

# EFFECT OF RETANNING AGENTS ON DRY HEAT RESISTANCE OF LEATHERS

by

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## ABSTRACT

To obtain acceptable dry heat resistance of leather by using proper retanning agents, the effect of typical retanning agents on dry heat resistance was investigated. The results indicated that the leathers retanned by different retanning agents have varying dry heat resistance, and the dry heat resistance is not always positively correlated with hydrothermal stability. Heating leather at 150°C for 30 min in the dry state led to minor damage to the crosslinking of collagen fibers, such as destruction of hydrogen bonds or other weak crosslinks. The increase of water content in leather exhibits negative effect on the dry heat resistance. Therefore, it was observed that the retanning agent that has lower hydrophilicity lead to higher dry heat resistance of leather. In addition, it seems that the retanning agents with good filling property and thermal stability are effective in achieving high dry heat resistance of leather.

## RESUMEN

Para obtener una aceptable resistencia al calor seco en el cuero mediante el uso de agentes de recurtición adecuados, el efecto sobre la resistencia al calor de los típicos agentes de recurtición fue investigado. Los resultados indicaron que los cueros recurtidos por diferentes agentes de recurtición han variando la resistencia al calor seco, y la resistencia al calor seco no está siempre correlacionada positivamente con la estabilidad hidrotermal. Calentar el cuero a 150°C durante 30 min en estado seco conduce a daños menores en la reticulación de las fibras de colágeno, tales como la destrucción de los enlaces de hidrógeno u otras reticulaciones débiles. El aumento del contenido de agua en el cuero exhibe efecto negativo en la resistencia al calor seco. Por lo tanto, se observó que el agente de recurtido que tiene menor hidrofilia conduce a una mayor resistencia al calor seco en el cuero. Además, parece ser que los agentes de recurtido con buenas propiedades de llenado y estabilidad térmica son eficaces en el logro de alta resistencia al calor seco del cuero.

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## INTRODUCTION

Thermal stability of leather includes hydrothermal stability and dry heat resistance, and they are essential properties to evaluate quality of leather.<sup>1,2</sup> Hydrothermal stability has received considerable attention due to the fact that it is considered as a key parameter to evaluate the tanning effectiveness<sup>2</sup>, while few studies have been published on dry heat resistance. But in fact, the hydrothermal stability gives little indication of performance of leather and leather products in processing and practical usage,<sup>3</sup> because leathers are often treated at a high temperature or used in hot environment in the "dry" state. For example, heat setting process in shoe manufacture generally sets shoes to a required shape by dry heating leathers at 120 - 130°C, and sole attachment process may involve a higher temperature (up to 170°C) if soles are attached by cementing, vulcanizing or injection molding.<sup>4</sup> Furthermore, determination of dry heat resistance has been required in automotive upholstery leather testing. Therefore, the investigation of dry heat resistance of leathers is necessary in consideration of their processing and practical usage of leather products.

Past research has demonstrated that water in hide and leather is closely linked to their thermal stability. For example, Yannas<sup>5</sup> and Luescher *et al*<sup>6</sup> found that a decrease in moisture content of tissues rich in collagen caused an increase in the melting temperature. More recently, Komanowsky<sup>7</sup> even observed an interesting phenomenon that the melting temperature of tanned leathers, including chrome, vegetable and formaldehyde tanned leathers, was lower than that of untanned hide when the moisture content of untanned hide was reduced below 30%. So it is reasonable to assume that water content is an important factor influencing dry heat resistance. In addition, it is well known that the dry heat resistance is usually evaluated by measuring the area loss of leather under dry heating conditions, while the hydrothermal stability is generally reflected by using the shrinkage temperature (Ts) of fully hydrated leather. Thus, it seems also reasonable to suppose that high dry heat resistance may not be accompanied by high hydrothermal stability.

Nowadays, retanning plays a more and more important role in leather making, because it can contribute to further stabilization of collagen fibers and good handle of leather, such as fullness, softness, elasticity and so on.<sup>8</sup> In order to meet customers' requirements, a wide variety of retanning agents is used in retanning process, which could bring about a difference in adsorption capacity of leather to water<sup>9</sup> and may influence the thermal stability closely related to the moisture content of leather.

Here, in order to give tanners some suggestions on choosing proper retanning agents for obtaining acceptable dry heat

resistance of leathers, we investigate the effect of typical retanning agents on dry heat resistance and compare it with that on hydrothermal stability. Moreover, we analyze the main properties of retanning agents, which may lead to the difference in dry heat resistance by determination of water content, and Fourier Transform Infrared (FTIR) Spectroscopy and Thermogravimetric (TG) analyses.

## EXPERIMENTAL

### Materials

Chrome tanned cattle hides (thickness 1.0 - 1.1 mm, Cr<sub>2</sub>O<sub>3</sub> 3.20%) were employed for retanning trials. All the chemicals used were of commercial grade.

### Retanning by using different retanning agents

Chrome tanned leather samples (dimensions 30 cm × 30 cm) cut from back region of the leather were processed in the procedures given in Table I.

### Characterization of leathers

After staking, the leathers retanned by different retanning agents were first conditioned at 25°C and 60% RH for 48h, and then sampled for the following analyses.

#### Analysis of dry heat resistance

Dry heat resistance was estimated by determining the percentage loss of area (shrinkage ratio) of leather according to the standard method with minor modification.<sup>10</sup> The test sample (dimensions 10 cm × 10 cm) was heated at 105°C ± 5°C for 8 h or 150°C ± 5°C for 30 min in an oven. The areas of leather before and after heating were recorded and the shrinkage ratio was calculated as:

$$\text{shrinkage ratio} = \frac{\text{area of leather before heating} - \text{area of leather after heating}}{\text{area of leather before heating}} \times 100\%$$

#### Analysis of hydrothermal stability

The hydrothermal stability (Ts) of the retanned leather was measured using a common shrinkage temperature recording instrument. The leathers after staking and those after the measurement of dry heat resistance were first wetted back in water, and then their Ts were determined.

#### Analysis of water content in leather

The leather sample was dried to constant weight in an oven at 105°C for at least 6 h, and the water content was calculated as:

$$\text{water content} = \frac{\text{original weight} - \text{dry weight}}{\text{original weight}} \times 100\%$$

In general, the water lost under this drying condition includes weakly bound water.<sup>11</sup>

**TABLE I**  
**Post tanning processes**

Process	Chemical	Offer/%	Time	pH
Washing	Water (35°C) Formic acid (85%)	300 0.2	30 min	3.0
Neutralization	Water (35°C) Sodium formate Sodium bicarbonate	150 1 1.5	30 min 20 min × 3, 30 min	5.5 - 6.0
Washing	Water	200	10 min	
Retanning	Water (35°C) Retanning agent* Formic acid (85%)	150 10 1	60 min 15min × 3, 30 min	4.0

**\*Retanning agent**

1 - phenol formaldehyde syntan; 2 - melamine formaldehyde syntan; 3 - acrylic resin; 4 - mimosa tannin;  
5 - chrome tanning agent (Cr<sub>2</sub>O<sub>3</sub> 23%); 6 - control, no retanning agent.

Fatliquoring	Water Synthetic fatliquor Formic acid (85%)	100 8 1	60min 20 min × 3, 30 min	3.5
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Horse up, sammimg, vacuum drying at 60°C for 3 min, hang- drying overnight, and staking.

### **Analyses of FTIR**

To investigate the effect of heating on the structure of leather, the leathers before and after the measurement of dry heat resistance were analyzed by FTIR. The FTIR spectra of leather grains were recorded in the wave number range of 4500 - 400 cm<sup>-1</sup> using attenuated total reflectance - Fourier transform infrared (ATR-FTIR) spectroscopy (Nicolet iS10, Thermo Scientific, USA).

### **Thermogravimetric (TG) analysis**

TG analysis is a thermal analysis technique, which measures a sample's weight as it is heated or cooled in a furnace. TG analysis is commonly used to determine mass loss or gain of materials due to decomposition, oxidation, or loss of volatiles (such as moisture).<sup>12</sup> In a desired temperature range, mass changes during heating indicate that the materials are no longer thermally stable. To investigate the thermal stability of retanned leathers, the TG measurement of leather sample was conducted using a TG analyzer (TG209F1, Netzsch, Germany) with a heating rate of 10°C / min in a nitrogen atmosphere.

### **Characterization of retanning agents**

All the retanning agents used in Table I were dried at 40°C for 6 h (acrylic resin was dried in the form of thin film). Then they were conditioned at 25°C and 60% RH for 48 h. Afterword, the measurements of water content and TG of the retanning agents were carried out by the same procedures as above.

## **RESULTS AND DISCUSSION**

### **Thermal stability of different retanned leathers**

As mentioned previously, the main purpose of this study was to investigate the effect of usual retanning agents on dry heat resistance of leathers. For this purpose, we first evaluate the dry heat resistance of leathers retanned with different retanning agents by using the shrinkage ratio after heating the leathers at 150°C ± 5°C for 30 min. It is evident that the shrinkage ratios of leathers retanned by all the organic retanning agents are less than that of the control, as shown in Figure 1. These results suggest that the organic retanning agents can improve the dry heat resistance of leather. But chrome tanning agent has little influence on dry heat resistance of leather.

Comparing Figures 1 and 2(a), it is found that high dry heat resistance is not accompanied by high hydrothermal stability, which strongly confirms our previous prediction. The dry heat resistance of the leathers retanned by phenol formaldehyde syntan, melamine formaldehyde syntan and acrylic resin is higher than that of the chrome retanned leather, while their hydrothermal stability is lower. It seems that the retanning agents with good filling property are more effective than those with only cross-linking ability in achieving high dry heat resistance. These results also prove that the determination of dry heat resistance is indispensable for an accurate estimate of the thermal stability of leather, especially in the "dry" state.

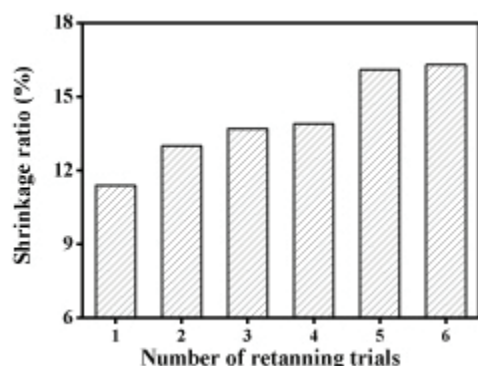


Figure 1. Dry heat resistance of retanned leathers after heating at 150°C for 30min.

1 - phenol formaldehyde syntan; 2 - melamine formaldehyde syntan; 3 - acrylic resin; 4 - mimosa tannin; 5 - chrome tanning agent; 6 - control, no retanning agents.

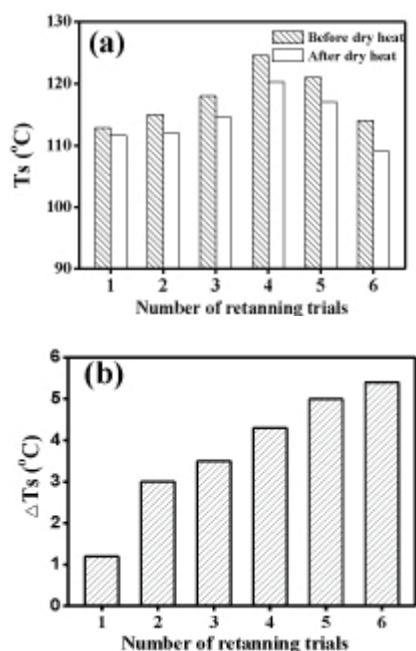


Figure 2. Hydrothermal stability of retanned leathers: (a) Ts before and after dry heat treatment; (b)  $\Delta T_s$ , difference between the Ts before and after dry heat treatment.

1 - phenol formaldehyde syntan; 2 - melamine formaldehyde syntan; 3 - acrylic resin; 4 - mimosa tannin; 5 - chrome tanning agent; 6 - control, no retanning agent.

After the measurement of dry heat resistance, the leathers were fully wetted back and then their Ts were determined. As shown in Figure 2(a), the dry heat treatment results in a slight decrease in Ts of leathers. But all the Ts of leathers after dry heat treatment are still higher than 109°C. As we know, the Ts reflects degree of crosslinking. The small change of Ts after dry heat treatment infers that dry heat treatment only causes minor damage to the crosslinking of collagen fibers, such as destruction of hydrogen bonds or other weak crosslinks.<sup>13</sup>

Furthermore, comparing Figures 1 and 2(b), it is shown that the effect of retanning agents on the Ts difference ( $\Delta T_s$ ) before and after dry heat treatment is very consistent with that on the shrinkage ratio. This fact suggests that the weak bonds among collagen fibers, which are easy to be broken during dry heat treatment, may be an important factor in enhancing dry heat resistance of leather.

### Analysis of leathers by FTIR spectroscopy

In order to further investigate the change of leathers resulting from dry heat treatment, the structures of leathers before and after dry heat treatment were characterized by FTIR spectroscopy. The FTIR spectra of the leather retanned by mimosa tannin before and after dry heat treatment are presented in Figure 3. It is obvious that the intensity of the broad band between 3500 and 3000  $\text{cm}^{-1}$  in the spectrum of the leather after dry heat treatment is lower than that before dry heat treatment, where this band is attributed to hydrogen-bonded OH and NH stretching vibrations<sup>14, 15</sup>. This result indicates that some hydrogen bonds between water molecules and collagen molecules were destroyed during dry heat treatment and that water molecules were desorbed from the collagen fibers.<sup>16</sup> In addition, similar results were found in the leathers retanned by using the other retanning agents (data not shown). The absorption peaks at 1650 and 1550  $\text{cm}^{-1}$  are almost identical in both the spectra of the leathers before and after dry heat treatment. According to Doyle *et al.*, the absorption peaks at 1650 and 1550  $\text{cm}^{-1}$  are assigned to the characteristic peaks of amide I and II in collagen, respectively.<sup>14</sup> Hence, it is probable that dry heat treatment has only a very slight effect on the secondary structure of leather.

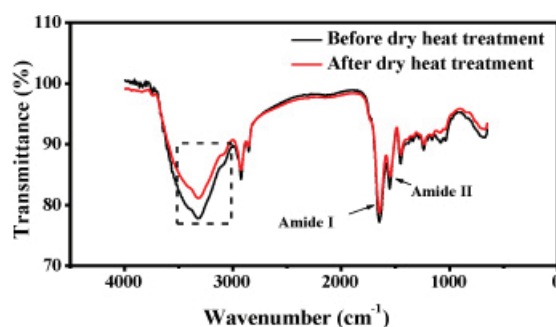


Figure 3. FTIR spectra of leathers retanned using mimosa tannin before and after dry heat treatment

### Effect of water content on dry heat resistance of leather

As we know, water in leather is usually linked to the thermal stability.<sup>5-7</sup> So we studied the effect of water content in leather on dry heat resistance in this section. Figure 4 provides the water contents of leathers retanned by different retanning agents and the shrinkage ratios of leathers after heating at  $105^\circ\text{C} \pm 5^\circ\text{C}$  for 8 h. It can be seen that the leathers retanned by different retanning agents have varying water contents as well as shrinkage ratios. The increase of water content in leather exhibits negative effect on the dry heat resistance.



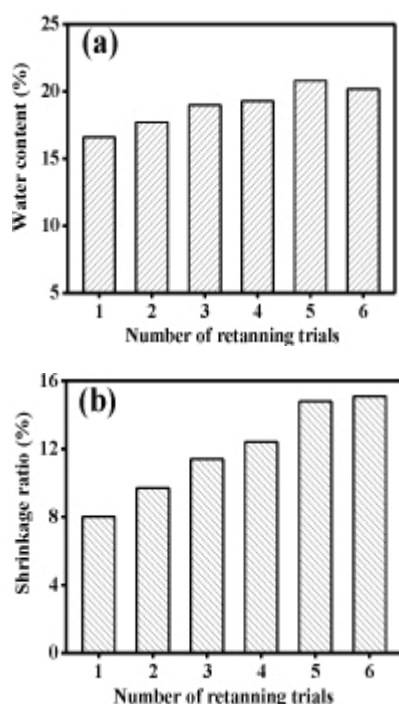


Figure 4. Water content (a) and shrinkage ratio (b) of retanned leathers.

1 - phenol formaldehyde syntan; 2 - melamine formaldehyde syntan; 3 - acrylic resin; 4 - mimosa tannin; 5 - chrome tanning agent; 6 - control, no retanning agent.

These results may be due to the fact that the water loss, which occurs during dry heat treatment, can result in a decrease in interfibrillar distance and therefore, lead to an area loss of leather. In other words, the interfibrillar distance is increased with increasing amount of bound water.<sup>17</sup> These results suggest that bound water in leather plays an important role in dry heat resistance of leather.

For understanding why water content in leathers was different when various retanning agents were used, we investigated adsorption capacity of retanning agents to water. The retanning agents were first dried at 40°C for 6 h, and then conditioned at 25°C and 60% RH for 48 h to obtain adsorption equilibrium of water. Finally, the water content of the retanning agents was measured as an indication of the equilibrium adsorption capacity of retanning agents to water. As can be seen in Figure 5, the equilibrium water contents of phenol formaldehyde syntan and melamine formaldehyde syntan are lower than those of acrylic resin, mimosa tannin and chrome tanning agent. This should be due to the fact that a large number of phenolic hydroxyl groups in vegetable tannin and carboxyl groups in acrylic resin are prone to form hydrogen bonds with water. The high water content in chrome tanning agent may be attributed to its high content of neutral salt that has strong adsorption ability to water. Obviously, the equilibrium water content of a retanning agent is positively correlated with the water content of leather being retanned, which implies that the hydrophilicity of retanning agents is a main factor influencing water content of leather, so as to affect dry heat resistance of leather. That is, a retanning

agent that has higher hydrophilicity would lead to a lower dry heat resistance of leather.

### TG analysis

The weight losses of retanned leathers and retanning agents are shown in Figure 6. The weight loss of leather between room temperature and 100°C, which mainly results from the weakly bound water loss, is much larger than that between 100°C and 250°C, as shown in Figure 6(a). Furthermore, it is interesting to

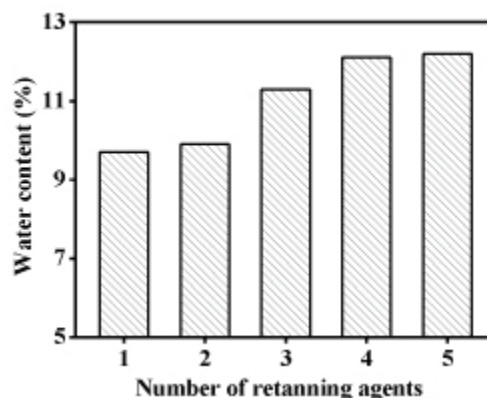
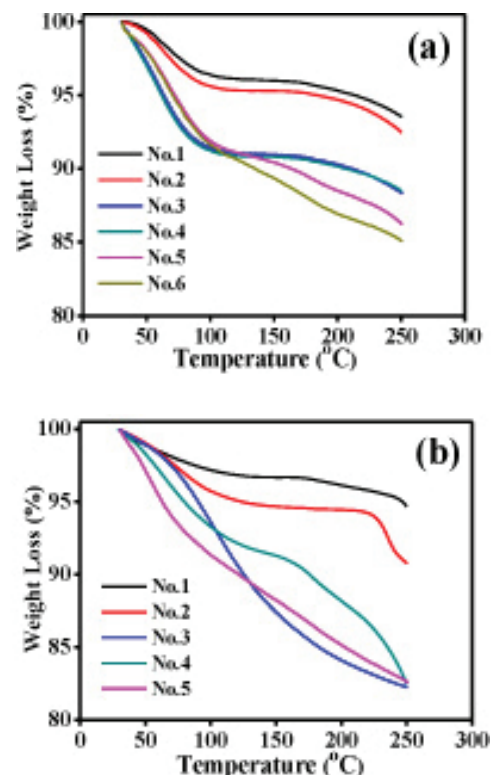


Figure 5. Water contents of retanning agents after conditioning at 25°C and 60% RH for 48 h. 1 - phenol formaldehyde syntan; 2 - melamine formaldehyde syntan; 3 - acrylic resin; 4 - mimosa tannin; 5 - chrome tanning agent.



TG curves of retanned leathers (a) and retanning agents (b). 1 - phenol formaldehyde syntan; 2 - melamine formaldehyde syntan; 3 - acrylic resin; 4 - mimosa tannin; 5 - chrome tanning agent; 6 - control, no retanning agents.

observe that the trend of total weight losses of retanning agents (Figure 6(b)) is positively correlated with that of leathers (Figure 6(a)), which is also consistent with that of the shrinkage ratios (Figure 1). This seems to imply that the thermal stability of retanning agents should be another factor influencing the dry heat resistance of leather.

### CONCLUSIONS

The dry heat resistance of retanned leathers is not always positively correlated with their hydrothermal stability. This phenomenon suggests that the factors influencing dry heat resistance are different from those influencing hydrothermal stability. The determination of dry heat resistance is necessary for accurate evaluation of the thermal stability of leather, especially in the "dry" state. Retanning by using retanning agents with good filling property, high thermal stability and low hydrophilicity is beneficial to obtain higher dry heat resistance of leather.

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