Preparation of Flame-Retardant Leather Pretreated with Pyrovatex CP

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ABSTRACT: Resistance to burning is one of the most useful properties that can be imparted to leather. Pyrovatex CP is rich in phosphorus and nitrogen and has been successfully used as a flame-retardant agent in the presence of etherified methylolated melamine (EMM). The effects of a finishing formulation containing Pyrovatex CP and EMM on the flame retardancy and other properties of modified leather have been studied under different conditions. The synergistic effect of the N/P ratio has been thoroughly investigated through the estimation of the nitrogen and phosphorus contents, and their impact on the flame retardancy, tensile strength, and elongation at break of the treated leather has been studied. An investigation of the different factors has led to the following conclusions: (1) the P and N percentages increase with increasing curing temperature and time, (2) increases in the Pyrovatex CP and EMM concentrations are accompanied by an enhancement of the P and N percentages, and (3) all samples exhibit loss in their tensile properties but within an acceptable range (20%). © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2039–2043, 2006

Key words: fibers; flame retardance; stabilization; thermogravimetric analysis (TGA)

INTRODUCTION

Today, leather through its many uses has become an essential commodity of man. Leather is a material that has reasonable mechanical resistance, good chemical stabilization, and acceptable thermal behavior. Now leather is widely used in furniture and clothing, so, considering the hazards of fire and cigarette ignition, we are trying to enhance the flame resistance of leather.

If leather is ignited and provided with sufficient oxygen and heat input, it will burn, as most organic polymers do. Flame-retardant treatments for leather merely increase the amount of oxygen or heat required for combustion. Flame-retardant leather is self extinguishing once the flame or heat source is removed. The utilization of phosphorus compounds chemically reacted with or deposited within the leather fibers represents the most significant contribution to the field of durable flame retardancy.[1] The compound *N*-methylol dimethyl phosphorus propionamide, a retardant finish, has been used in the United States since 1968.[2]

It has been known for over 30 years that phosphorus compounds can retard flame in cellulosic textiles. Recently, most durable fire-retardancy finishing has been done by the application of organophosphorus compounds.[3–5] The results illustrate that phosphorus and nitrogen are synergistic in flame-retardant finishes.[6] There is general agreement that acid-forming phosphorus compounds are very effective in preventing flaming. Their action has been attributed to a protective charring at a subflame temperature, which prevents ignition.[7]

We undertook this work to investigate the effect of phosphorus-based flame-retardant compounds containing nitrogen atoms on the treatment of leather samples and to improve their flame retardancy. Flame-retardant finishing was carried out according to the pad–dry–cure method with finishing formulations consisting of Pyrovatex, etherified methylolated melamine (EMM), and the catalyst $(NH_4)_2SO_4$ at different concentrations. After the finishing process, the samples were monitored for nitrogen and phosphorus contents. The work was further extended to include the characterization of treated leather samples with respect to the flammability, tensile strength, and elongation.

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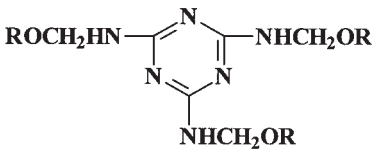
EXPERIMENTAL

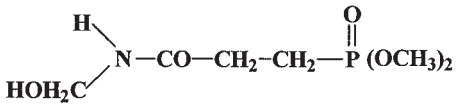
Materials

Chrome-tanned crust leather hide was supplied from a commercial tannery in the Misr-El-Kadima region, where most Egyptian tanneries exist.

EMM, under the commercial name Cassurit HML, was kindly provided by Hoechst AG (Berlin, Germany). Pyrovatex CP, with 50% active material, supplied by Ciba–Geigy (Basel, Switzerland), was used as the flame-retardant agent:



(EMM)



(Pyrovatex CP)

Flame-retardant finishing treatment

The finishing formulation consisted of EMM (50–80 g/L), Pyrovatex CP (100–200 g/L), and H_3PO_4 (20 g/L). Finishing was carried out according to the pad–dry–cure method. The finishing treatment was carried out under different conditions, as detailed in the text. The treated samples were washed at 60°C for 15 min before analysis.

Evaluation of the sample properties

The extent of the reaction of Pyrovatex CP with leather was expressed as the nitrogen and phosphorus contents. The nitrogen content was determined according to the kjeldahl method.[8] The phosphorus content was determined according to the methods described by Olsen[9] with a PerkinElmer (Berlin, Germany) Lambda 2 spectrophotometer during the project "Micronutrients and Other Plant Nutrition Problems" at the National Research Center (Cairo, Egypt).

The flame retardancy was monitored according to the vertical test method.[10]

The thermogravimetric analysis (TGA) of treated and untreated leather samples was carried out from 30 to 700°C/min under a nitrogen atmosphere at a heating rate of 10°C/min with a Shimadzu (Tokyo, Japan) TGA-50.

The flammability properties were evaluated with the ASTM oxygen index method[11] for measuring the minimum oxygen concentration to support candlelike combustion of different products.

Dumbbell-shaped specimens (5 cm × 1 cm with a 4-mm neck width) were used for the measurement of the ultimate tensile strength and elongation at break. These tests were carried out with an Instron model 1195 machine according to the standard method at the Polymer Department of the National Research Center. The crosshead speed was 50 mm/min.

RESULTS AND DISCUSSION

Nitrogen and phosphorus contents

Figures 1–4 show the nitrogen and phosphorus contents of the crust leather when finishing was performed with the pad–dry–cure method.

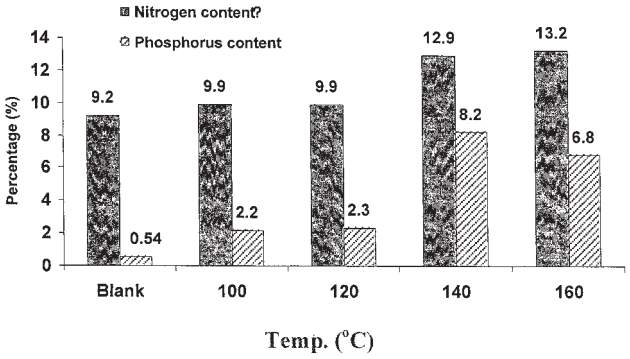


Figure 1 Effect of the curing temperature on the nitrogen and phosphorus contents ([Pyrovatex] = 150 g/L; [EMM] = 70 g/L; $[H_3PO_4]$ = 20 g/L; time = 10 min; pickup = 100%).

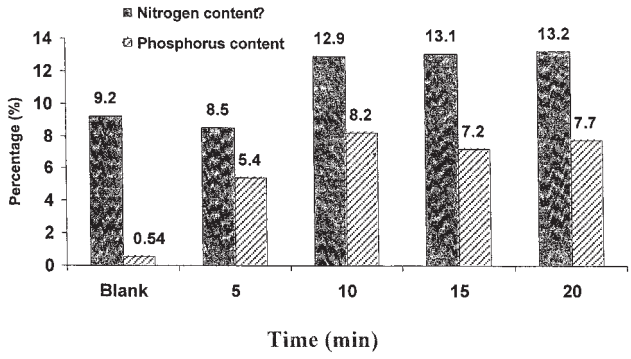


Figure 2 Effect of the curing time on the nitrogen and phosphorus contents ([Pyrovatex] = 150 g/L; [EMM] = 70 g/L; $[H_3PO_4]$ = 20 g/L; temperature = 140°C; pickup = 100%).

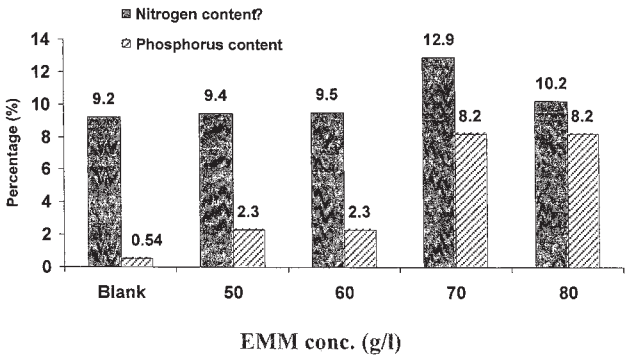


Figure 3 Effect of the EMM concentration on the nitrogen and phosphorus contents ([Pyrovatex] = 150 g/L; [H_3PO_4] = 20 g/L; time = 10 min; pickup = 100%).

Figures 1 and 2 show that the nitrogen and phosphorus contents are significantly higher with increasing curing temperature or time, respectively; this means that for better fixation, the reaction of Pyrovatex CP requires a higher temperature and a longer contact time between the reactants.

Figure 3 shows the variation of the nitrogen and phosphorus contents of the treated leather samples with the EMM concentration. The nitrogen and phosphorus contents increase as the EMM concentration increases. This is rather interesting and implies that EMM can enter the reaction and can act as a bridge between Pyrovatex CP and leather.

Figure 4 shows the dependence of the nitrogen and phosphorus contents of the crust leather samples on the concentration of Pyrovatex CP. Increasing the concentration of Pyrovatex CP causes a significant enhancement of the nitrogen and phosphorus contents of the treated samples. It is thought that increasing the Pyrovatex CP concentration will directly result in the greater availability of its molecules to enter the vicinity of the leather.

Flammability

Table I shows that the use of Pyrovatex and EMM in finishing leather produces flame-retardant properties before and after washing, and better flame retardancy is obtained with higher nitrogen and phosphorus contents.

The results also show that the use of Pyrovatex CP in conjunction with EMM is an example of a commercially successful finish based on this concept. Thermochemical studies have indicated that if phosphorus and nitrogen atoms are directly linked, their flame-retardant effectiveness might be enhanced. Among compounds in which P—N linkages are present, some have been claimed as flame-retardant finishes.

TGA

The thermogravimetric curves for untreated leather and leather treated with Pyrovatex CP are shown in Figure 5. For untreated leather, an initial weight loss of 15% can be observed from 50 to 150°C and is apparently associated with adsorbed water (stage 1 in Table II). After this process, the leather fibers are stable up to 360°C, beyond which a one-step thermal degradation process can be observed (stage 2). The weight loss in this stage is 33.68% with a thermal degradation temperature of 463°C. The weight residue at 650°C is 33.67%. With respect to the treated sample ([N] = 12.46%, [P] = 8.52%), the initial weight loss is 10%, and this indicates that it has less water than the unmodified one. The main decomposition also occurs in a one-step thermal degradation process. The weight loss in this stage is 24.7% with a thermal decomposition temperature of 435°C. The weight residue at 650°C is 51.87%.

On the basis of the previous discussion and the data summarized in Table II, we can conclude that the thermal stability of leather is quietly improved after chemical modification.

Limiting oxygen index (LOI)

The LOI value of the untreated leather sample is 36, which is lower than that obtained (44) for the leather treated with Pyrovatex CP ([N] = 12–46%, [P] = 8.52%). These results show the improvement in the flame-retardant properties of the leather samples after the treatment.

Mechanical properties of treated leather

Tables III–VI show the effects of the treatment conditions on the tensile strength and elongation at break of leather treated with Pyrovatex CP. The results make it evident that the tensile strength and elongation at break are lower after the treatment than before the treatment; that is, the tensile strength and elongation

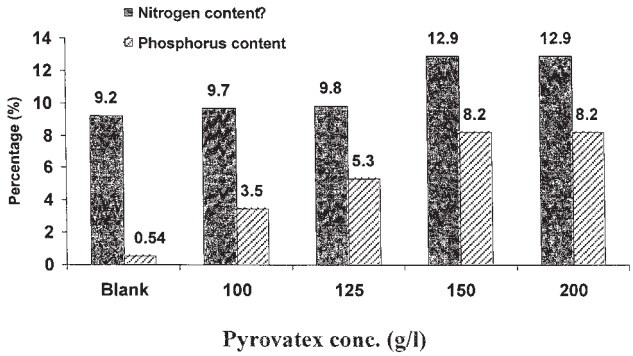
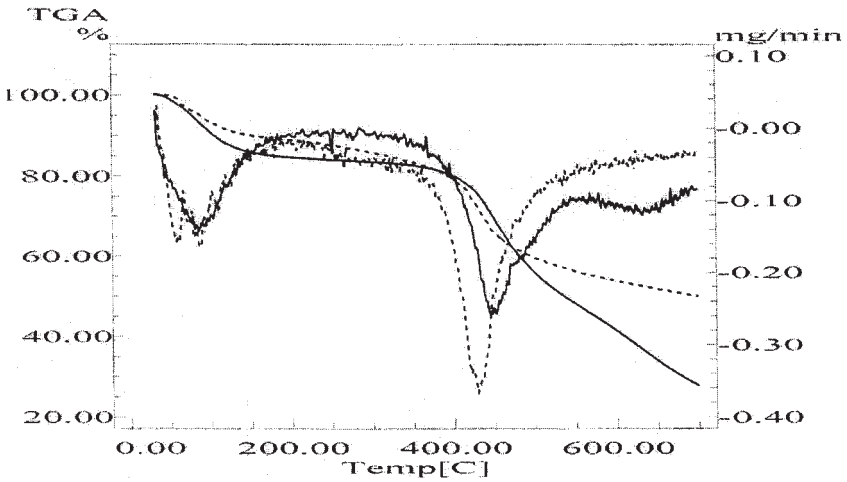


Figure 4 Effect of the Pyrovatex concentration on the nitrogen and phosphorus contents ([EMM] = 70 g/L; [H_3PO_4] = 20 g/L; time = 10 min; temperature = 140°C; pickup = 100%).



. **Figure 5** Thermogravimetric analysis (TGA) for the leather samples: (- - -) untreated leather and (—) treated leather.

at break of the treated leather samples are generally lower than those of the untreated samples.

These results may be attributed to the penetration of Pyrovatex molecules within the leather structure as well as the formation of the polymer deposit; this leads to an increase in the leather stiffness and a decrease in its elasticity.

CONCLUSIONS

The results show that Pyrovatex CP can be successfully used as a flame retardant for leather.

TABLE I
Effect of Treatment, Expressed as Nitrogen and Phosphorus Contents, on the Flammability of Leather Samples Treated with CP

Treated samples		Flammability
N (%)	P (%)	charred length (cm)
9.4	2.3	0.2
9.8	5.3	0.2
12.9	8.2	0.0
Untreated sample		0.5

TABLE II
Percentage Weight Loss of Treated and Untreated Leather Samples Produced by Thermogravimetric Analysis

	Stage 1		Stage 2		Residue
Leather type	T_1	M_1	T_2	M_2	at 650°C (%)
Untreated sampled	91.4	15.3	463	33.68	33.67
Treated sample	88	10.02	435	24.7	51.8

T_1 and T_2 = temperature of the maximum degradation rate (°C); M_1 and M_2 = percentage mass loss in each stage of degradation.

TABLE III
Effect of Curing Temperature on the Mechanical Properties of Leather Treated with Pyrovatex CP

Treatment temperature (°C)	Tensile strength	Elongation at break (%)
100	9.9	65.2
120	8.28	62.9
140	8.73	62.9
160	—	—
Untreated samples (blank)	13.03	90.6

[CP] = 150 g/L; [EMM] = 70 g/L; [H_3PO_4] = 20 g/L; time = 10 min; pickup = 100%.

TABLE IV
Effect of Curing time on the Mechanical Properties of Leather Treated with Pyrovatex CP

Treatment time (min)	Tensile strength	Elongation at break (%)
5	11.34	81.5
10	8.73	62.9
15	7.28	48.47
20	8.58	59.5
Untreated samples (blank)	13.03	90.6

[Pyrovatex] = 150 g/L; [EMM] = 70 g/L; [H_3PO_4] = 20 g/L; temperature = 140°C; pickup = 100%.

TABLE V
Effect of EMM Concentration on the Mechanical Properties of Leather Treated with Pyrovatex CP

EMM concentration (g/L)	Tensile strength	Elongation at break (%)
50	12.11	81.5
60	9.91	65.2
70	8.73	62.9
80	7.72	51.2
Untreated samples (blank)	13.03	90.6

[CP] = 150 g/L; [H_3PO_4] = 20 g/L; temperature = 140°C; time = 10 min; pickup = 100%.

TABLE VI
Effect of Pyrovatex CP Concentration on the Mechanical Properties of Leather Treated with Pyrovatex CP

Pyrovatex CP concentration (g/L)	Tensile strength	Elongation at break (%)
100	9.91	65.2
125	8.73	62.9
150	8.73	62.9
200	7.72	51.2
Untreated samples (blank)	13.03	90.6

[EMM] = 70 g/L; [H_3PO_4] = 20 g/L; temperature = 140°C; time = 10 min; pickup = 100%.

A typical treatment bath (100% wet pickup, 150 g/L Pyrovatex, 70 g/L EMM, and 20 g/L H_3PO_4) can be applied to crust leather. A typical cure lasts for 10 min at 140°C after drying.

Such finishes have the disadvantages of imparting excessive weight to materials that have to be transported and imparting stiffness and some loss in strength.

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