The Formation of Tanning Matrix and Combination Tanning Synergistic Effect

Hui Chen, Jie Yi, Ka Li, Zhihua Shan*

National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, P.R. China

Abstract: The produce of Combination Synergistic Effect by combination tannage using two kinds of tanning agents can improve the hydrothermal stability of collagen protein. The relative experiments have testified that Combination Synergistic Effect may result from the formation of Tanning Matrix by two kinds of tanning materials. The Tanning Matrix possesses high hydrothermal stability which can prevent the transformation of collagen protein when heated. At the same time, the Tanning Matrix can combine with collagen fibres through active groups. The building of Combination Synergistic Effect can build up the tanning mechanism of leather science and engineering and make non-chrome tanning method into reality.

Key words: combination synergistic effect; tanning matrix; collagen protein

1 Introduction

The Synergistic Effect would occur with two non-chrome materials combination tannage and could improve the hydrothermal stability remarkably. The research had proved that it was because that there formed the Tanning Matrix between two tanning agents. Because of stable structure, good resistance to heat stability, the Tanning Matrix can prevent the collagen molecule from conformation conversion when heated. In order to get more detailed information, the formation process, structure and resistance to heat stability of the Tanning Matrixes including metal-organic materials, organic-organic materials should be studied respectively. If the Tanning Matrix can be explained clearly, it would contribute to establish non-chrome tanning process and probe the resistance to heat materials of protein matters[1,2].

The leather-making is about one century; special scientists are researching the mechanism of tanning process. Up to now, some theories have been proved, but others still can't be explained reasonably. Generally speaking, the definition of tanning mechanism is the chemical characteristic of raw collagen is changed after the treatment of chemicals. Among the physical and chemical parameters, hydrothermal stability is the most important one. So, the theory of tanning mechanism is based on the change of hydrothermal stability [3,4,5].

2 The Combination Tannage

Today 90% of all leathers are manufactured with chrome tanning agents. So far chrome salt is used widely in leather-making because of its excellent features; no any other single tanning agent can displace it completely. However, tanners are finding it increasingly difficult to comply with emerging regulations with respect to the chrome content of effluent as well as the disposal of chrome containing solid wastes such as sludges, shavings, leather trimmings and buffing dust. In some countries there are restrictions on the use of chrome-tanned leathers for certain purposes. On the other hand, its toxicity on organism and environment is the disputed talking for people. Consequently, many researchers in this field have explored alternatives to the traditional chrome tanning system. The ideal tanning agent to rival chrome

*Corresponding author. Phone:+86-(0)28-85407289. E-mail:zhihuashan@sohu.com

should incorporate the following features[6-10]: high hydrothermal stability, lower metal salts, white or pale coloured, lightfast and low environment impact. Oxazolidines, a new class of tanning agent has been developed and patented. Alternative organometallic aluminum complexes were also studied and a patent established for the application of basic aluminum fomate with polycarboxylic acid. To solve these problems, scientists tried to looking for some no-chrome tanning agent consciously. Since there was no any other single tanning agent can substitute for chrome tanning agent, they made a method that some no-chrome metal materials and other materials with the property of tanning can be combined and applied to leather-making which was the initial concept of combination tannage. After that, the combination tannage was developed step by step, the perfect combination tannage definition is to two kinds of tanning agents with weaker tanning properties are made use of in leather-making which can achieve a higher hydrothermal stability and the effect was called Synergistic Effect. The foremost study of combination tannage was only limited with two kinds of tanning agents whose amounts are more than that of single tanning agent when used, so the initial Synergistic Effect was thought bond combination between tanning agents.

Some experiments had indicated that the shrinkage temperature(Ts) can be increased after the collagen of leather was modified, if some no-chrome metal salts and polyphenolic structure act with collagen. General organic materials including formaldehyde, glutaraldehyde, oxazolidine and catechin that the Ts of leather were between 84~87 ℃ , as the Ts of the wet blue can exceed 100 ℃ by glutaraldehyde, oxazolidine or catechin. Now aluminium ion(Al) -vegetable combination tannage is often used which can make the Ts up to 125℃. During 1940s Englishmen produced high resistant hydrothermal stability leather, Germen and American produced no-chrome shoe leather and top grade car seat leather with glutaraldehyde and vegetable combination tannage.

Frey and Beebe(1940) started the research of the combination tannage of vegetable and aluminum. In 1983, Waldo E.kallenberger also studied the combination tannage of vegetable and aluminum and found that especially control of pH and of the aluminum complex employed, the higher Ts of leather can be got. Tannaing agents with a polyphenolic substance followed by the application of dissolved metal salts, specifically vegetable tannins followed by aluminum salts, produces unexpectedly high thermal stability and acid resistance in the final leather(Fig.1).

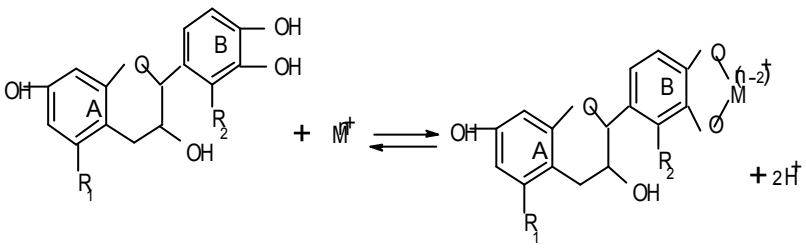

Fig.1 The reaction mechanism between combination tanning agents

The leather produced by the vegetable tannins or aluminum alone has more limited properties. These individual tanning agents have relatively weak tanning properties, especially the aluminum salts. The Synergistic Effect is produced by the combination of two relatively weak tanning materials, i.e., vegetable tannins and aluminum is well established. It is important that the knowledge to determine the most probable mechanism of reaction between collagen and the combination of vegetable tannins and aluminum salts. If the aluminum is an essential substance responsible for the high stability, the future work should be well-designed, combination tannages which include aluminum. On the other hand, if the vegetable tannins

are the main source of the high stability of the leather, the potential applications can be very great by developing combination of polyhydroxyphenyl compounds (polyphenolics) with reactive compounds that may or may not have tanning properties alone. Since vegetable tannins have great affinity for many metals, but very few metals possess tanning capabilities, the obvious demonstration of the lack of importance of the protein-metal interaction would be to produce a very heat-stable collagen using weak tanning or non-tanning metals and vegetable tannins. This is exactly what was done in these experiments. The results indicated that metals (divalent or polyvalent ions) produces exceptionally stable leathers, not because of coordination covalent links between tannins and collagen, but rather because the metals react with tannins to produce a tightly fit network around the collagen network. The result is two intimately entangled network which possess even greater stability than the collagen network which has only been stabilized by crosslinks within itself, such as chrome tanning[11-15].

The possible reactions during the tanning-retanning operation of collagen, with two different tanning agents, can be summarized as follows: A reaction may occur between individual tanning agents and the protein molecules with "no reaction" occurring between individual tanning agents; A reaction may occur between the tanning agents and the protein molecules with a "single reaction": occurring between individual tanning agents; A reaction may occur between the tanning agents and the protein molecule with a "complexing reaction" occurring between individual tanning agents; A reaction may occur between one tanning agent and the protein molecules with a "polymerization reaction" occurring between tanning agents[16,17].

These reasonable theories still don't explain why those materials without tanning property can produce higher hydrothermal stability.

3 The Formation of Tanning Matrix

It's for a long time that people believed hydrothermal stability of tanned collagen was up to the cross-linkage of tanning materials and skin collagen. The single combination tannage without change the Ts of collagen and the shrinkage of collagen is because of the broken of cross-linkage. The theory was proved unreasonable after A.D.Covington researched the Al-NMR spectrum in 1989. After the tanned leather by Al(III) achieved the Ts they compared the Al-NMR spectrum pre-shrinkage and post-shrinkage of collagen[18-23], there was not any change, which indicated the shrinkage of leather is not because of the broken of Al(III)-collagen side link group.

So, it can be hypothesized that the reaction of shrinkage is like the broken of hydrogen bond of collagen or leather which showed the shrinkage is independent of the process of tanning. The high hydrothermal stability through combination is the result of Synergistic Effect. Tanners were enlightened by the review that they think that tanning if the Tanning-matrix can be shaped which not only increased Ts but only more conveniently for form of combination tanning materials. It is believed that the Synergistic Effect is concerned with the combination of bonds between tanning agents and collagen, if the strength of bonds is increased such as offering valence force and adding the number of linkage which can improve the hydrothermal stability of collagen. It seems reasonable referring to the relationship between tanning agents and collagen. As for single metal tanned leather, the hydrothermal stability is dependent on the fastness and amount of linkage. As for inorganic tanning agents, the results of Cr(III),Fe(III)and Al(III) can give logical explanation. From the combination of stability with protein the sequence is Cr(III) > Fe(III) > Al(III), the tanned ending is $Ts_{(Cr(III))} > Ts_{(Fe(III))} > Ts_{(Al(III))}$. If adding the amount of vegetable tanning agent when tanned with pure vegetable, the Ts of leather can achieve 86 ℃. If combination tannage with vegetable and metal salts(Cr(III),Fe(III)and Al(III) respectively), the Ts obtained was Ts(Cr-vegetable) >

Ts(Fe-vegetable) > Ts(Al-vegetable). The above conclusion also indicated that there existed the relationship between tanning agent the bond strength and amount of collagen[24-28](Fig.2).

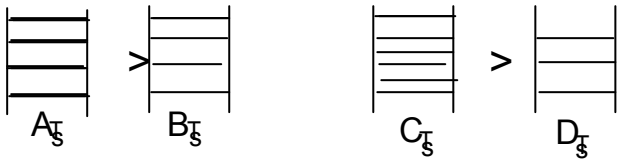

Fig. 2 The influence of bonds combination on the Ts

The further research disagreed the viewpoint, because it can't explain some atmosphere when combination tannage. For example, when tanned with the combination of Al-vegetable, the highest Ts is 125℃, the optimal pH=4.0~4.2. So according to above viewpoint, we believe that Ts is from the bonds combination of Al(III) and collagen basically. Under the situation the strength of bonds combination is better than that of single vegetable tanning. It is known that Al(III) compounds with the carboxyl group of collagen when tanning. But the Ts of Al(III)-vegetable combination is still 125℃ after cutting the carboxyl group of collagen[9]. In fact, even some metal ions without any the tanned characteristic such as Co(II), Mg(II) and Ni(II) combined with vegetable, the Ts can achieve about 100℃[10],which disobeys the relationship between the metal salts and the bond combination strength of collagen. On the other hand, on the assumption that the structure A(Fig.3) can improve the Ts to 108℃ with Al combination[11],which explains that the phenolichydroxyl, the amino of collagen and tipebond form the firm hydrogen. But from the Fig.1, we can also find after the structure B acts with Al the Ts is 106℃ which agreed with above the point. Except some multi-phenolic, multi-carboxyl organic materials, the metal can produce same Synergistic Effect with glutaraldehyder, oxazolidine and vegetable tannin. Aquino reported that the Ts can near 100℃ with combination of THPS and melamine. All facts can be made clear by the theory of the strength and amount of bond[29-31].

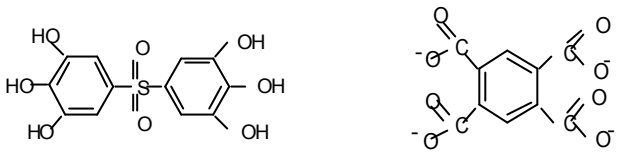

Fig.3 The formation of Tanning Matrix with organic materials and metal

For the mechanism of combination tannage there are two guesses, one is the structure stability of collagen molecule referring to Gustavson's point, Berman, etc. think if the conformation stability of collagen three helix can be strengthened that the hydrothermal stability can be increased, the stability depends on the super molecule stable internet with the hydroxyl-proline. After that, Copper and Weir did some experiments according to the energy change of collagen thermal deformation, they analyzed the activation kinetic parameters of three helixes such as entropy and enthalpy and believed that the hydrothermal stability of collagen was dependent on those parameters directly. They also tested the activation parameters of collagen with Cr(III), Zr(III), Al(III), Fe(III) and formaldehyde tanning and the declining order of Ts is same as that of activation entropy and enthalpy. The collagen tanned with Cr(III) is the highest, followed by Zr(III). These points accorded with single tanning with those tanning agents but tanning property still lies on the combination of tanning agents and collagen. It is also unreasonable to illuminate the Synergistic Effect by the theory. The other guess is that the Poly-Strut Firm Structure among collagen fibre or called Tanning Matrix by Covington.(Fig.4) produces the Synergistic Effect[32-34].

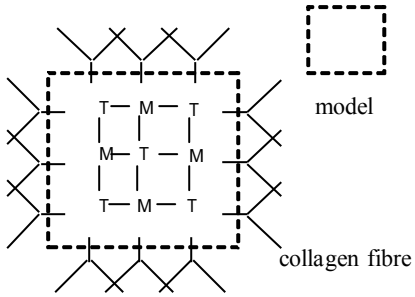

Fig.4 The Poly-Strut Firm Structure/Tanning Matrix T-vegetable tannin; M-metal ion

The Tanning Matrix formed by covalent bonds and the thermal deformation temperature is higher than that of collagen. These Tanning Matrixs were embedded in the fibre of collagen and combined with collagen fibre powerfully. Before thermal deformation happened the Tanning Matrix can support the collagen structure and prevent the conformation from converting which can produce higher Ts. In fact in 1997, after Ramasami from BSLT team researched the compound structure of Cr(III) salts, they put up one complete new theory, they think the reason of high Ts depends not only on the linkage of compounds and skin collagen, but also the formation of the three helix stable structure through the hydrolyzation polymer of Cr(III) hydrous ions. By X-diffraction, it had made sure that the weak binding strength between the three-dimensional Cr(III) hydrolyzed ligand polymers or Tanning Matrix and the collagen. Covington quoted Kronik and Cook's studies about the solidified bones and animals' shell of collagen, these mine materials didn't react with collagen, but phosphorus lime hydroxide penetrated the fibre and made the temperature of thermal deformation to 155 ℃, which indicated that it did the temperature thermal deformation of collagen and described the meaning of Tanning Matrix.

In 1914, Povorrin employed Ts as the judgment of tanning effect. Since last 70s, it has been proved that the thermal denaturalization shrinkage temperature of collagen protein is the converting point of phase, when the temperature reaches to the point, the special conformation of protein fibre or multieptide changed, the length or volume started to shrink obviously, as Mannich theory from macromolecule science, there are three methods to improve the thermal stability of macromolecule :A) strengthen the Tanningity (such as applying to Tanning chain to resistant heat and ring materials);B)carry out the linkage(such as controlling the space of chain action and possibility);C)producing the crystal(for only the crystalloid). From practical combination tannage results and existent theories, we can conclude that two kinds of tanning agents can produce firm combination and stable structure such as Tanning Matrix, the Tanning Matrix can combine with skin collagen and near the fibre, fill in the fibre interspace and support the conformation of fibre. When the skin collagen heated, if internal Tanning Matrix can't be destroyed, the conversion of collagen fibre conformation will be prevented which strengthens the Tanningity of collagen fibre and makes the Ts increase. So, it is reasonable that the combination Synergistic Effect is because of Tanning Matrix or Poly-Strut Firm Structure, which accords with Mark theory[35-37].

We also found that not all combination tannages in leather-making can form the Tanning Matrix and produce Synergistic Effect. Talking of chrome and vegetable or formaldehyde tanning agents, they were used as tanning-retanning or retanning-filling processes. So, furthermore research and experiments needed to make use of Tanning Matrix or Poly-Strut Firm Structure. the following are the detailed problems, firstly, make sure the optimal composition of Tanning Matrix including the structure characteristic and formation condition, secondly, find the difference of resistance to heat between the being Tanning Matrix of the skin collagen's outside and inside. Thirdly, develope the optimal condition of the formation of

Tanning Matrix including the amount of tanning agents, outside and inside conditions of collagen and the reaction order with collagen, etc.. All factors will bring the influence on the Ts, stability of leather in practice.

In order to make the no-chrome into realization, it's necessary to research the composing of Tanning Matrix and mechanism of being in the collagen which can improve the stability of collagen. The new Tanning Matrix cannot only enrich the tanning theory of leather science and engineering, but also develop new-fashioned, perfect combination tanning agents. The Tanning Matrix can make no-chrome clean process into industrial production. It can also contribute to the research of chemicals' modifying and biology organization of collagen protein in other fields.

4 The Outlook of Tanning Matrix Application

It's very important to investigate the component of the Tanning Matrix and understand the mechanism of Synergistic Effect for replacing chrome tanning completely. And the theory can build up the tanning mechanism of leather science and engineering and make non-chrome tanning method into reality. We can get some inspiration from the application of modified protein and information for biology medicine.

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