Optimization and Design of Tanning Process Using Zr-Al-Ti Complex Tanning Agent

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Abstract

To solve the pollution of chrome in the process of making garment leather, goat pelts after pickling were tanned by Zr-Al-Ti complex tanning agent which was independent development. The optimum process conditions were found: the dosage of Zr-Al-Ti complex tanning agent was 12%, initial pH was 2.6-2.8, pretanning agent was modified glutaralde-hyde, tanning temperature was 35℃,tanning time was 4h，final pH was 4.0.Shrinkage temperature of leather tanned on such conditions was 93.6℃. Zr-Al-Ti complex tanning agent has the potential to replace the conventional chrome tanning agent. Otherwise, the pollution of chrome to people and environment were eliminated in process and leather products waste. The corresponding leather can meet the demand of garment leather. This work suggests the feasibility to exploit a new way for chrome-free cattle garment leather.

Keywords：Zr-Al-Ti Complex Tanning Agent ；Chrome-free tanning；Process；Optimization.

1 Introduction

As is well known, chrome-free tanning has become the research focus, due to the pollution and scarcity of chrome[1-5]. The major area of our research lab is about chrome-free tanning and other leather clean technology. We researched the chrome-free complex tanning agent earlier in the industry which can get rid of the chrome pollution at the source and satisfied the requirement of green chemistry[6-10].

Preliminary study showed that major factor effecting hydrothermal stability of chrome-free tanned leather were pretanning agent, mechanic effect, ratio, dosage of Zr-Al-Ti complex tanning agent, initial pH value ,final pH value, temperature and time[11-12]. Parameter optimization can improve the absorption and effect of Zr-Al-Ti complex tanning agent. The optimal combination of all the parameters can make the best tanning property. By single

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factor experiment, we figure out the tanning technological conditions' effect on tanning property of Zr-Al-Ti complex tanning agent, which will make guide to the application of Zr-Al-Ti complex tanning agent.

2 Experimental Procedures

2.1 Materials

Modified glutaraldehyde and cation oil were CP grade without any further purification. Goat pelts after pickling and Zr-Al-Ti complex tanning agent made by our own research lab.

2.2 Instruments

Drums(GSD，Φ=400mm) equipped with automatic controls of speed and temperature, Wu Xi Xinda Light Industry Machinery Co., LTD. Digital leather shrinkage temperature tester (MSW-YD4), Electronic Research Laboratory pf Shanxi University of science and technology.

2.3 Experimental method

2.3.1 Effect of mechanic action on shrinkage temperature

The drum rotational speed was adjusted to 10rpm, 15rpm, 20rpm, 25rpm, 30rpm on the condition that other parameters were the same. After tanned, the Ts of crust leather were detected and the effect of mechanic role on shrinkage temperature was analyzed.

2.3.2 Effect of ratio on shrinkage temperature

The ratio was adjusted to 0, 0.5-0.6、0.8-1.0、1.2-1.5、1.8-2.0 on the condition that other parameters were the same. After tanned, the Ts of crust leather was detected and the effect of ratio on shrinkage temperature was analyzed.

2.3.3 Effect of dosage of Zr-Al-Ti complex tanning agent on shrinkage temperature

The dosage of Zr-Al-Ti complex tanning agent was 4%、8%、12%、16%、20% on the condition that other parameters were the same respectively. After tanned, the Ts of crust leather were detected and the effect of dosage of Zr-Al-Ti complex tanning agent on shrinkage temperature was analyzed.

2.3.4 Effect of tanning temperature on shrinkage temperature

The temperature was normal temperature, 45-55℃、55-60℃ on the condition that other parameters were the same respectively. After tanned, the Ts of crust leather was detected and the effect of temperature on shrinkage temperature was analyzed.

2.3.5 Effect of initial pH value on shrinkage temperature

The initial pH value was 2.0-2.2、2.6-2.8、3.0-3.2 on the condition that other parameters were the same respectively. After tanned, the Ts of crust leather were detected and the effect of initial pH value on shrinkage temperature was analyzed.

2.3.6 Effect of final pH value on shrinkage temperature

The final pH value was 3.6-3.8、3.8-4.0、4.0-4.2 on the condition that other parameters were the same respectively. After tanned, the Ts of crust leather was detected and the effect of final pH value on shrinkage temperature was analyzed.

2.3.7 Effect of pretanning on shrinkage temperature

The pelt was pretanned by cation fat, modified glutaraldehyde ,nothing on the condition that other parameters were the same respectively. After tanned, the Ts of crust leather was detected and the effect of pretanning on shrinkage temperature was analyzed

2.3.8 Effect of tanning time on shrinkage temperature

The tanning time was 1、2、3、4、5、6h on the condition that other parameters were the same, respectively. After tanned, the Ts of crust leather was detected and the effect of tanning time on shrinkage temperature was analyzed.

3 Results and Discussion

3.1 Tanning technological conditions' effect on tanning property of Zr-Al-Ti complex tanning

3.1.1 Effect of mechanic action on shrinkage temperature

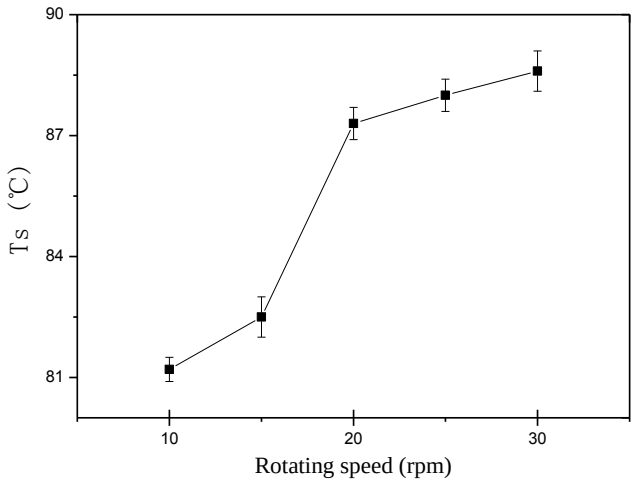

Figure1 effect of rotational speed on shrinkage temperature

The mechanic action of drum and ratio can make the tanning agent infiltrate through pelts, because that curve of pelts make micropores open and close which can speed up infiltrate and absorption of tanning agent. Many factors can influence mechanic action, such as size of drum, ratio, rotational speed and time.

As can be seen from figure1, with the rotational speed became faster, the Ts became higher on the condition that other parameters were the same. However, when the rotational speed was over 20rpm, the Ts increased slowly. When the rotational speed was 30rpm, the Ts were the highest. But if the rotational speed was too fast, the pelts would be rubbed heavily, causing damage of pelts. Especially when the ratio was small, the temperature would increase causing tanning agent combine with pelts on the surface. Considering all the conditions, the optimal rotational speed was 20 rpm.

3.1.2 Effect of ratio on shrinkage temperature

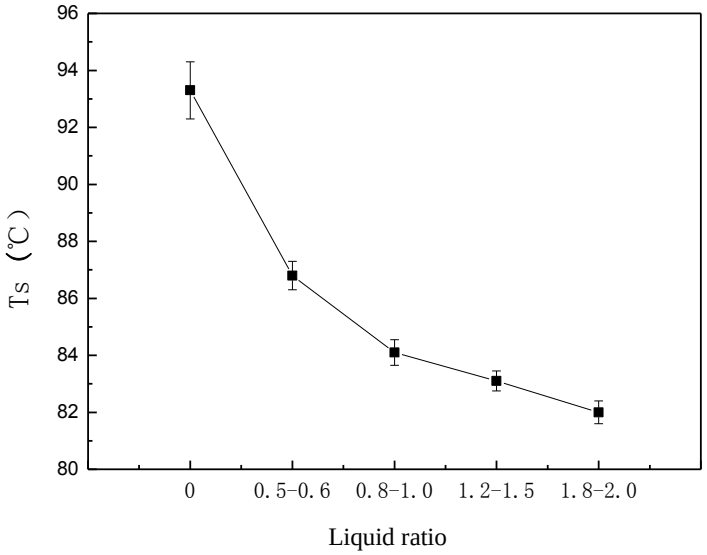

Figure2 effect of ratio on shrinkage temperature

Except mechanic action, diffusion also affects the infiltrate of Zr-Al-Ti complex tanning agent. Diffusion related to concentration of solution. The ratio smaller, the concentration higher, the infiltrate faster. The ratio was increased at later period. Zr-Al-Ti complex tanning agent was diluted and coordination faster. The molecular becoming bigger, which was in favor of combing Zr-Al-Ti complex tanning agent with pelts, enhancing tanning effect.

As is shown in figure 2, with the ratio becoming smaller, the Ts became higher. Decreasing the ratio would make the concentration of Zr-Al-Ti complex tanning agent increase, and the infiltrate became faster. Otherwise, when the ratio decreased under 0.5, the absorption rate of Zr-Al-Ti complex tanning agent increased observably. Amount of water liquor was also decreased. But the mechanic action was increased, and drum load increasing,

which could damage the drum. Considering all the conditions, the optimal ratio was 0.5.

3.1.3 Effect of dosage of Zr-Al-Ti complex tanning agent on shrinkage

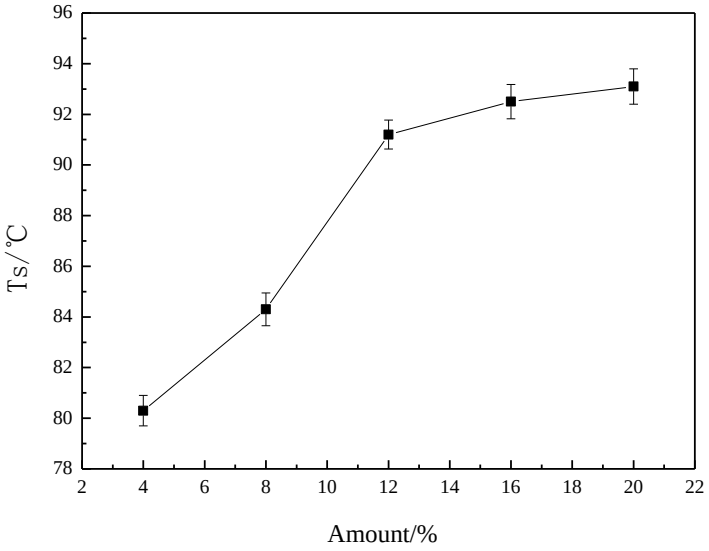

Figure3 effect of dosage of Zr-Al-Ti complex tanning agent on shrinkage

As is shown in figure3, with the dosage of Zr-Al-Ti complex tanning agent increasing, the Ts became higher. Higher dosage of Zr-Al-Ti complex tanning agent would make the concentration higher and make the infiltrate became faster, enhancing tanning effect. When the dosage of Zr-Al-Ti complex tanning agent increased above12%, the Ts increased slowly. What's more, increasing the dosage of Zr-Al-Ti complex tanning agent will increase costs. Considering all the conditions, the optimal dosage was 12%.

3.1.4 Effect of tanning temperature on shrinkage temperature

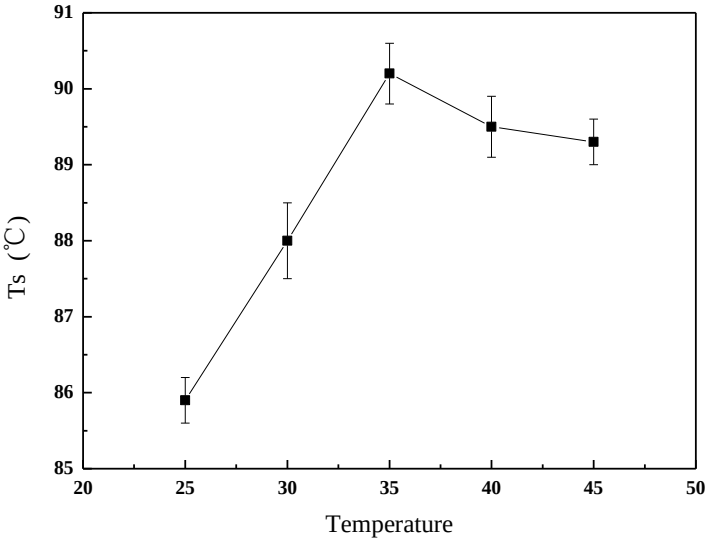

Figure4 effect of tanning temperature on shrinkage temperature

Normally, with the temperature increasing, the chemical reaction rate will increase the same as tanning. The temperature was normal temperature at the initial stage. This is better for the infiltrate. At the later stage, adding hot water to increase the temperature, speeding up the Zr-Al-Ti complex tanning agent hydrolyzing and coordinating big molecular and promoting the combination between Zr-Al-Ti complex tanning agent and collagen.

As is shown in figure4, the Ts gradually increase with the temperature increasing from normal temperature to 35℃. When the temperature was 35℃-45℃, the Ts changed small. But compared with Ts of that tanned at normal temperature, the Ts increased by a big margin. If the solution's temperature was too high, the pelts may denatured and molecular of Zr-Al-Ti complex tanning agent and collagen will become too big because of the coordination of Zr-Al-Ti metal complex, causing over tanning on the surface. If the temperature was too low, it's bad for combination between Zr-Al-Ti complex tanning agent and collagen. It shows that at the later stage of tanning, increasing temperature had effect on Ts. But when the temperature reached 35℃, increasing the temperature had less effect on Ts.

3.1.5effect of initial pH value on shrinkage temperature

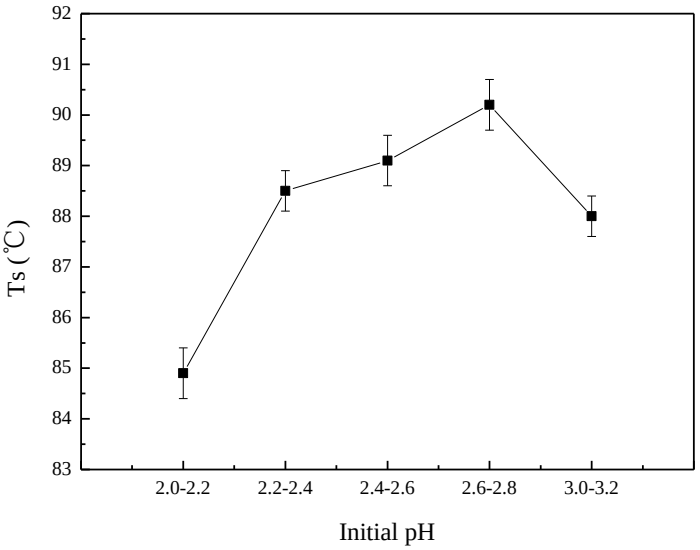

Figure5 effect of initial pH value on shrinkage temperature

As everyone knows, the key of tanning was controlling charge of collagen. pH of solution had close relation with the collagen's charge. When the initial pH was too low, it is hard for the hydrolyzing and coordinating of Zr-Al-Ti metal complex. The molecular was smaller and was easy to infiltrate into the pelts. But if the initial pH was too low, at later stage of tanning, there would be many problems, such as increasing the basification time, increasing the dosage of dicarbonate, hard to reach the final pH. When the initial pH was too high, it is easy for the hydrolyzing and coordinating of Zr-Al-Ti metal complex. The molecular was bigger, causing over tanning on the surface, which would make the grain rough.

As is shown in figure5, the Ts increase first and then decrease, with the increasing of initial pH. This is mainly because that when the pH value was too low(under2),carboxyl of collagen was unionizing and tanning agent could combine with collagen hardly. So it is in favor of infiltrate of Zr-Al-Ti complex tanning agent. With the increasing of pH, degree of ionization of carboxyl on the side chain of collagen increased, making the Zr-Al-Ti metal complex combine with collagen abundantly. If increase the pH, it is easy for the coordinating of Zr-Al-Ti metal complex and make the molecular bigger, causing precipitation. When the pH value was 2.6-2.8, the combination between Zr-Al-Ti metal complex and collagen could reach the highest.

3.1.6 Effect of final pH value on shrinkage temperature

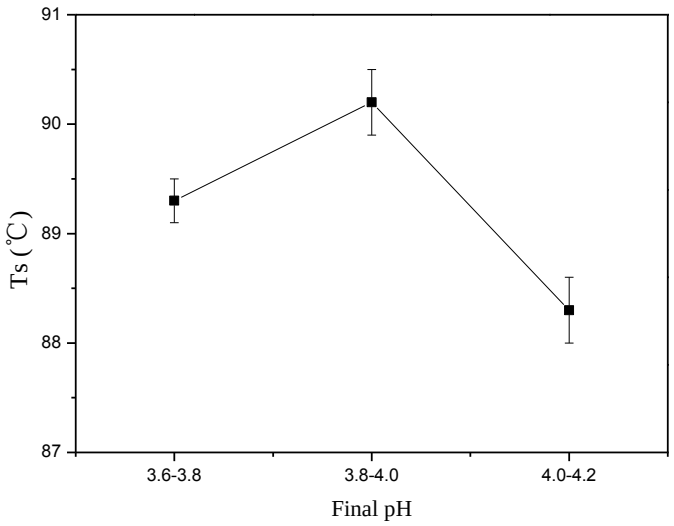

Figure6 effect of final pH value on shrinkage temperature

Basification is a process of adding alakalies, promoting hydrolyzing and coordination of Zr-Al-Ti complex tanning agent, speeding up the process of tanning. When Zr-Al-Ti complex tanning agent infiltrated through pelts completely, the pH value of solution should be increased, for promoting the absorption, combination and crosslinking.

As is shown in figure6, when the final pH value was 3.6-3.8, Ts of crust was 89.2℃. when the final pH value was 3.6-3.8, Ts of crust was 90.2℃.With the final pH value increasing, the Ts of crust increased. The major reason was that when the pH increased, it was easy for the coordinating of Zr-Al-Ti metal complex and makes the molecular bigger. The tanning agent was easy to combine with collagen, adding the tanning property. Ts of crust also increased. When the final pH value was4.0-4.2 , Ts of crust was only 88.3℃. That might because adding too much alkali, which could not distribute even, making more Zr-Al-Ti complex tanning agent combine with the pelts on the surface. This would cause over tanning on the surface.

3.1.7 Effect of pretanning on shrinkage temperature

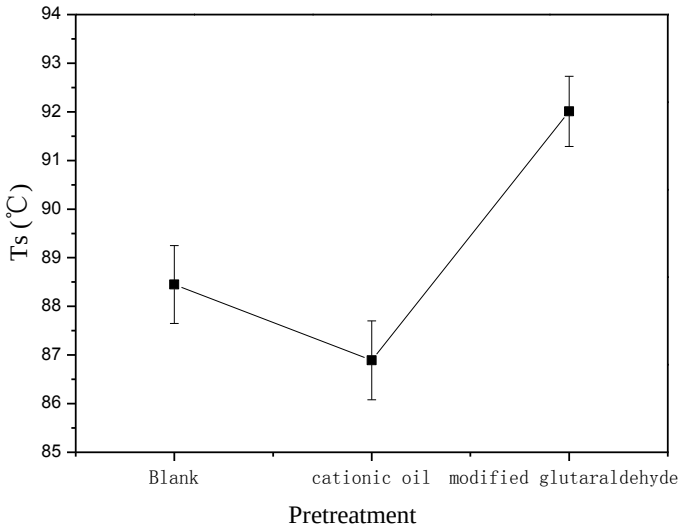

Figure7 effect of pretanning on shrinkage temperature

As is shown in figure7, Ts of pelts pretanned by modified glutaraldehyde was higher than that pretanned by cation fat and nothing. One reason was that α-amino group and ε-amino group of collagen had reaction with modified glutaraldehyde, making positive charge decrease, which was in favor of the coordination between carboxyl of collagen and cation of Zr-Al-Ti complex tanning agent. The other reason was that it could finalize the design of collagen fibers slightly. That is better for the permeating of Zr-Al-Ti complex tanning agent.

3.1.8 Effect of tanning time on shrinkage temperature

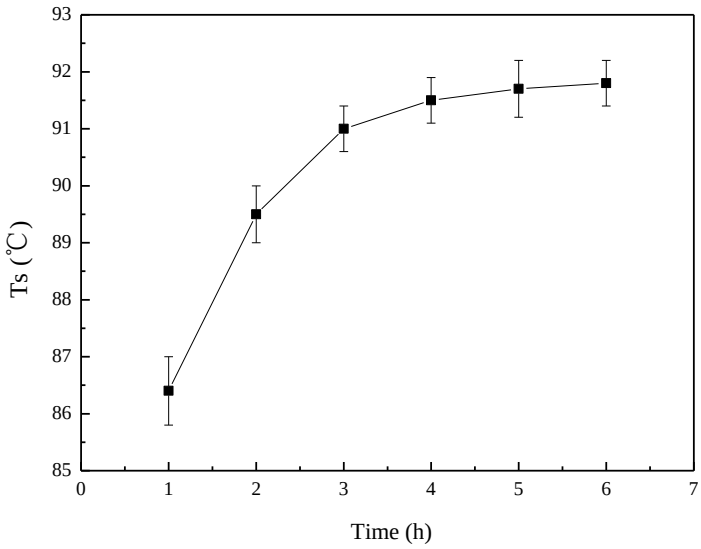

Figure8 effect of tanning time on shrinkage temperature

Tanning system of Zr-Al-Ti complex tanning agent was a balance system. Adding tanning time would make more Zr-Al-Ti complex tanning agent combine with the pelts. As is shown in figure8, with the tanning time (1-4h) increasing, Ts of crust increase. But when the time over 4h, Ts of crust only increased slightly. Considering the costing and efficiency, the optimum tanning time was 4h.

4 Conclusions

In this research, the Zr-Al-Ti complex tanning agent was used for tanning Goat pelts after pickling, the optimum process conditions were found: dosage of Zr-Al-Ti complex tanning agent was 12%, initial pH was 2.6-2.8, pretanning agent was modified glutaralde-hyde, temperature was 35℃.Shrinkage temperature of leather tanned on such conditions was the highest, 93.6℃. Zr-Al-Ti complex tanning agent had the potential to replace the chrome tanning agent and could solve the chromium salt pollution.

Acknowledgements

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