THE APPLICATION OF A PHOSPHORUS-NITROGEN FLAME RETARDANT RETANNING AGENT

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In order to improve the fire resistant of leather to meet the condition of higher fire-safety requirement, a phosphorus-nitrogen flame retardant retanning agent (M-THPS-U for short) was synthesized. The vertical flame test, oxygen index test, smoke density, mechanical properties, thicken rate, and shrinkage temperature were used to evaluate the property of M-THPS-U, and the dosage of M-THPS-U was optimized at the same time. Furthermore, the hide powder acting with M-THPS-U was used to study the flame resistant effect in detail by thermogravimetry (TG). The results showed that the fire resistance of leather was improved obviously by using 5% of M-THPS-U. With the increase of M-THPS-U dosage, the mechanical properties were dropped, but the fire resistance, thicken rate, and shrinkage temperature were raised. The thermogravimetry results indicated that the fire retardant could promote the fire resistance of leather by accelerating leather fiber into char. In short, not only does M-THPS-U improve the fire resistance of leather, but it also has retanning and filling effects.

Keywords: leather, phosphorus-nitrogen flame retardant, retanning

INTRODUCTION

Leathers have a better fire resistance than cloth and plastic materials in normal situation. The oxygen index of the leather untreated by flame retardant is between 21% and 27%, which is a self-extinguishing material (Ou, 2002). There is no melt dropped during the leather burning process, but the flameless combustion time is long and a lot of smoke together with nasty smell is emerged. The demands for fire-safety are increasing, so the leather must be treated by fire retardant to improve flame resistance (Huang, 2005).

A lot of flame retardant had been synthesized and applied to improve fire resistance of leather (Ling *et al.*, 2012), especially phosphorus-nitrogen flame retardant (Wang *et al.*, 2006), because it had the synergistic effect on fire resistance with two fire retardant elements, which was a hot area of research in recent years (Huang *et al.*, 2004). In this research, a phosphorus-nitrogen flame retardant retanning agent (M-THPS-U for short) was synthesized by using tetrakis hydroxymethyl phosphonium sulfate (THPS), urea, formaldehyde and sodium bisulfite. Because there were two fire retardant elements in M-THPS-U, the flame resistance was excellent. On the other hand, a lot of active groups such as hydroxymethyl were existed, which made it had good performances of retanning and filling.

EXPERIMENTAL

Materials

Shaved goat wet blue with average thickness of 1.0mm was made in the lab as a

common process. Other chemicals used for leather processing were commercial grade, and reagents used for analysis and synthesis were research grade.

Preparation of M-THPS-U

72g urea and 81.3g THPS were put into a round-bottom flask, then some distilled water was added into the system and the flask was stirred at 80°C for 2 hours. After cooling down to the room temperature, a 0.5mol/L NaOH solution was used to adjust the pH to about 8.5. 59.1g formaldehyde and some water were added, then the system was stirred at 65°C and reflux condensation was processing at the same time. Another 31.2g sodium bisulphite was added again for 50min to get the M-THPS-U. The M-THPS-U was colorless oily liquor and the solid content was about 45%.

Preparation of Fire Resistant Leather

The shaved goat wet blue was treated by M-THPS-U as shown in Table 1.

Table 1. The process of flame retardant leather

Process	Materials	T/°C	Dosage %	t/min	Remark
Washing	Water	35	200		
	Penetrant agent		0.3	10	
	Degreasing agent		0.2	20	Drain
Washing	Water	25	200	10	Twice, Drain
Neutralizing	Water	35	200		
	HCOONa		0.5	20	
	NaHCO3		0.9	60	pH: 6.0, Drain
Washing	Water	25	200	15	Drain
Fire retardant*	Water	35	150		
	M-THPS-U		X	60	
	HCOOH		1.2		pH: 4.0～4.2, Drain
Washing	Water	25	200	10	Twice, Drain
Drying					

*The leather was not treated by M-THPS-U used as a control.

Preparation of Fire Resistant Hides Powder

The hide powder (slightly chromed, chrome content was about 0.1%) and water (the mass was about 500% of hide powder) were mixed in a flask at room temperature for 4 hours to allow hide powder swelling. 10% M-THPS-U (based on the solid content) was acted with hide powder in thermostatic water bath oscillators at 30°C for 3 hours. After washing by distilled water some times and filtration, the hide powder treated by M-THPS-U was dried in a vacuum drying oven at 40°C for 5 hours. The hide powder was not treated by M-THPS-U was used as control.

Testing Methods

FT-IR Test of M-THPS-U

The M-THPS-U was purified by absolute alcohol, and after drying in a vacuum drying oven, the white solid was obtained. The samples were ground with KBr and made into pellets, then a Nicolet10 FT-IR (American Thermo Scientific Corporation)

was used to scan in the wavelength range of 400-4000cm^{-1} for 32 times, and the data was recorded.

TG/DTG of Hide Powder

The treated and control hide powder were dried at 40°C for 24 hours. A NETZSCH TG 209 F1 thermogravimetric analyzer (Germany) was used for analysis. The samples were put into Al_2O_3 crucibles and heated at 10°C/min in a N_2 atmosphere (flow N_2:100mL/min); the range of temperature was from 40 to 800°C. After the test, the TG curve was derivative, and the DTG curve was obtained.

Sampling for Flammability Test

A set of samples, including 5 pieces for the vertical flame test, 5 pieces for oxygen index test and 3 pieces for smoke density test were taken from each treated and control leather pieces. The samples for the vertical flame test were 51 mm by 317.5 mm, and their long axis was perpendicular to the backbone. Oxygen index test samples were 52 mm by 140 mm and samples for smoke density test were 50 mm by 52 mm. The prepared samples were stored in a chamber at 20±1°C and 65±2% relative humidity for 48 h and then the thickness of each sample was measured.

Flammability Test

The vertical flame, the oxygen index and the smoke density of all the samples were tested according to ALCA Method E50, ASTM D 2863-77 and GB/T 8627-1999 respectively.

Mechanical Properties and Shrinkage Temperature (Ts) Test

The leathers were sampled and conditioned as the standard method. The tensile strength and tear strength of leather were tested by tensile machine (AI-7000S, China) following the standard method. The shrinkage temperature was tested by Shrinkage Temperature Tester (MSW-YD4, China) with the bath of glycerin (75%). Each value was an average of two which were along and across the backbone.

RESULTS AND DISCUSSIONS

FT-IR of M-THPS-U

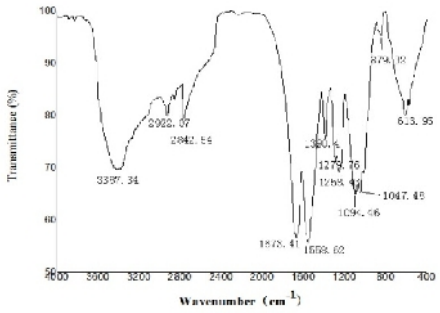

Figure 1. The FT-IR of M-THPS-U

Figure 1 showed the main absorption of M-THPS-U. The peak at 1047cm^{-1} was the -CH_2OH, which indicated that the hydroxymethyl was appeared in M-THPS-U. The peak at 3387cm^{-1} was due to the C-N stretching vibration of M-THPS-U, showing the urea acting with formaldehyde. The peak at 1258cm^{-1} was the characteristic absorption peak of –OH. The peak at 879cm^{-1} was due to the S=O stretching vibration of M-THPS-U, indicating sulphonation reaction happening. All these results indicated that M-THPS-U had been synthesized as expected.

Thermogravimetry of Hide Powder

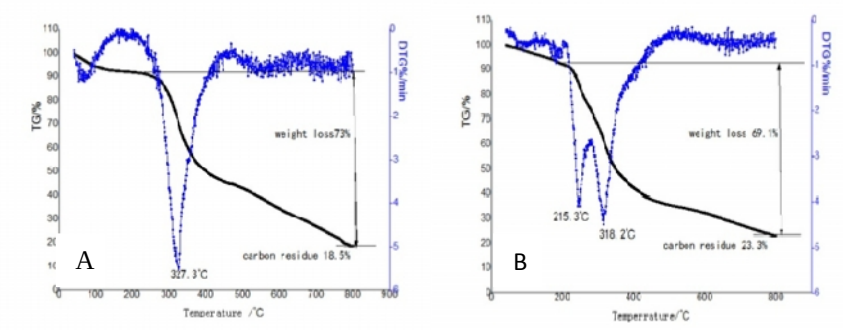

Figure 2. The TG curves of the hide power (A was treated sample, B was control)

As shown in figure 2, control hide powder was break down rapidly at 327.3°C, the weight loss was 73% during the process, and the carbon residue was only 18.5% at 800°C. The flame retardant hide powder had two rapid weight loss stages; there were 215.3°C and 318.2°C, and the carbon residue was 23.3% at 800°C. These results indicated that M-THPS-U could increase the carbonization of collagen fiber, and decrease the weight loss. According to Van Krevelen' theory, there was a liner relation between flame resistant effect and carbonization, the higher carbonization, the better flame resistant effect. The carbon residues were observed by optical microscope also proved these proofs. Furthermore, the DTG curve showed that M-THPS-U could slow down the decomposition velocity of leather and enhance the thermal stability of fire resistant leather.

The Flammability of Fire-Resistant Leather

Table 2. The vertical combustion of leather

Dosage of M-THPS-U	Flame combustion (s)	Flameless combustion (s)	Char length (cm)	Weight loss (%)	Oxygen index (%)	Smoke density (%)
0%	2.68	16.48	0.89	4.19	27.5	54
3%	1.06	0	0.64	3.32	30.6	48
5%	0	0	0.56	3.08	32.1	45
7%	0	0	0.52	2.91	32.9	44

As shown in Table 2, with the increasing of M-THPS-U, the flame combustion, flameless combustion, char length and weight loss were all decreasing, and the oxygen

index of leathers treated by M-THPS-U were increasing. When the dosage of M-THPS-U was 5% (based on the weight of wet blue), the flame combustion, flameless combustion were zero second, the char length and weight loss were 0.56cm and 3.08%, which were decreasing by 37% and 26% compared with control respectively.

Compared with control, the oxygen index was increasing by 11%~20% respectively. The smoke density was decreasing with the using of M-THPS-U, especially the dosage of M-THPS-U was 7%. During the combustion process, the collagen fiber was dehydrated by the M-THPS-U to form a loose carbon to isolate heat and oxygen, which could cut down the smoke and raise the oxygen index. The dosage of M-THPS-U was higher, the flame resistant effect was better, indicating that M-THPS-U could be used for making high quality fire resistant leather.

The Mechanical Properties, Ts and Thicken Rate of Leather

Table 3. The mechanical properties, Ts, and thicken rate of leather

Sample	Tensile strenth (Mpa)	Tear strenth (N/mm)	Elongation (%)	Ts (°C)	Thicken rate (%)
Control	25.4	73.5	32.7	109.1	0
M-THPS-U 3%	23.1	63.7	33.4	112.8	6.3
M-THPS-U 5%	21.8	59.5	31.2	114.3	8.1
M-THPS-U 7%	19.7	57.5	30.6	113.7	8.9

As shown in Table 3, with the dosage of M-THPS-U increasing, the mechanical properties were decreasing, but the Ts and thicken rate were rising. M-THPS-U was consisted of many active groups which could act with collagen. Stress concentration was created by these cross-links between collagen fibers, which could lower the mechanical properties. The thicken rate reflected filling effect and the increasing of Ts expressed the tanning effect. The leather treated with M-THPS-U was thicker and had higher Ts, showing that M-THPS-U had filling and tanning effect.

CONCLUSIONS

After treated with M-THPS-U, the smoke density, flame combustion, flameless combustion, char length and weight loss of leather were decreasing and oxygen index was rising, indicating M-THPS-U had excellent flame retardance; the shrinkage temperature and thicken rate of leather were increasing, showing M-THPS-U had filling and tanning effect. In sum, M-THPS-U could use for making high performance fire resistant leather.

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