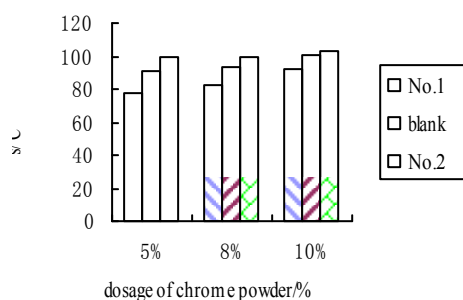


Fig.3 The relation of chrome powder dosage and Ts

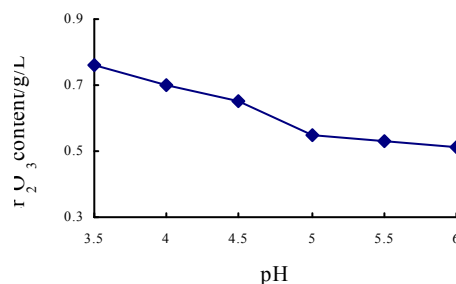


Fig.4 The relation of pH and content of Cr<sub>2</sub>O<sub>3</sub> in float

As shown in Fig.3, when HP-I was added before chrome powder, Ts of leather was higher than that of adding after chrome powder; if HP-I was used before chrome powder, Ts of leather was higher than that of without HP-I; if HP-I was used after chrome powder, Ts of leather was lower than that of without HP-I. In the same procedure, Ts continuously increased following the increase of chrome powder dosage. In addition, when HP-I was added before chrome powder, the grain of leather was thin and full. But when adding HP-I after chrome powder, the grain of leather was rough and the color of waste liquid was deep blue. So the effect of using HP-I before chrome powder was better.

There were large numbers of carboxyl in HP-I, so HP-I could combine with Cr<sup>3+</sup> and the molecule of assistant and Cr<sup>3+</sup> became big. If HP-I was used after chrome tanning, it combined with Cr<sup>3+</sup> and formed macromolecule which was not benefit for penetrating into leather. So they combined on leather surface and it was not favorable for absorption and fixation of chrome. Meantime, the stability of collagen network structure was prevented and Ts was less than that of traditional chrome tanning. When using assistant before chrome powder, HP-I could penetrate into hides which solved the penetration of chrome complex macromolecule. HP-I combined with collagen fibers by hydrogen bond. A large numbers of carboxyl in HP-I molecule increased reaction point between collagen fiber and chrome complex, as a result, tanning effect was improved and Ts slightly increased. The reason was that the dosage of chrome tanning agent was too few. In the same technics, with the increase of chrome powder dosage, the network structure of collagen fibers was strengthened and Ts continuously increased. So HP-I should be used before chrome tanning and the pH was between 2.5 and 3.0. When HP-I penetrated into hides and combined with collagen fibers, chrome powder was added. After chrome powder and assistant completely penetrated, slow basification facilitated further absorption and combination of chrome. So adding HP-I before chrome powder was optimum.

### 3.2 The effect of pH of basifying on application of HP-I

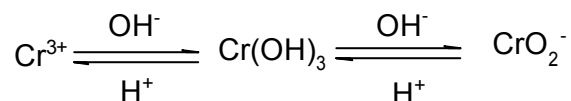
Fig.5 The relation of pH and chrome absorption ratio

Fig. 6 The relation of pH and Ts

The pH of chrome tanning liquid directly influenced penetration of chrome complex and combination of

chrome and collagen fiber, so pH must be carefully controlled in tanning process. In the experiment the relation of pH of basifying and chrome absorptivity were studied. Finding out optimum pH of basifying which gave attention to chrome absorptivity and quality of leather had practical significance.

As shown in Fig.4, along with the increase of pH, the  $\text{Cr}_2\text{O}_3$  content in chrome tanning wastewater gradually reduced. This was because chromium took on following balance under different pH.



Chrome oxide was an amphoteric oxid. The study showed that when pH was more than 4,  $\text{Cr}^{3+}$  salt could form  $\text{Cr}(\text{OH})_3$  deposition. When pH was 6.5,  $\text{Cr}(\text{OH})_3$  completely deposited and  $\text{Cr}^{3+}$  concentration was very low. When pH was more than 10,  $\text{Cr}(\text{OH})_3$  deposition began to dissolve. When pH reached to 14,  $\text{Cr}(\text{OH})_3$  deposition completely dissolved. For different  $\text{Cr}^{3+}$  complex, above pH range was different. But no matter which  $\text{Cr}^{3+}$  complex, under pH 7.5~10 the solubility of  $\text{Cr}(\text{OH})_3$  was the least. When pH was lower, the hydroxyl concentration in solution the basicity of chrome complex were very low, hydrolyzation of chromium salt was slow and molecule was small. The small molecule complex was benefit for penetrating into skin and went against combination. If pH was continually increased, the increase of hydroxyl caused coordination reaction; as a result, chrome complex with bigger basicity was produced. The second-step hydrolyzation of chrome complex completed under pH 3~4. With the increase of basicity, hydroxyl coordination reaction of chrome complex made bridge bond form and relative molecular weight increase. The macromolecule chrome complex was not benefit for penetration, but for combination with collagen. When pH was bigger than 4, the third-step hydrolyzation gradually carried out. So chrome complex in wastewater would gradually produce  $\text{Cr}(\text{OH})_3$  deposition and carboxyl had combined with chrome in skin was extracted from complex. During basifying the increase of pH and basification made more carboxyl enter inner chrome complex. Meantime, ionization degree of carboxyl, combination capability with cationic chrome complex increased and fixation to  $\text{Cr}^{3+}$  increased. In a word, when pH was among 3.5 to 6, chrome complex in chrome tanning liquid was absorbed by hides or became chromic hydroxide deposition. So  $\text{Cr}_2\text{O}_3$  content in waste liquid would continuously reduce.

As were indicated in Fig.5, with the increase of pH of basifying, chrome absorptivity continuously increased.

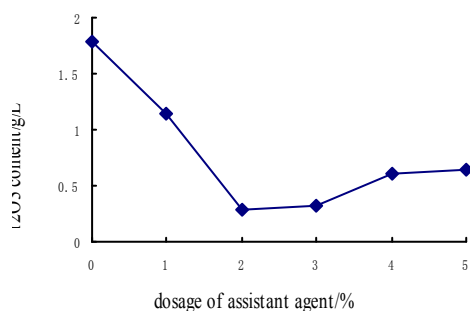


Fig.7 The relation of dosage and content of  $\text{Cr}_2\text{O}_3$

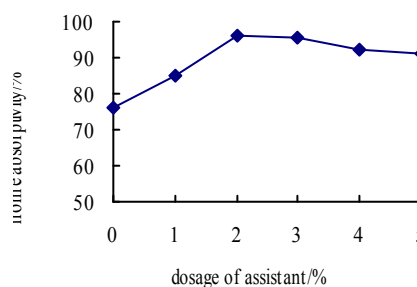


Fig.8 The relation of assistant dosage and absorption ratio

As were indicated in Fig.6, with the increase of pH of basifying, Ts of leather increased, and then reduced. When pH was from 3.5 to 4.5, chrome complex in hides combined with carboxyl in collagen and assistant agent,

crosslink between collagen fibers and tanning effect increased, so Ts gradually increased. When pH increased to 6.0,  $\text{Cr}^{3+}$  became chromic hydroxide deposition and the carboxyl even was substituted from chrome complex.  $\text{Cr}^{3+}$  combined with collagen fibers reduced, the strength of collagen network structure stability was prevented, as a result, Ts gradually reduced. So the optimum pH of basifying was 4.0~4.2.

### 3.3 The effect of HP-I dosage on chrome absorptivity

If the dosage of HP-I was too few, the effect was not obvious; but if it was too much, the cost would increase. The most important was that many assistants that was not absorbed by hides were easy to form macromolecule with chromium salt in basifying, as a result, the penetration of chrome tanning agent was prevented. So the dosage of HP-I was discussed.

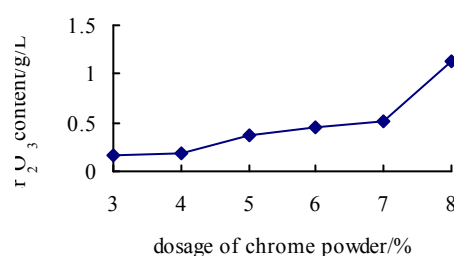
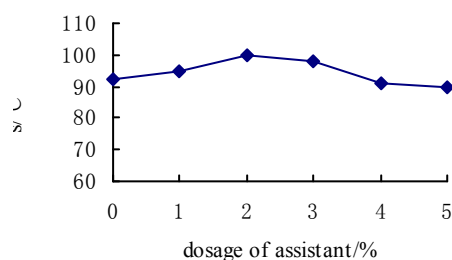


Fig.9 The relation of assistant dosage and Ts

Fig.10 The relation of chrome dosage and content of  $\text{Cr}_2\text{O}_3$

As were shown in Fig.7 and Fig.8, when the dosage of assistant was less than 2%, along with the increase of assistant dosage,  $\text{Cr}_2\text{O}_3$  content in chrome tanning wastewater reduced and chrome tanning agent absorptivity increased. When the dosage of assistant was more than 2%,  $\text{Cr}_2\text{O}_3$  content in chrome tanning wastewater increased, and chrome tanning agent absorptivity reduced.

As shown in Fig.9, when the dosage of assistant was less than 2%, the increase of HP-I made the increase of chrome absorptivity, multi-point combination and Ts. When the dosage of assistant was more than 2%, the increase of HP-I made the reducing of Ts. Considering above indexes and cost, the dosage of HP-I was 2%.

### 3.4 The effect of chrome powder dosage on chrome tanning agent absorptivity and leather properties

The dosage of chrome powder could influence chrome tanning agent absorptivity, so it was necessary to research the effect of chrome powder dosage on application.

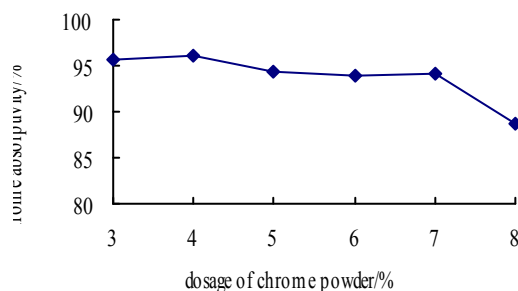


Fig.11 The relation of chrome dosage and chrome absorption ratio

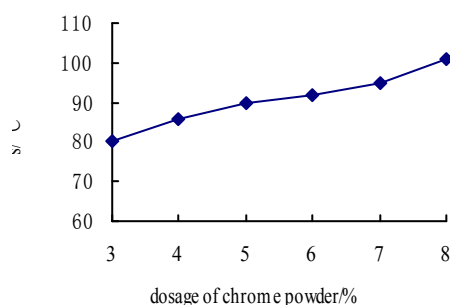


Fig.12 The relation of chrome dosage and Ts

As were indicated in Fig. 10, with the increase of chrome powder,  $\text{Cr}_2\text{O}_3$  content in waste liquid continuously increased. The more the dosage of chrome powder, the more of the  $\text{Cr}_2\text{O}_3$  content.

As were shown in Fig. 11, with the increase of chrome powder, chrome tanning agent absorptivity continuously reduced. The more the dosage of chrome powder, the less the chrome tanning agent absorptivity.

As were indicated in Fig.12, with the increase of chrome dosage, Ts continuously increased. Considering  $\text{Cr}_2\text{O}_3$  content, chrome tanning agent absorptivity and Ts, the dosage of chrome powder was 5%. Under the condition the application effect could equal with that of traditional chrome tanning.

#### 4 Conclusions

The optimum technics of HP-I was shown as follows. HP-I should be added before chrome powder. When adding HP-I, the pH of basifying was 4.0~4.2 and the optimum dosage of HP-I was 2%. When the dosage of chrome powder was 5%, Ts equaled with that of traditional chrome tanning.

#### Acknowledgments

The authors would like to thank the support of National Natural Science Foundation of China (20676075 and 20876090) and the doctoral foundation of educational ministry (20060708002).

#### References

- [1] Young H. Kim, Owen W. Webster. Hyperbranched polyphenylenes. *Macromolecules*, 1992, 25: 5561.
- [2] K. Ishizu, D. Takahashi, H. Takeda. *Novel Polymer*, 2000, 41: 6081.
- [3] P. J. Flory. *J. Am. Chem. Soc.*, 1952, 74: 2718.
- [4] Y. H. Kim, O. W. Webster. *J. Am. Chem. Soc.*, 1990, 112: 4592.
- [5] Wang Xuechuan, Qiang Taotao, Ren Longfang. *China Leather*, 2005, 34: 14.
- [6] Wang Xuechuan, Qiang Taotao, Ren Longfang. *JSLTC*, 2006, 90: 54.
- [7] Wang Xuechuan, Qiang Taotao, Ren Longfang. *China Leather*, 2006, 35: 43.
- [8] Li Guoying, Luo Yi, Zhang Mingrang. *Leather Science and Engineering*, 2000, 20: 12.
- [9] Gang Yang, Mitsutoshi, and Masa-aki Kakimoto. *Macromolecules*, 1999, 32: 2215.
- [10] V. R. Reichert, L. J. Mathias. *Macromolecules*, 1994, 27: 7024.
- [11] Yu Shijun, Zhao Hongxia, Li Ruisheng. *Chemistry bulletin*, 2003, 12: 843.
- [12] M. Jikei, S. H. Chon, M. Kakimoto. *Macromolecules*, 1999, 32: 2061.
- [13] X. C. Wang, T. T. Qiang, X. Z. Yuan, L. F. Ren. *Proceedings of the 7th Asian International Leather Conference of Science and Technology*, 2006: 906.