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Preparation of Flame Resistant Retanning Product for Glove Leather

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Abstract—Leather gloves are very light leather used for protection against various risks. A flame-resistant product is needed to increase its flame resistance of the natural leather. In this study, 02 flame resistant retanning products had been prepared utilizing waste leather protein extract with phosphoric acid and formaldehyde. These products had been applied at the retanning stage during leather processing. The utilization of phosphorus compounds chemically reacted with or deposited in leather fibers represented the most significant contribution in durable flame retardancy. The final prepared leathers had been characterized for different physical properties such as radiation and electric heat resistance, flame spread resistance and impact of spatter. These products had been found to be compatible with the commercial flame-resistant products. The thermal behavior of prepared leathers showed significant resistance.

Keywords—Flame resistant leather; Glove leather; Leather solid waste; Protection; Protein recycling

1. INTRODUCTION

Leather is usually used at different places according to the requirements. The finished leather is not combustible material. However, when the leather is used for safety purposes, higher fire resistance is a special requirement of customers. The flame resistance increases with the additional chemical treatment [1]. The flammability of leather treated with various retanning agents, fat liquors, and flame retardants has been closely investigated and it has been found that all flame retardants affect the flammability and other physical properties of leather up to different levels [2-4]. Finishing has also been investigated where it was found that the pigments in a finish improve the resistance when compared to the resin alone, but the conventional finish decreases the flame resistance of the leather [5]. Leather is regularly used in industrial clothing to provide thermal protection. This type of industrial clothing must also protect against a spatter of molten metal and stand a short contact time with flame. Radiant heat protection is also needed with arc welding. The main objective of the present study is the development of dual action flame resistant and retanning product for leather. The suitability of the applied flame retardant is assessed by estimation of various thermal behaviors and the physical properties of resulted leather after comparison with commercial flame-retardant products.

2. EXPERIMENTAL SECTION

2.1. Materials

The raw waste of chrome shavings was collected from the open *SITE* area of Korangi sector 7-A which was discarded without any further treatment. Wet blue from goat skins was processed by conventional chrome tanning process for application of the prepared flame-resistant formulation. The chemicals were purchased from the local market. Phosphoric acid and Formaldehyde solution were purchased from Merck®.

2.2. Instrumentations

An autoclave (series 155-9653) model YX-24LM was used for protein extraction. Determination of each amino acid in isolated protein samples was performed using an amino acid analyzer from Technicon Instruments Corporation, New York (AOAC 18th Edition), 2005. The instrument was first calibrated by analyzing a standard mixture of the known percentage of amino acids and subsequently, the samples were analyzed. The universal test of the Tinius Olsen HKS model was used. The softness was checked by a Softness tester from SATRA, Company. Thermal behavior tests were carried out on the locally fabricated instrument.

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2.3. Application of flame resistant formulation

Three Goat skins were processed to wet blue by a conventional chrome tanning process. Each formulation (10% based on the shaved weight of each wet blue) was applied to each wet blue goat skin in the tannery area as described in **Table 1.** Finally, the leathers from three different processes were removed from the drums without washing, placed flat on a drying board in such a way that the flesh side down and air dried for 24 h at room temperature.

Table 1. Application of retanning /flame resistant formulation

Operation	Process	Run time/control
Float	1. 300% water at 35^0C 2. Drain	Run 20 min.
Float	1. 200% water at 35 ˚C 2. 0.3% Acetic acid	Run 20 min; pH 3.8
Re- chrome	1. 4.0% basic chromium sulphate	Run 120 min
	2. 0.5 % Sodium bicarbonate	Run 30 min; Leave overnight
	3. Drain	
Float	1. 300% water at 35 ˚C	-
Neutralize	1. 1.5% Sodium formate	Run 30 min
	2. 1.5% sodium bicarbonate	pH 6.5
	3. Drain	
Float	1. 300% water at 350 °C	-
Retan/retard	2. 10% Prepared Flame retardant*	Run 60 min
Fatliqour	1. 4% Fish based product	Run 60 min
	2. 6% Synthetic oil based product	-
Acidify	1. 1.5% Formic acid	Run 30 min

*Flame retardant Retanning product was applied as treatment 1, 2, & 3) at the same drum conditions.

2.4. Procedure

Before testing all prepared leather, samples were conditioned at 20±2 °C and 50±5 % Relative Humidity. Thermal behavior tests of the leathers were measured by the standard ISO-15025:2002, EN ISO 11611. The tensile strength and elongation at break of leathers were measured by IUP-6, EN ISO 3376:2002, and Tear load was measured by IUP-8, BS EN ISO 3377-2:418, 2002. The softness was measured by a non-destructive method using a softness meter according to EN ISO 172589, 2002.

2.5. Preparation flame resistant formulation

The flame-resistant formulation was prepared by the extracted protein from chrome shavings, formaldehyde, and phosphoric acid. Firstly, the protein and formaldehyde were mixed for 5 min. Then, ortho-phosphoric acid was added. The acid serves as a catalyst. The weight ratios were 22 parts by weight of protein from chrome shavings, 51 parts by weight of formaldehyde (4% solution), and 7 parts by weight of ortho-phosphoric acid. The formulation was prepared at 65-70 °C with continuous stirring for 20 min. It was a light-yellow colored liquid. After preparation, the pH of the formulation was adjusted to 6.0 for the application in leather. The second product was prepared with 6% formaldehyde solution while the others were the same. The third formulation was purchased from the local market ERHA Flame FR-01 from TFL Company, used for flame retardant leather. It was a white colorless liquid in appearance.

3. RESULT AND DISCUSSION

Chrome shavings were collected from the Basic Chromium Sulphate tanning process of leathers and subjected to an alkaline hydrolysis process as provided in materials and methods. After the hydrolysis process was completed, the hydrolyzed protein was filtered through a fine muslin cloth and stored in a refrigerator (4 °C) until it was used for experimental work. Meanwhile, residue solid chrome cake was separated after filtration and used to prepare a recycled tanning agent. The alkaline hydrolysis of chrome-tanned solid wastes generated various hydrolyzed protein-rich amino acids. The results showed that the percentage of glycine, proline, and aspartic acid was 15.09%; 11.88%; and 6.44%; respectively. While the lower percentage of methionine and serine 0.36% and 0.50%, respectively, were found. Consequently, the experiments were conducted to utilize the amino acids-rich protein into a valuable intumescent product for leather. However, the functional properties of extracted protein may be affected by pH, salt concentration, and other chemical modifications [6].

Table 2. Thermal behaviour tests of prepared leathers

Formulation*	Radiation heat resistance[1]	Electric Resistance[2]	Flame spread[3]		Impact of spatter[4]
			After flame time (sec)	After glow time (sec)	
01 Product 1	Class 2	Class 2	8	1	3
02 Product 2	Class 2	Class 2	106	80	3
03 Prosuct 3	Class 2	Class 2	182	145	3

*Leathers conditioned at 20±2 °C , Relative humidity 85±5 %; (1)ISO 8942-2002; (2) EN 1149-2; (3) ISO 15025-2000; (4) ISO 9150

The results of the final prepared leathers are presented in **Table 2**. The findings show that the impact of spatter, radiation heat, and electric resistivity were similar in each of the three types of leathers. Still, the flame spread was significantly reduced using the protein-based flame-resistant product 01, as shown in **Table 2**.

In addition to reducing the fire spread, it was important that any prepared leather should be commercially acceptable in terms of physical and tactile properties. Therefore, physical testing of prepared leathers using standard test methods was also carried out to evaluate the effect of the application of each prepared product on leather. The results are presented in **Table 3.**

Table 3. Physical characteristics of prepared leathers

Formulation	Tensile Strength (N/mm^2)	Elongation (%)	Tear Load (N)	Softness (mm)
Product 1	21.0	137.0	76.5	9
Product 2	25.5	106.8	60.4	10
Prosuct 3	18.1	80.6	40.2	8

The physical testing results as presented in Table 3 show that the leather processed using the intumescent flame-retardant product was quite satisfactory when compared to the other leather in terms of physical properties. The superior fire retarding properties of the protein-based product might be due to the phosphoric acid esterification, dehydration of the polymer, and then the formation of a carbonaceous protective layer that protects the leather from burning [7].

It has been studied previously that when leather is ignited and provided with sufficient oxygen and heat, its burning behavior is like any other organic polymer. The flame-retardant leather is self-extinguished, 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 [8]. There is a general agreement that acid-forming phosphorus compounds are very effective in preventing fires. Their action has been attributed to a protective charring at a sub-flame temperature, which prevents ignition. Intumescent are the special form of flame retardants with phosphoric compounds. These flame retardants work through the exact interaction of the three main components, this system leads to an expansion process in which a large volume high carbon protective layer is built which protects the substrate/material from the heat attack [9].

These chemicals can retard the burning process by cooling through an endothermic process either by forming a protective layer and excluding oxygen or by diluting the fuel in the solid and gaseous phase or by breaking the continuity of the free radical combustion process by breaking down the polymer to reduce the viscosity which enables a withdrawal from the flame and preparation of carbon layer on the polymer surface by dehydration [10-11]. These are some possibilities for the mechanism of action of applied intumescent flame retardant. However, the mechanisms that strengthen this high performance are further under investigation and required to know the exact mechanism of action.

4. CONCLUSION

The results of thermal behaviour tests showed that all the 03 Flame Resistant Retanning products had different flame retardant effects on the prepared leathers due to the difference in formulation. The prepared formulation from protein of leather wastes showed better thermal behaviour results as well as other physical characteristics of leather due to presence of amino groups of the extracted protein and phosphorus groups of the products which is suitable for apply in retanning process. The prepared protein based intumescent flame retardant product is environment friendly and did not show any negative influence on leather properties.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

The experimental work conducted by BZ. BAS and UN were coordinated in the finalization of manuscript.

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