



Increasing the thermal behaviour of leather using a modified chrome hydrolysate

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A low cost and easily manufactured product based on chrome leather hydrolysate has been developed that is very effective as a fire retarding agent. This product can be applied in the same manner as a retanning agent and shows good leather making possibilities.

Leather is often used in industrial clothing to provide thermal protection. Normally, this is in the form of hoods, aprons, sleeves, gloves and gaiters that are designed to protect the head, body, arms, hands and legs. This type of clothing must also provide protection against a spatter of molten metal, and withstand a short contact time with flame. Radiant heat protection is also needed with arc welding.

Flame resistance of leathers

Flame retardation is a process by which the normal degradation or combustion of a substrate is altered by the addition of certain chemicals. These flame retardant chemicals can be formulated to be more resistant to ignition, or to slow the rate of flame-spread in a major flame initiated by some other source.

Generally, leather has significant flame resistance when compared to other materials such as plastics and synthetic fabrics¹. Due to this property, the scope of flame resistant leather has become an increasingly significant issue², and many investigations have taken place regarding these properties.

The flammability of leathers treated with various retanning agents, fatliquors and flame retardants has received close attention, and it has been found that all flame retardants influence both the flammability and other physical properties of leather to different levels³⁻⁵. Finishing has also been investigated where it was found that the pigments in a finish improve

resistance when compared to resin alone, but that a conventional finish decreased the flame resistance of the leather⁶. And many other investigations to increase flame resistance have taken place, although there is often a lack of comment on the properties of the leather as a result of these treatments.

The role of intumescent products

Intumescent products are products that swell and increase in volume when exposed to heat, typically producing a light char that is a poor heat conductor and retards heat transfer. These chars are often carbonaceous, and so effective that intumescent are often used in passive fire protection. Other applications can include water based paints and coatings⁷.

With these properties in mind, a flame retardant protein based product was developed that was high in polyhydroxy groups, phosphorus and nitrogen, all known to be effective in flame retardancy. The objective was that this intumescent would serve both as a flame retardant and as a retanning agent, and that the final leather should be assessed both for flame retardant and leather related properties using standard methods⁸.

The product was made in the following manner:

- Protein hydrolysate was isolated following alkaline hydrolysis of chrome shavings.
- This hydrolysate was warmed to 60°C.

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Panel 1: Chemicals used in producing a fire retardant product

Chemical	Parts by weight
Protein hydrolysate	22
Formaldehyde	71
Phosphoric acid	7
Resorcinol	20

- Formaldehyde and phosphoric acid were added together slowly and continuously over 30 minutes with continuous stirring.
- A freshly prepared solution of resorcinol in water was then similarly added.
- The reaction continued for 15 minutes under the same condition, then cooled to room temperature.
- The pH of the new product was adjusted to pH6.0.

The final product was water soluble and yellow in colour; the chemicals used in its production were of commercial quality, and the amounts used are listed in *Panel 1*.

It has also been reported that magnesium sulfate could also improve the thermal resistance of leather⁹ so this was also considered suitable for evaluation.

Panel 2: Retanning/fire retardancy process

Operation	Materials	Run time/ control
Float	200% water at 35°C	Run 20 min
	Drain	
Float	200% water at 35°C	
	0.3% Acetic acid	Run 20 min Ph 3.8
Rechrome	4.0% Basic chromium sulfate	Run 60 min
	0.5 % Sodium bicarbonate	Run 30 mins Leave overnight
	Drain	
Float	200% water at 35°C	
Neutralise	1.5% Sodium formate	Run 30 min
	1.5% Sodium bicarbonate	pH 6.5
	Drain	
Float	200% water at 35°C	
Retan/retard	12% Protein based product	Run 60 min
Fatliquor	4% Fish based product	Run 60 min
	4% Synthetic oil based product	
Acidify	1% Formic acid	Run 30 min

The retanning/fire retardancy process

Wet blue goat skins prepared within PCSIR were selected for the trial purposes, and then shaved to 0.8mm. They were then retanned using 12% of the protein based product as set down in *Panel 2*.

The process was then repeated in a second trial where the protein based product was replaced with 12% magnesium sulfate. A third retannage was then performed, but without any retanning agent to act as a control. Finally, the leathers from the three different processes were removed from the drums without washing, placed flat on a drying board flesh side down, and air dried for 24 hours.

Reduced flame spread

In addition to reduced fire spread, it was essential that any leather produced should be commercially acceptable in terms of physical and tactile properties. Tear load, percentage elongation and tensile strength were measured using ISO methods⁹⁻¹², and the results are presented in *Panel 3*.

This shows that the leather processed using the novel flame retardant product was quite acceptable when compared to the other two leathers in terms of physical testing methods. The leathers were also assessed by leather experts and were considered to be softer, more full and smoother (scale rating 1-10) than the other two leathers.

Thermal behaviour was assessed using standard test methods⁸. The findings show that the impact of spatter, radiation heat and electrical resistance was similar in each of the leathers, but the flame spread was significantly improved by use of the protein based product. These findings are presented in *Panel 4*.

This superior fire retarding properties of the protein based product may be due to the phosphoric acid esterification, dehydration of polymer and then formation of a carbonaceous protective layer which protects the leather from burning¹³. However, the mechanisms that underpin this high performance are not clear, and further investigations are taking place. ●

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Panel 3: Physical properties of leathers

Sample	Tensile Strength N/mm ²	Elongation %	Tear Load N	Softness (mm)	Colour	Fullness	Grain Smoothness
Control leather	18.1	80.6	40.2	8	8	7	7
Magnesium Sulfate	29.9	103.8	60.4	8	8	8	8
Protein based Flame Retardant composition	22.0	147.0	76.5	9	8	9	8

Panel 4: Thermal behaviour of leathers

Leather type	Radiation Heat Resistance ⁽¹⁾	Electric Resistance ⁽²⁾	Flame Spread ⁽³⁾		Impact of Spatter ⁽⁴⁾
			After flame time	After glow time	
Control leather	Class 1	Class 1	180 sec.	145 sec.	2
Magnesium Sulfate	Class 2	Class 2	105 sec.	80 sec.	3
Protein based Flame Retardant product	Class 2	Class 2	7sec.	1 sec.	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

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