Characterization and Mechanism of Zinc Salts as Tanning Agents

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Abstract

Zinc has important biological functions as one of the essential trace elements to human. The Zinc tanning agent could produce white leathers with properties comparable to the chrome tanning agent, and the tanning agents based on Zinc salts were prepared using different masking agents such as sodium formate, sodium acetate, sodium tartrate and potassium hydrogen phthalate. The selection of the zinc tanning agents has been optimized based on the properties like hydrothermal stability and percentage exhaustion of zinc. The results indicated that zinc sulfate can be used as tanning agent under acidic conditions (50g/L, pH=3, 25°C) and is an effective and superior method. Moreover, Sodium citrate (0.1mol/L) was selected as masking agent compared with other masking agents. The hydrothermal stability was improved effectively with the action of masking agent.

Introduction

Tanning is one of the most important processes in leather production, which plays an important role in the change of the rawhide performance. Tanning agents are chelated with the leather collagen in peptide bond so that the stability of the hide can be more firmly.[1] The general tanning methods include the chrome tanning, the aluminum tanning, the aldehyde tanning, the vegetable tanning, the oil tanning, the combination tanning, etc. The chrome tanning is the most predominant method of tannage in commercial leather production all over the world. Different tanning agents result in different tanning characteristics.[2] Chrome tanned leather have the highest hydrothermal stability and mechanism relative advantages. However, a number of studies show that chromium (III) are toxic at high levels under certain ligand environments,[3,4] and chromium(IV) is a known carcinogen. Besides, a series of disadvantages usually occur in chrome tanning process, such as the darker color, poor oxidation resistance, and the environmental pollution. Though it's still difficult to find other tanning methods to replace chrome tanning completely until now, exploration of new types of tanning materials which can reducing chrome-pollution is the trend of research in leather industry.

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The ideal tanning materials should exhibit the following features: good hydrothermal stability, white or pale color with light fastness, low environmental impact, comparable costs and versatile basis for different leather types.[5] In past researches, B. Madhan studied the combination tanning method of zinc combination tanning and achieved some positive results.[6,7] This paper focused on the conditions of tanning used zinc independently and the influence of masking agents to zinc tanning. It's well known that zinc has important biological characteristics as one of the essential trace elements to human. The possible optimal combination ways between the zinc and protein are not only investigated widely in the field of biological, medicine and food, but also are of great significance to the leather industry of sustainable development and clean production. Biological researches found that zinc ions and short peptide segments, which compose special structural domain of biomacromolecules, form a stable combination under certain conditions.[8] It has the characteristic of maintaining the stability of the structure of polypeptide. These protein fragments were defined by Biological Sciences as zinc finger protein, which can bind to amino acid sites specially and regulate the body's physiological function. The zinc finger proteins exist in a huge number of organisms such as animals, plants and fungi in the form of tetrahedron, which is connected by zinc as coordination center. These researches will be the significant references to study zinc-tanning mechanism. The binding sites and steric configuration of zinc and collagen can be measured and speculated by relevant biotechnology.

In the field of medicine and animal feeding science, the amino acid chelated zinc is of considerable significance and is being widely used in practical applications. Depending on the different types of amino acids, the zinc amino acid chelates can be divided into single zinc amino acid chelates (e.g., zinc glycinate, zinc lysine) and compound zinc amino acid chelates (i.e., metalloprotein). In theory, the compound zinc amino acid chelates are more conducive to living organisms because of the diverse range of amino acids. Which is essential for the maintaining basic functions of organisms is more than a specific amino acid; a variety of zinc amino acid can play the bio-functions in different tissues and organs of living bodies. As the adding auxiliary agents, the compound zinc amino acid chelates affords a further broader field of application. Besides, the bioavailability of compound chelates is obviously higher than single chelates, which had been testified by the animal experiments. All of these researches mentioned provide the possibility to handle the shavings produced by zinc tanning. That will reduce the pollution from the chrome-tanned leather wastes, which are difficult to deal with.

The main factors affecting the chelating reaction involve the conditions such as the concentration of agents, pH value, temperature and the reaction time. There is a wide variation of chelate rate from 30% to 90% with different structures and processes. Therefore, the choice of appropriate reaction conditions is important to the binding rate of zinc-collagen, also for the zinc tanning effect in leather production.

This paper revealed the tanning effect of zinc agent with masking agents and the binding capacity of zinc with collagen. If the finish-leather tanned by zinc can meet the requirements, it benefits not only to reduce the pollution from tanning wastewater but also to increase the available range of leather shavings.

Experimental Procedures

Equipment

YP402N-electronicbalance, PH meter and UV-Vis spectrophotometer were obtained from Shanghai Scientific Instrument Co, Ltd. ZDI-water bath oscillator and The HH-zk2 constant temperature water bath were purchased from Zhengzhou Penglai Instrument Co, Ltd. Magnetic stirrer, Volumetric flask, Beaker, Separatory funnel, Pipette and Scanning electron microscopy were all obtained from Tianjin Jiangtian Instrument Co, Ltd.

Materials

Bated goat pelts were used as raw material. The chemicals used for tanning process were of commercial grade and the chemicals used for analysis of tanning spent liquors were of analytical grade. The masking agents were of analytical grade such as Sodium formate, Sodium acetate, Sodium citrate, Sodium tartrate and Potassium phthalate.

Preparation of Zinc Ion Measuring Reagent

Preparation of Dithizone in Carbon Tetrachloride Solution

Dithionite ($C_{13}H_{12}N_4S0$ (0.25g) was dissolved in 250ml of carbon tetrachloride as stock solution of 0.1% (m/v) dithizone carbon tetrachloride. It can be stored in the brown regent bottle and placed in the refrigerator. The stock solution(10.0ml) was transferred to a 100 ml volumetric flask①, and diluted with distilled water to volume. Then solution (4.0ml) was transferred to a 100ml volumetric flask② and got the 0.0004% (m/v) solution. The 0.0004% (m/v) dithizone carbon tetrachloride can be got and it should be prepared at the time before used.

Preparation of Sodium Acetate Buffer Solution

Sodium acetate ($CH_3COONa•3H_2O$) (68g) was weighed and added to volume in 250ml volumetric flask, acetic acid and water was mixed at the ratio of 1:7. Two kinds of solution were mixed in equal volumes. The mixture was extracted by the dithizone carbon tetrachloride several times until the extract liquor turned to green, and then washed with carbon tetrachloride to remove excess dithizone.

Preparation of Sodium Thiosulfate

Sodium thiosulfate ($Na_2S_2O_3$•$5H_2O$) (25g) was weighed and added to a 100ml volumetric flask. The solution was extracted with dithizone carbon tetrachloride until the extract liquor showed green, and then washed with carbon tetrachloride to remove excess dithizone.

Preparation of Tanning Reagent

The zinc tanning agent was prepared with different kinds of zinc salts and at different concentration. The zinc salts used as tanning agent include zinc sulfate, zinc acetate, zinc chloride, etc. The zinc tanning solution was prepared as shown in the Table 1.

Zinc Standard Curve

Zinc particles (99.9%purity) (0.1g) was dissolved with 5ml hydrochloric acid and added to a 1000ml volumetric flask. The zinc standard stock solution was prepared and the zinc concentration of this solution is 100μg/ml.

Transferred 10.0ml of the zinc stock solution to a 1000ml volumetric flask, and diluted with distilled water to volume. The zinc concentration of the solution was 1μg/ml.

TABLE I
Type and concentration of zinc tanning agent.

Type	Weight (g)	Volume (ml)	Concentration (g/L)
Zinc acetate	42.21	500	25
	84.42		50
	126.63		75
	168.84		100
Zinc sulfate	55.31	500	25
	110.62		50
	165.93		75
	221.24		100
Zinc chloride	26.62	500	25
	53.24		50
	79.86		75
	106.48		100

Transferred 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 of 1μg/ml zinc solution to the separating funnel, and the absorbance was got according to the Dithizone spectrophotometry method. The zinc standard curve was measured and plotted as Figure 1.

The Optimal Conditions of Zinc Tanning Procedure

The Selection of the Zinc Tanning Agent

The pickling leather were tanned by different zinc tanning agents such as zinc sulfate, zinc acetate, zinc chloride as the comparison experiment. The zinc tanning agent could be selected preferably according to the hydrothermal stability of the wet-white. The zinc absorption rate of the leather was calculated by the amount of zinc in the solution before and after tanning.

The Selection of the Zinc Concentration on Tanning Process

Leather was tanned by zinc agents of different concentrations. It was set to be 25g/L, 50g/L, 75g/L and 100g/L. According to the hydrothermal stability of the wet-white, the appropriate concentration was selected and refined in a suitable range.

The Selection of a Suitable pH Range

Leather was tanned by zinc agents at different pH's, from 2 to 6, and the pH interval degree was 1. The hydrothermal stability of the wet-white can help to choose the suitable pH range.

The Selection of the Masking Agent for Zinc Tanning

The masking agents used commonly in leather production include sodium formate, sodium acetate, sodium citrate, sodium tartrate, terephthalic acid sodium, etc. The suitable masking agent and the optimal concentration were selected to make the effect of zinc tanning better.

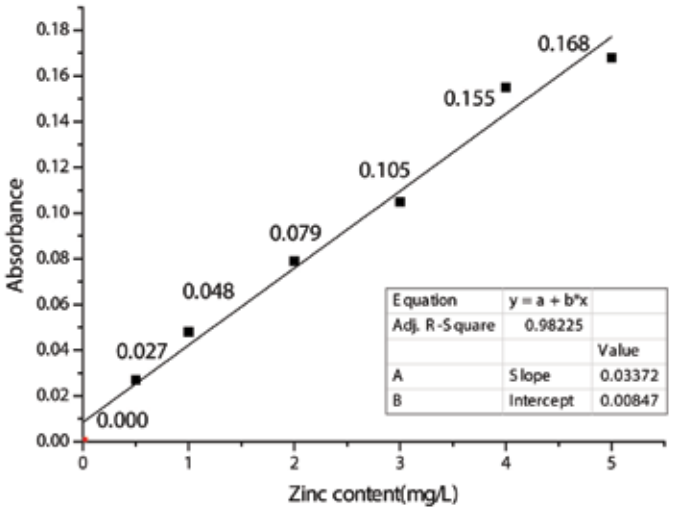

Figure 1. The zinc standard curve.

Results and Discussion

Hydrothermal Stability of Wet Leather Tanned with Zinc Salts

Choose zinc sulfate, zinc acetate, zinc chloride as tanning agents, and the pickling goat skin was tanned with them separately. As are shown in the Table 2 and Table 3, zinc sulfate has the most firmly combination with leather collagen in all the experimental zinc tanning agents. The long pair electrons exist in sulfate ions, and they can form polynuclear complexes with zinc ions. Therefore, the opportunity for the formation of multipoint binding is improved, which result in a better effect than other zinc salts.

TABLE II
The hydrothermal stability of different concentration of zinc tanning agent.

Concentration (g/L)	Zinc sulfate (°C)	Zinc acetate (°C)	Zinc chloride (°C)
25	66	58	54
50	68	60.5	58
75	68	59.5	58.5
100	68	65.5	60.5

There is no obvious change of the shrinkage temperature when the concentration is higher than 50g/L. Therefore, the selection of the optimum concentration is 50g/L in the zinc tanning process, and the concentration was used in the follow-up experiments.

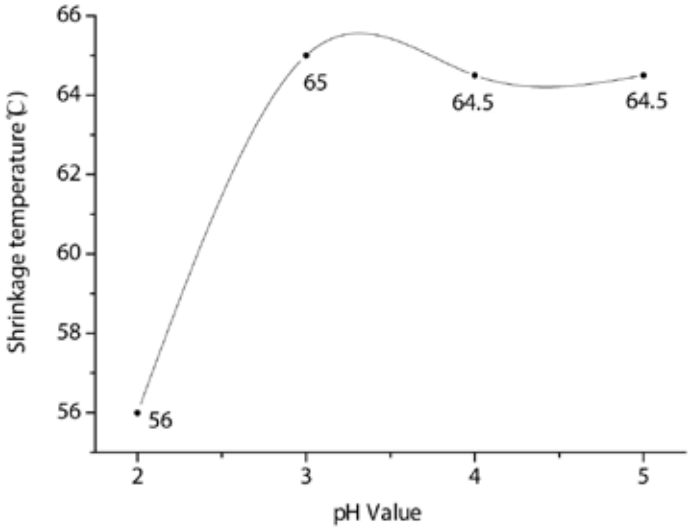

Figure 2. The influence of the pH to the zinc tanning when the concentration is 50g/L.

TABLE III
The selection of the zinc agent's species.

Reagent species	Zinc sulfate	Zinc acetate	Zinc chloride
Initial concentration (g/L)	50	50	50
Final concentration (g/L)	14.47	21.77	49
Hydrothermal stability after tanning (°C)	68	63	58
Utilization ratio (%)	71.05	56.46	2

Zinc absorption rate is desirable at a concentration of 50g/L. The suitable pH is 3, but the effect didn't show significant change in the range of pH 3- 5, The shirnkage temperature of leather rises significantly after zinc tanning and all the data above prove that the zinc salt has the tanning function.The effect of early tanning was not very ideal but the hydrothermal stability can be improved in the re-tanning process. Furthermore, the zinc tanning separately would be very conducive to the treatment of the shavings of the wet-white produced in the tanning process.

The Effects of Masking Agent

In the leather production, monocarboxylic acid salts and dicarboxylic acid salts are used as masking agents. Monocarboxylic acid salts include the formate salts and the acetate salts, while dicarboxylic acid salts include citrate salts, tartrate salts and phthalates salts, etc. The masking agents for experiments were selected with sodium formate, sodium acetate, sodium tartrate, sodium citrate and potassium hydrogen phthalate. As is shown in Table 4, sodium citrate is the best masking agent used in zinc tanning compared with other experimented masking agents.

The Principle of Zinc Tanning

Collagen is the main ingredient of the leather. The polypeptide chain consists of three winding peptide chains, and the peptide chains are constituted by the repetition structure of small peptide (Gly-X-Y). Gly-Pro-Hyp is the most commonly tripeptide sequence.[9] Gly accounts for about 33% which is the predominant amino acid component composed the leather collagen.[10] The combined form of zinc ions and amino acids is chelating. The steric configuration of zinc and collagen is inconclusive. However, the molecular structure can be determined by reference of the structure of zinc and histidine (Figure 3).

In the Figure 3, there are 3 covalent bonds and 2 electrovalent bonds in a molecular of the complex, and the hybridized orbital of Zn^{2+} is sp^3d. Zinc was combined with amino groups

TABLE IV
Hydrothermal stability the masking agent's species in zinc tanning process.

Reagent species	Ts1 (°C)	Ts2 (°C)	Ts3 (°C)	Ts4 (°C)	Ts5 (°C)
Sodium formate	68	68.5	69	68.5	69
Sodium acetate	66	68.5	69	71	70
Sodium tartrate	63	63.5			
Sodium citrate	78	81	66.5	66.5	66
Potassium hydrogen phthalate	59	61	64	68.5	

[1]The concentration of the 1-5 test groups is 0.05mol/L, 0.10mol/L, 0.15mol/L, 0.20mol/L and 0.25mol/L.
[2]The sodium tartrate can not be dissolved completely when the concentration is higher than 0.1mol/L.
[3]The potassium hydrogen phthalate can not be dissolved completely when the concentration is 0.25mol/L.

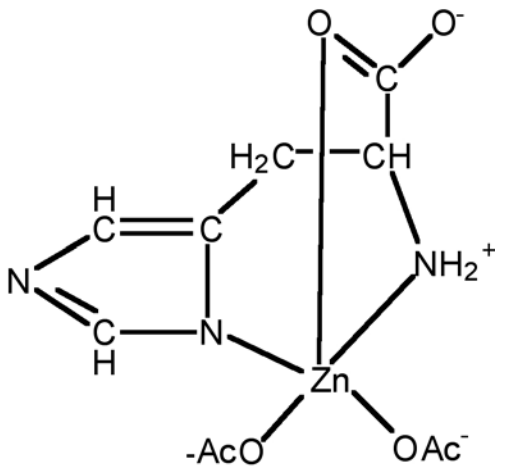

Figure 3. The structure of the amino acid chelated zinc.

so that the carboxyl groups were still capable to combine with other tanning agents. Therefore, the retanning process was able to improve the hydrothermal stability to meet the requirements successfully.

The principle of zinc tanning is that: zinc penetrates the leather under acidic condition and attracted by the positively charged amino-ion on the peptide chains. Then amino-ions and zinc will have coordination reaction and generate coordinaton compounds firmly when the distance is appropriate. According to the positive electrical property of wet-white hides, the fatliquoring and dyeing can be more effectively. Utilization of fatliquors and dyes are improved as well as chrominance of dyeing wastewater and residual quantity of fatliquor are reduced. All of these contribute to the treatment of the wastewater on leather production.

CONCLUSIONS

This research revealed that zinc has tannage effects and the masking agents can be helpful to zinc tanning. As the results, the optimum concentration for zinc tanning is 50g/L and the preferable pH is about 3.Sodium citrate is selected as the masking agent and used at the concentration of 0.1mol/L. The stability of the leather is better because of the linkage of ligand bond between the amino ions and zinc ions. According to the combination of the amino-ions and zinc agents, the physical properties of the wet-white hides were changed. All binding sites of carboxyl groups were free which benefited the retanning processed by chrome-zinc retanning agents. Besides, the positive electrical property of wet-white hides was in favor of the fatliquorting and dyeing.

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