Study on Characterizes and Tanning Property of THPS and Fe(Ⅱ) In-situ Cooperative Substance

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Abstract: In the sake of chrome-free tanning system, a new more environmental-friendly combination tanning system has been developed. The in-situ cooperative substance from ferrous sulfate and tetra hydroxymethyl phosphonium sulphate (THPS) was synthesized of different mole ratios between the two materials. By testing the UV and FT-IR absorption spectra of the Fe(Ⅱ)-THPS compounds in the job method, it can be found that the most possible mole ratio of *n*(Fe(Ⅱ)) : *n*(THPS) was 1 : 3. And the combining site between these two materials was the $-SO_3-$ of THPS. At last, pickled sheep skin was tanned with solo $FeSO_4$, solo THPS, $FeSO_4$ and THPS, Fe(Ⅱ)-THPS compound. The results show that the hydrothermal stability of leather tanned with cooperative substance was higher than that of leather tanned with single tanning agents, and its shrinkage temperature can reach to 90℃. And the gained leather had poor resistance to storage and oxidation.

Key words: THPS; Fe(Ⅱ); Tanning Property; Hydrothermal Stability; Cooperative Substance

1 Introduction

Using of chrome salts tanning agent in leather-making industry is being questioned owing to the reports emerging on the poor distribution, the toxicity and remaining in the waster water associated with it [1-3]. Many studies based on less chrome and chrome-free technologies have emerged during the past 10 years. And the combination tannage using more than one tanning agent was thought as the potential substitutes for chrome tanning [4]. The combining use of organic tanning agents and organic tanning agents, organic tanning agents and inorganic tanning agents, inorganic tanning agents and inorganic tanning agents has been applied for many years. Among the mineral materials, aluminum, zirconium, copper and iron are the potential metal substitutes for chrome. Tanning system based on aluminum had been explored [5-7]. Due to loss of strength and darkening of color on ageing of iron tanned leather [8, 9],

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ferrous sulfate was chose as one composition of combination tannage in this work. Then, combining with ferrous sulfate, the reducing agent preventing the oxidation of ferrous ion, THPS was selected to the second composition.

THP salts which used as fire retardant were the most usual chemical assistants, and the textile treated with THP salt have the following features, such as good wash ability, excellent absorptivity to dyestuff and resistance to constringency [10-13]. There are lots of active hydroxymethyl group which ensure THP salt can condensate with amine mass to form the stable organic compounds. Because of its efficient, broad-spectrum, harmful-less and biodegradable characteristics, the usage of THP salt in the chemical field is extensive.

In this study, the compound Fe-THPS has been synthesized. By testing the compound's UV and FT-IR spectrum, the most possible mole ratio of Fe^{2+} and THPS could be determined. Studies on tanning properties of THPS and Fe-THPS compound were carried out as an alternative tanning to the traditional chrome tanning system. The shrinkage temperature of leather tanned with solo ferrous sulfate, THPS and Fe-THPS compound reveals the cross-linking properties of the compound, which disclosure the tanning mechanics of combination tannage.

2 Experimental

2.1 Materials

All chemicals used for leather processing were of laboratory grade. Ferrous sulfate and citric acid purchased from Yixing Chemicals Co., Zhejiang were used. Tetrakis hydroxymethyl phosphonium sulphate (THPS) (Figure1) purchased from Rhodia Chemicals Co., England was used. Sodium bicarbonate purchased from Ningbo Chemicals Co., Zhejiang was used. Pickled sheepskins were used for tanning trials.

2.2 Synthesis of compounds

Mass of ferrous sulfate and THPS were weighted to ensure the mole ratio are 2∶1, 1∶1, 1∶2, 1∶3 and 1∶4, the organic acid as stabilizing agent of Fe^{2+}. The materials were mixed in volumetric flask, keeping the flask at 30℃, pH3.0 for 2 hours. The reaction produces are the Fe-THPS compounds with different mole ratio.

2.3 Analysis of compounds

2.3.1 UV analysis

Using the Job method [14], the possible mole ratio of Fe^{2+} and THPS can be determined. According to the volume in table, the ferrous sulfate (0.25 mol/L) and THPS (0.25mol/L) were transferred to volumetric flask, and the absorption of liquor gained from 25℃ thermostat water

bath for 2 hours should be tested at wavelength of 300 nm.

Tab.1 The volume of Fe (Ⅱ) and THPS

$v(FeSO_4)$/mL	v(THPS)/mL	f [1)]
10	0	0
6.7	3.3	0.5
5	5	1
3.3	6.7	2
2.5	7.5	3
2	8	4

1) f = c(THPS)/c(Fe(II))

2.3.2 FT-IR analysis

The FT-IR spectra of THPS and compound with optimum mole ratio were tested by liquor titration method. The samples were scanned 15 times in the spectrum 670 FT-IR instrument.

2.4 Tanning power

The amount of every tanning agent and pH of every tannage were shown in table 2, in which A represented ferrous sulfate, B represented THPS, C was Fe-THPS compound, and D was pickled skin. According to the weight of tanning agents and skin, the pickled liquor was added to ensure the enough float, and the react temperature was 35℃.

Tab.2 The proportion of different materials

Method	Weight	pH	Remark
A+D	20%	2.5~3.0	The final pH should adjusted to 3.5
B+D	10%	3.0	Final pH is 6.0
A+D/+B	10%+5%	2.5~3.0	A+D(pH2.8,4h,adjust pH to3.5),add B(pH3.0, then pH5.5)
B+D/+A	5%+10%	3.0	B+D(pH3.0,6h,adjust pH to6.0), add B(pH2.5, then pH5.5)
C+D	10%	3.0	Final pH is 5.5

3 Results and discussion

3.1 Optimum ratio of component mole

Figure 1, whose X ray is f (the concentration ratio of Fe^{2+} and THPS), Y ray representing the absorption can be gained by the Job method. And the corresponding f to maximum A is the optimum mole ratio of Fe and THPS.

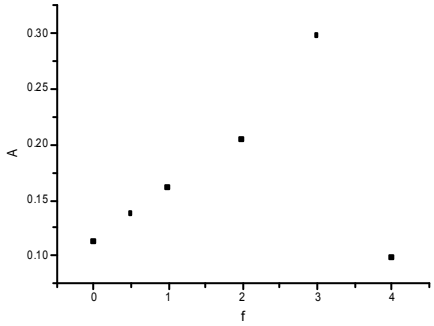

Fig.1 Job curve of Fe^{2+} and THPS

The figure 1 can reflect the fact that the absorption of compound will rise with the increase of mole ratio when f was 0 to 3.0. And the absorption arrives to maximum when f is 1/3. The result can illustrate that the mole ratio of THPS and ferrous sulfate is 3:1.

3.2 FT-IR spectrum

The FT-IR spectra of solo THPS and optimum mole ratio compound have been shown in figure 2.

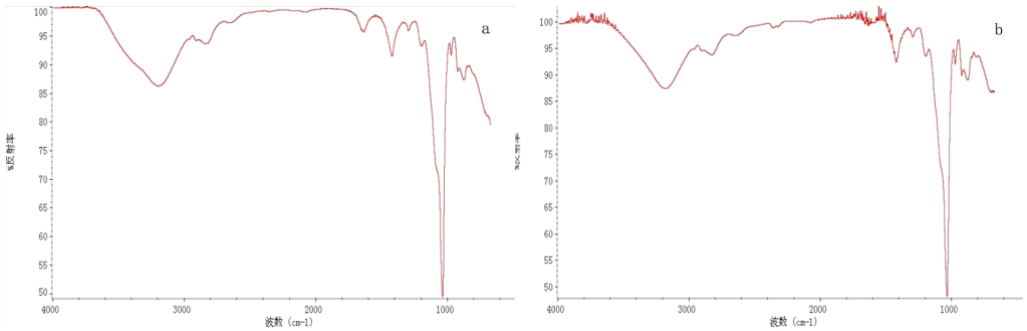

Fig.2 FT-IR spectra of THPS and Fe-3THPS at pH3.0 (a THPS; b THPS-3Fe)

From the spectra of solo THPS and Fe-THPS compound, it can be found that most of absorption peak of compound is similar with THPS. For example, the 3015.2 cm^{-1} and 3178.5 cm^{-1} represent the stretching vibration of hydroxyl group in image a and b respectively, and the 2793.7 cm^{-1}, 2793.4 cm^{-1} indicate the stretching vibration of -CH-. Meanwhile, 1080.5 cm^{-1} and 1047.8 cm^{-1} list the stretching vibration of -C=O. All of these data show that the bonding site between ferrous ion and THPS is not the hydroxymethyl of THPS. And according to the FT-IR spectra in figure 2, it can be presumed that the bonding position is $-SO_3-$ of THPS.

3.3 Tanning properties of tanning agents

The shrinkage temperatures of leather tanned with different methods have been listed in table 3, and the color also have been described. In this table, drying treatment means 50℃, 3 hours at the thermostatic oven.

Tab.3 Ts and color of leather aged with different tannage

Feature	Methods				
	$FeSO_4$	THPS	Fe(II)→THPS	THPS→Fe(II)	Fe(II)-THPS
Ts/℃	70.5	81.9	91.1	93.7	94.0
color	light brown	white	brown	dark brown	brown
Dried Ts/℃	66.1	81.2	89.2	92.1	92.4
Dried color	brown	light brown	brown	dark brown	brown

Shrinkage temperature of the collagen fiber is a measure of hydrothermal stability of the matrix being formed by cross-linking agent and raw collagen. There are much carboxyl group, amino group and other active groups in the lateral chain of peptide chain which is the units of the collagen, and the stability of modified collagen can be enhanced only when the tanning agent does combine with the active sites of collagen firmly. The increase in shrinkage temperature represents an in increase in the stability of the matrix through the interaction processed between collagen and tanning agents. From the data of table 3, it can be concluded that the cross-linking properties of solo tanning agent is week, such as the shrinkage temperatures of leather tanned with ferrous sulfate and solo THPS only are 70.5℃ and 81.9℃ respectively. However, the temperature of combination leather can be enhanced markedly, which is 91.1℃ for Fe then THPS leather, 93.7℃ for THPS then Fe leather, which show that the sequence of the two tanning agents have a little influence on the hydrothermal stability of leather. From these data, we can suppose that the reaction sites of ferrous sulfate and THPS with collagen are different. This phenomenon indicates that the compound can form the tanning matrix with excellent rigidity with collagen active sites, which ensure the outstanding thermal stability.

Shrinkage temperature of leather tanned with big dimensional agent is very low even the rigidity of the tanning agent is excellent, which means the penetrating step and the molecular size of tanning agent is important in the process of tanning. After drying, the leather whose tanning agent have ferrous sulfate will change in shrinkage temperature and color because of the moisture and oxygen. And the temperature will decrease, the color will darken. For example, the shrinkage temperature of leather tanned with compound is 93.7℃, which reduces to 92.1℃ after drying treatment. The reason can be suppose that the combination between compound tanning matrix and collagen is feeble.

4 Conclusions

The optimum mole ratio of THPS and Fe is 3:1. There are 4 hydroxymethyl groups in THPS, which ensure its strong reaction with other active materials, but the combining site between these two materials is the $-SO_3-$ in THPS.

The hydrothermal stability of leather tanned with the two tanning agents and compound is better than leather tanned with any solo tanning agent. The highest shrinkage temperature of leather tanned with solo ferrous sulfate or solo THPS only can reach to 81.9℃, and the shrinkage temperature of combination tannage leather is higher than 90℃. Contribution of compound to hydrothermal stability of leather is the best one. Similar with solo ferrous sulfate tannage, the color of leather tanned with the compound and combination tanning agents will darken with ageing. Meanwhile, the shrinkage temperature will decrease, and leather tanned with solo ferrous sulfate is the most obvious one.

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