Behavior of Leather as a Protective Heat Barrier and Fire Resistant Material

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ABSTRACT

Leather is a natural material with many applications: automotive, domestic upholstery, buildings, aviation, maritime, personal safety, etc. For each of these sectors, fire behavior is a field of particular interest. Unfortunately, there are many testing methods and different flammability standards depending on material application and end use. Therefore, there are different ways of approaching the whole flammability issue. In this work, different approaches for analyzing the fire resistance of leather are examined: (i) influence of the type of tannage, (ii) influence of the type of leather, (iii) influence of the type of retannage, (iv) influence of the type of fatliquor, and (v) influence of the use of flame retardants. The results indicate that leather presents natural fire resistance. However, the type of leather, type of tannage, retannage and fatliquor effect the flammability behavior of leather. In addition, the use of flame retardants slightly improves the smouldering properties of leather.

RESUMEN

El cuero es un material natural con muchas aplicaciones: tapicería para automóvil, tapicería doméstica, para arquitectura, para transporte aéreo, para marítimo, para seguridad personal, etc. Para cada uno de estos sectores, el comportamiento al fuego es un campo de especial interés. Desafortunadamente, hay muchos métodos de prueba y diferentes normas de inflamabilidad dependiendo de la aplicación del material y su uso final. Por lo tanto, hay diferentes caminos para abordar el tema de la inflamabilidad en su conjunto. En este trabajo, diferentes enfoques para el análisis de la resistencia al fuego del cuero son examinados: (i) la influencia del tipo de curtición, (ii) la influencia del tipo de piel, (iii) la influencia del tipo de recurtido, (iv) la influencia del tipo de engrase, y (v) la influencia de la utilización de agentes retardantes de combustión. Los resultados indican que el cuero presenta una resistencia natural al fuego. Sin embargo, el tipo de piel, el tipo de curtido, recurtido y engrase afecta el comportamiento de la inflamabilidad del cuero. Además, el uso de retardantes de formación de llama mejora ligeramente las propiedades de lenta combustión del cuero.

Introduction

Fire resistance is a critical property for some materials to ensure the personal safety and reduce the risk of property damage. It has been shown that approximately 6-24 million fires per year worldwide are produced, with 100.000 deaths per year from fire, and a yearly total cost of fire-related accidents of around 400 billion €.¹ The analysis of fire statistics suggests that roughly 80 percent of the fire accidents are associated with the occurrence of flashover. Flashover is the sudden transition from a relatively small, slowly developing fire spreading systematically to a much larger and dangerous fire. Reducing the risk of flashover can be equated with reducing fire spread, fire growth, and the maximum value of the heat release rate.²

To counteract these losses economically and to pre-empt the anticipated increase in fire-related deaths and injuries, new fire safety technologies and performance-based codes are needed; these can be achieved with a higher level of understanding of the dynamics of fire and with more certain measurement methods. All fires are different, and a single fire scenario or fire test will never cover the whole range of fires types and correspond to a single fire behavior. Most fire science and hence most fire testing is focused on specific protection goals: preventing sustained ignition, limiting the contribution to fire propagation, or acting as a fire barrier.

Most fire testing methods in existence are centred in promoting specific realistic fire scenario and monitor a specific fire hazard rather than determining the properties of the material. Moreover, fire researchers have traditionally used textile or polymeric upholstery materials to study its flammability.3-7 However, upholstery leather is a natural material considered a very high-tech product that is progressively being used to a larger extent in different sectors: automotive, domestic upholstery, buildings, aviation, maritime, personal safety, etc. There are previous studies on leather as a fire resistant material.8-14 Robert M. Lollar conducted impregnation tests to evaluate flame retardants⁸. Kadir Donmez and W.E. Kallenberger described the testing of leather for flame/glow retardance by analyzing the effect of various factors on flammability of leather and the effectiveness of the diverse flame retardants and process variations.9 Huang Zan et al., studied the flammability of leather with different retanning agents, fatliquors and flame retardants on pigskins¹⁰⁻¹² Ryszard Koslowski et al., conducted flammability tests on natural and artificial leather.¹³ Also, it must be acknowledged that several companies have been patenting flame retardants and fireproofing processes for many years.¹⁵-²⁵ Our contribution is based on different approaches for analyzing the fire resistance of leather: (i) influence of the

type of tannage, (ii) influence of the type of leather, (iii) influence of the type of retannage, (iv) influence of the type of fatliquor, and (v) influence of the use of flame retardants.

Several methods can be used to protect materials more effectively against attack by fire. An efficient way is to use flame retardants directly incorporated in the materials or in a coating covering their surface. The mode of action is generally attributed to the formation of a heat barrier at the surface of the materials, decreasing heat transfer from the flame and/or from the external heat flux to the substrate.²⁶

There are many different flame retardants, and these work in a number of different ways. Some flame retardants are effective on their own; other products are used mainly or only as synergists, acting to increase the effect of other types of flame retardant. In general, the types of compounds used for fire-retarding materials include halogenated flame retardants containing chlorine or bromine atoms, antimony trioxide, phosphorous flame retardants, nitrogen flame retardants, intumescent coatings¹ and inorganic flame retardants.^{1,9}

EXPERIMENTAL

Material

Five types of leather were tested: sheepskin, goatskin, bovine leather, double-face, and fireproof artificial polyurethane laminate. The chemicals used in the operations were those normally used in the leather industry. The experimental results were obtained as the average value of three different measurements.

Methodology

Five series of fire tests were conducted to assess the burning behavior of leather:

- 1. To analyze the influence of the type of tannage in smouldering properties, Spanish pickeled sheepskins were cut into two sides by the backbone. The left sides were employed to carry out a chrome tannage, whereas the right sides were used to perform a vegetable tannage. In both types of tannage the fire tests were conducted before fatliquoring and after fatliquoring. The tanning operations are shown in Table I.
- 2. To assess differences in fire resistance depending on the type of leather employed, four types of leather on wet-blue were purchased from three tanneries sited in Igualada (Spain). The post-tanning operations carried out are detailed in Table II. Additionally, fireproof artificial polyurethane laminate was tested.

¹Intumescent coating is a fire retardant coating that, when heated, causes a foam produced by non-flammable gases, such as carbon dioxide and ammonia, forming an insulating barrier when exposed to heat.

- 3. To examine the influence of the type of retannage in burning resistance, Spanish sheepskins on wet-blue were cut into two sides by the backbone. The left sides were employed to carry out the post-tanning operations without the use of any retanning product, and the right sides were used to perform the different retannages under study. These post-tanning processes are shown in Table III.
- 4. To evaluate the influence of the type of fatliquoring in fire properties, also Spanish sheepskins on wet-blue were cut into two sides by the backbone. The same methodology explained above was carried out. The post-tanning processes are detailed in Table IV.
- 5. Finally, the same procedure was followed to study the influence of the use of flame retardants. The post-tanning processes are shown in Table V.

Evaluation

Flammability standards and methods are in constant state of evolution and the protocol varies depending on material application and end use. The flammability tests range in size from small scale and bench scale, using equipment such as Bunsen burners or heat radiators of different type and shape.

Fire test can be categorized in the following types:

- a) Fire resistance tests to determine whether a structure can withstand the effects of fire.
- b) Non-combustibility tests to screen the materials which burn from those which do not.
- c) Ignitability tests, which enable to determine the ease with which materials ignite.
- d) Reaction to fire tests to determine some fire properties such as fire load, flame spread, heat release rate, etc.
- e) Smoke production tests to ascertain whether the materials produce smoke when burning.
- f) Test for toxicity to analyze gases emitted by materials on fire.

Additionally, the influence of different treatments or materials on fire performance is usually determined by comparing the relevant flammability parameters explained above, as obtained for both untreated /unmodified material and treated/modified material.²⁷

In this work, we adopt the JAR/FAR 25853(b) standard. Materials used in the interior of aircraft have to comply with Joint Aviation Regulation (JAR)/Federal Aviation Regulation (FAR) Part 251. In compliance with JAR/FAR 25853 (a) and (b), where JAR/FAR 25853 (a) covers ceiling panels, wall

panels, gallery structures, etc. and (b) covers floor covering, textiles, seat cushions, padding and other fabrics, the test method is as follows: a minimum of 3 specimens are tested hung in vertical position and exposed to a Bunsen burner flame at the lower end of the specimen (a) materials for 60 seconds and (b) materials for 12 seconds. In Figure 1 is shown a sketch of the method of analysis. The specifications are detailed in Table VI.²⁸

[11 JAA/FAA is an harmonization initiative between Europe and United States to enhance the global aviation safety. JAR stands for Joint Aviation Requirements. The JAA (Joint Aviation Authorities) is an associated body of the European Civil Aviation Conference representing the civil aviation regulatory authorities of a number of European States who have agreed to cooperate in developing and implementing common safety regulatory standards and procedures. The JAA is responsible for the development and application of common provisions (so called JAR) as well as of procedures concerning the safety and operation of aircrafts. FAA represents the United States aviation regulatory authorities.]

RESULTS AND DISCUSSION

The results obtained in the fire tests comparing the type of tannage are shown in Figures 2 and 3.

These results indicate that leather has a natural fire resistance since in the worse case scenario the chrome tanned sheepskin without fatliquoring presents a burn length of only 3 cm, whereas the JAR/FAR 25853 (b) specifications require a value lower than 20 cm. Vegetable tanned sheepskin offers a better fire behavior than chrome tanned sheepskin. Specifically, a 70% reduction in the burn length is obtained when working with vegetable tannage. This is due to the fact that there are less interstitial voids. To examine the fibrous structure of the leather samples we use the scanning electron microscopy Jeol JSM 6400. As can be seen in Figure 4, the fibrous structure of chrome tanned sheepskin and a vegetable tanned sheepskin is very different. Chrome tanned leather

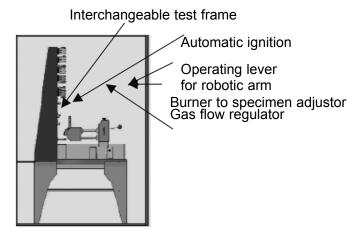


Figure 1. – Sketch of method of analysis.

TABLE I
Tanning formulations (on pickeled sheepskins)

	Chrome	Vegetable		
Degreasing	Carronic	veBetasie		
Water 35°C	100%	100%		
NaCl	10%	10%	rotate - 10' °Bé = 8.0	
Degreaser (Corilene DEN-50) ¹	2%	2%	rotate - 60'. Drain, wash	
Water 35°C	200%	200%	Totate 100 : Drain, wasii	
NaCl	10%	10%	rotate - 10' °Bé = 7.0	
Sodium bicarbonate	1%	1%	rotate - 60° pH = 6.8	
Degreaser (Corilene DEN-50) ¹	3%	3%	rotate - 60° pH = 5.0 . Drain, wash	
Water 35°C	100%	100%	Totate - 00 pri - 5.0. Drain, wasii	
NaCl	10%	10%	rotate - 10' °Bé = 7.0	
No ionic surfactant (Bemanol D) ¹	1%	1%	rotate - 30', Drain, wash	
Water 35°C	100%	100%	Totate - 30 , Diani, wash	
NaCl	10%	10%	rotate - 10' °Bé = 7.0. Drain, wash	
Pickel	1070	1070	Totale - 10 *Be = 7.0. Drain, wash	
Water 35°C	100%	100%		
NaCl	10%	10%	rotate - 10' °Bé = 7.0	
HCOOH (1:10)	1%	1%	rotate - 20'	
		+	rotate - 60'. Drain	
H ₂ SO ₄ (1:10)	0.4%, pH=3.5	—, pH = 3.8	rotate - 60 . Drain	
Tanning Water 35°C	100%	100%		
			10° oP (7 0	
NaCl	10%	10%	rotate - 10' °Bé = 7.0	
HCOOH (1:10) Chrome salt 33%	0.5%	 _	rotate - 10' pH = 3.3	
	7%	 _	rotate - 60'	
Fungicide (Cortimol FUN) ²	0.3%	 -	rotate - 30' pH = 2.1	
Sodium bicarbonate (slowly)	2.5%	<u> </u>	rotate - 30' pH = 3.9	
Naphtalene sulphonic ac. (Sinektan ACCN) ¹	-	4%	rotate - 20'	
Mimose	-	3%		
Quebracho	 -	3%		
Tara		3%	201	
Water 35°C		50%	rotate - 30'	
Mimose	<u> </u>	3%		
Quebracho	_	3%	2015	
Tara		3%	rotate - 90' Drain	
Neutralization	1,000/			
Water 35°C	100%	 -	20) 11 5 / D 1	
Neutralization syntan (Neutrigan) ²	1%	<u> </u>	rotate - 30' pH = 5.4. Drain, wash	
Fatliquoring	Lanny	Lanny		
Water 50°C	200%	200%		
Sulphated oil (Salem GC) ¹	2%	2%		
Sulphited oil (Corilene F275) ¹	2%	2%	(0)	
Emulsion fatliquor (Corilene W-30) ¹	1%	1%	rotate - 60'	
HCOOH (1:10) (slowly)	3%	3%	rotate - 40' pH = 3.6. Drain, wash	
Rest (24 h), drain, conditioning, stacking				

¹ Provided by Stahl by Holdings ² Provided by BASF Aktiengesellshaft

TABLE II
Post-tanning formulations for different types of leather

Degreasing Water 40°C Degreaser (Corilene DEN-50)¹	300% 0.5% 0.3%	 - -	-		
Degreaser (Corilene DEN-50)¹	0.5%		_		
		_		1	
	0.3%	i	1—	_	
HCOOH (1:10)		—	_	_	rotate - 30'. Drain
Washing		<u> </u>			
Water 40°C	_	300%	300%	300%	
Surfactant agent (Bemanol D) ¹	_	0.5%	0.5%	0.5%	
HCOOH (1:10)	_	0.3%	0.3%	-	rotate - 30'. Drain
Retanning and neutralization	·				
Water 35°C	150%	150%	150%	150%	rotate - 5'
НСООН	_	_	0.4%	0.4%	rotate - 10', pH = 3.2
Chrome 33%	4%	4%	4%	4%	rotate - 60'
Sodium formiate (1:10)	1%	1%	1%	1%	rotate - 30', pH = 3.4
Sodium formiate (1:10)	1%	1%	1%	1%	
Naphtalene sulphonic acid (Sinektan ACCN) ¹	2%	2%	2%	2%	rotate - 45', pH = 3.7
Neutralization syntan	1%	1%	1%	1%	rotate - 15'
Neutralization syntan (Neutrigan) ²	1.5%	1.5%	1.5%	1.5%	rotate - 30'. Drain, wash
Water 40°C	100%	100%	100%	100%	
Styrene maleic r. (Renektan ITF) ¹	3%	3%	3%	3%	rotate - 20'
Melamine resin (Renektan BN) ¹	3%	3%	3%	3%	rotate - 30'
Fatliquoring					
Water 60°C	200%	200%	200%	200%	
Synthetic beef tallow	2%	2%	2%	2%	
(Corilene F345E) ¹	5%	5%	5%	5%	
Sulphated oil (Salem GC) ¹	5%	5%	5%	5%	rotate - 60'
Lanoline (Corilene UL) ¹	3%	3%	3%	3%	rotate - 40'
HCOOH (1:10) (slowly)					pH = 3.6, Drain, wash
Rest (24 h), sammying, conditioning and stacking					

¹ Provided by Stahl by Holdings ² Provided by BASF Aktiengesellshaft

contains on its interior a large amount of empty hollows in the form of microscopic channels located among the tanned fibres. These empty spaces make way for the oxygen to pass through them with relative ease, which in turn increases the contribution to fire propagation. Instead, the vegetable tannage adds a large amount of tanning agent to allow both the increase in diameter of the fibres and the reduction of the interfibrillar spaces; thus, limiting the contribution to fire propagation.

Also, it is interesting to compare the results obtained before and after fatliquoring. The results indicate that fatliquoring

in chrome tanned sheepskin enables the enhancement of the fire properties (-20% burn length), whereas in vegetable tannage worse results are obtained (+33% burn length).

Figure 5 shows that the presence of fatliquoring agents in vegetable sheepskin causes the increase in diameter of the fibers. However, the said fibers are more porous and therefore the interfibrillar spaces increase in size. In like manner, the fibers in chrome sheepskin have also increased their diameter, although these are more compact and consequently the interfibrillar spaces have been reduced. Despite this, vegetable sheepskin shows a better behavior to burning.

TABLE III

Post-tanning formulation for different types of retanning products (on wet-blue sheepskin shaved at 1.0 mm)

Washing		
Water 40°C	300%	
Surfactant agent (Bemanol D)	0.5%	
HCOOH (1:10)	0.3%	rotate - 30' Drain
Only for Zirconium		
Water 35°C	100%	
HCOOH (1:10)	0.4%	rotate - 10' pH = 3.0
Zirconium salt¹	10%	rotate - 180', Drain and wash with acidulate water
Neutralization		
Water 35°C	150%	
Sodium formiate (1:10)	1%	rotate - 30'
Sodium bicarbonate (1:20)	1%	rotate - 60', pH = 5.8, Drain, wash
Retanning		
Water 40°C	100%	
Retanning agent ¹	15% (liquid) 12% (solid)	rotate - 30'
Fatliquoring		
Water 60°C	200%	
Sulphated oil (Salem GC)	2%	
Sulphited oil (Corilene F275)	2%	
Emulsion fatliquor (Corilene W-30)	1%	rotate - 60'
HCOOH (1:10) (slowly)	3%	rotate - 40', pH = 3.6, Drain, wash
Rest (24 h), sammying, conditioning and stacking		

¹ Syntan: Synektan WFN provided by Stahl by Holdings

Mimose Melamine resin: Renektan BN provided by Stahl by Holdings

Acrylic resin: Renektan ZY Stahl by Holdings

Styrene maleic resin: Renektan ITF provided by Stahl by Holdings

Zirconium: Blancorol ZB33 provided by Bayer.

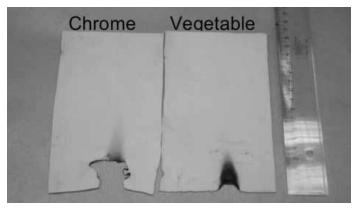


Figure 2. – Sheepskins after flammability test.

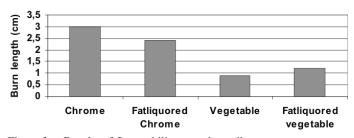


Figure 3. – Results of flammability tests depending on the type of tannage.

Since the previous results appear to indicate that the filling of the interstitial voids can be an influential factor to the enhancement of leather reaction to fire tests, a further comparison of the behavior to burning of different types of

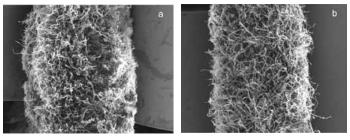


Figure 4. – Micrograph of cross-section of chrome (a) and vegetable (b) sheepskins without fatliquoring.

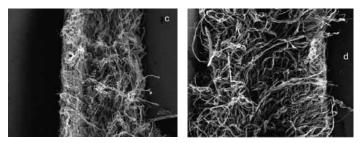


Figure 5. – Micrograph of cross-section of chrome (c) and vegetable (d) sheepskins with fatliquoring.

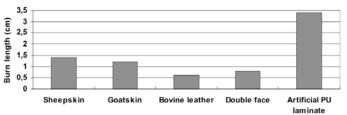


Figure 6. – Results of flammability tests depending on the type of leather.

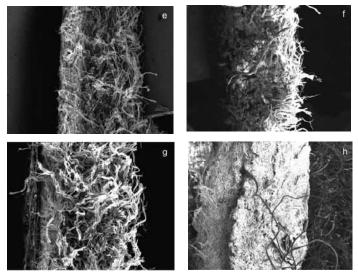


Figure 7. – Micrograph of cross-section of sheepskin (e), bovine leather (f), goatskin (g) and double-face (h).

leather was made, that is: sheepskin, goatskin, bovine leather, double-face and an artificial polyurethane laminate. The results can be seen in Figure 6 and 7. It can be seen in the graph and the micrograph of the cross-section of the different types of leather that bovine leather, which is more compact

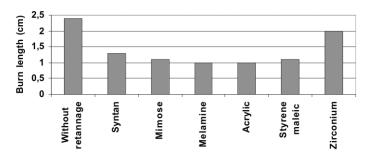


Figure 8. – Results of flammability tests depending on the type of retannage.

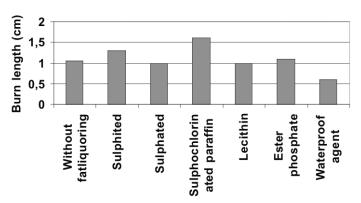


Figure 9. – Results of flammability tests depending on the type of fatliquoring.

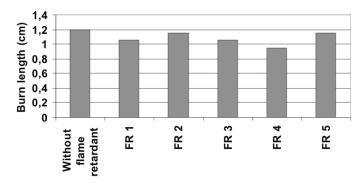


Figure 10. – Results of flammability tests depending on the type of flame retardant.

than the other types, presents only 0.6 cm of burn length. On the contrary, sheepskin is the one with the most widely open structure and presents +57% more of burn length than bovine leather. It is worth observing the low value obtained when using double face. As can be seen in Figure 7h, double-face presents a very compact fibrous structure. This is due to the fact that no dehairing or deliming is employed with this type of leather. Apart from the removal of the epidermis together with the wool, a weakening of the fibrous structure occurs in this operation through the splitting of fibers into fibrils. It can also be observed that artificial polyurethane laminate shows

TABLE IV

Post-tanning formulation for different types of fatliquoring products (on wet-blue shaved at 1.0 mm)

Washing		
Water 40°C	100%	
Surfactant agent (Bemanol D)	0.5%	
HCOOH (1:10)	0.3%	rotate - 30', Drain
Neutralization		
Water 35°C	150%	
Sodium formiate (1:10)	1%	rotate - 20'
Sodium bicarbonate (1:20)	1%	rotate - 60'
Fatliquoring		
Water 60°C	200%	
Fatliquor ¹	6%	rotate - 60'
HCOOH (1:10) (slowly)	3%	rotate - 40', pH = 3.6, Drain, wash
Rest (24 h), sammying, conditioning and stacking		

¹ Sulphated oil: Salem GC provided by Stahl by Holdings Sulphited oil: Corilene F275 provided by Stahl by Holdings

Sulphoclorinated paraffin: EX-63118 provided by Stahl by Holdings

Lecithin: Salem LCN provided by Stahl by Holdings

Ester phosphate: Corilene PEL provided by Stahl by Holdings Waterproof agent: Corilene WP-1 provided by Stahl by Holdings.

+82% more of burn length than bovine leather. This is further evidence to confirm that leather has natural resistance to fire.

Another important point is that the results obtained when comparing the types of leather are different than those obtained when comparing the type of tannage. Therefore, it can be deduced that the post-tanning operations modify the results of the fire tests. It is due to this that it was decided to further proceed with the study of the influence of retanning agents on the one hand, and that of fatliquoring agents on the other. From this point onwards, all the tests were carried out using chrome tanned sheepskins since it is the type of leather that grants the least satisfactory results.

Firstly, we performed a comparison of different retanning agents: syntan, mimosa, melamine resin, acrylic resin, styrene maleic resin and zirconium. The results obtained are detailed in Figure 8.

As can be seen in the graph, retanning agents reduce the burn length in all cases. However, such improvement in fire tests results varies with regard to the type of retanning product used. The best results are obtained using acrylic resin and styrene maleic resin. These are the resins that fill the fibres the most and give less interstitial voids to the leather. On the

contrary, when working with zirconium +50% burn length is obtained compared with both acrylic resin and styrene maleic resin. Thus, it is confirmed again that the filling of the interstitial voids is an essential factor that leads to the enhancement of leather reaction to fire tests.

Secondly, to evaluate the influence of the type of fatliquoring in fire properties, the following fatliquors were compared: sulphited oil, sulphated oil, sulphochlorinated paraffin, lecithin, ester phosphate and a waterproof agent. All the tests were carried out using chrome tanned sheepskins. The results obtained are shown in Figure 9.

The results indicate that the type of fatliquoring used may cause a change in flammability test results. As can be observed in the graph, sulphited oil and sulphochlorinated paraffin produce worse results. Sulphated oil, lecithin and ester phosphate barely modify the results, and the waterproof agent enhances the results of the tests.

The function of fatliquoring agents is to maintain the fibres separated and lubricated so that they can slide with ease. During the process of fatliquoring, two phenomena occur: penetration, which is a physical process, and fixation, during which chemical reactions take place. The fat deposits in the protein chains, inside the fibrils, in a similar manner as

TABLE V
Post-tanning formulation for different types of flame retardant (on wet-blue shaved at 1.0 mm)

Washing		
Water 40°C	200%	
Surfactant agent (Bemanol D)	0.5%	
HCOOH (1:10)	0.3%	rotate - 30', Drain
Retanning and Neutralization		
Water 35°C	150%	rotate - 5', pH = 4.2
HCOOH (1:10)	0.4%	rotate - 10' pH = 3.0
Chrome 33%	4%	rotate - 60'
Sodium formiate	1%	rotate - 30'
Sodium formiate	1%	
Naphtalene sulphonic ac. (Sinektan ACCN)	2%	rotate - 45' pH = 3.7
Neutralization syntan	1%	rotate - 15'
Neutralization syntan (Neutrigan)	1.5%	rotate - 45', pH = 5.0, Drain, wash
Water 40°C	100%	
Styrene maleic resin (Renektan ITF)	3%	rotate - 20'
Melamine resin (Renektan BN)	3%	rotate - 30'
Fatliquoring		
Water 60°C	200%	
Synthetic beef tallow (Corilene F345E)	2%	
Sulphated oil (Salem GC)	5%	
Lanoline (Corilene UL)	5%	rotate - 60'
HCOOH (1:10) (slowly)	3%	rotate - 40', pH = 3.6, Drain, wash
Fireproof (without float)		
Flame retardant ¹	12%	rotate - 60', Drain
Rest (24 h), sammying, conditioning and stacking		

¹ Amonium polyphosphate: Bemanol FPA provided by Stahl by Holdings

Sulphamic acid with urea: ERHA FLAM FR01 provided by TFL Inorganic halogen compound: Sella Tec Safe provided by TFL

Antimony oxide-halogenated dispersion: Flacavon H 14/587 provided by Schill + Seilacher

Bromine halogenated compound: AMSPERSE FR-PAW provided by CADES S.A.

TABLE VI Jar/Far 25853 (A) And (B) Specifications

Class	(a)	(b)
Burn length	≤ 150 mm	≤ 200 mm
Afterflame time	≤ 15 s	≤ s
Flame time of drippings (if any)	≤ 3 s	≤ s

chrome or a vegetable tannin do. A fatliquoring agent can be of anionic, cationic or ionic nature, depending either on the treatment it has been subjected to or on the type of emulsifier that has been added to the fatliquoring agent. At large, the chemical or electrochemical affinities that occur are the following: the polar valence between the anion and cation or else between one ion and one permanent dipole; the formation of hydrogen bonds; the formation of complexes; the attraction between dipoles.

Due to the fact that the composition of fatliquoring agents is highly variable and both their penetration and fixation depend on their origin, the treatments they have been subjected to, the conditions set by the process, etc., further studies will have to be conducted. These studies will focus on the influence of the type of fatliquoring on flammability tests.

Finally, five types of flame retardants were compared: ammonium polyphosphate (FR1), sulphonic acid with urea (FR2), inorganic halogen compound (FR3), antimony oxide-halogenated dispersion (FR4), bromine halogenated compound (FR 5). The results obtained can be seen in Figure 10.

As can be inferred from the results obtained, all the flame retardants tested can enhance the flame resistance of leather. However, as explained in the introduction section, these retardants work in a number of different ways. The efficiency of flame retardants depends on both their absorption and a proper dosage. Under the conditions of this experiment, in which all the products tested are used following the same formulation and conditions, the antimony oxide- halogenated dispersion appears to be the best flame retardant for use in sheepskin under the conditions of work studied. Specifically, using the antimony oxide- halogenated dispersion, -25% burn length is obtained.

CONCLUSIONS

The aim of this study was to find out about the behavior of leather as a protective heat barrier and fire resistant material. Through the comparison between different types of retanning products, different types of fatliquoring agents and different types of flame retardants, a further aim was to learn how these affect the post-tanning operations in fire performance. The results indicate that leather presents natural fire resistance. However, each type of leather presents a different resistance to fire; this is determined by the compactness of the fibres. Thus, bovine leather is the type that presents the best fire behavior. In addition, the type of tannage applied has a strong influence on the limitation of fire propagation. This is also due to the difference in fibrous structure which each different tannage produces. To this effect, a vegetable tannage offers a better resistance to fire. In the same way, a retannage enhances fire resistance due to the modification of the fibrous structure, which results in enhanced fire behaviour when working with acrylic resin and styrene maleic resin. These resins are the retanning agents which allow for a better filling of the fibers and grant greater compactness. On the other hand, fatliquoring agents have different effect on flammability tests since each type of fatliquor has a different boiling point, ignition point, penetration and fixation. Finally, the use of flame retardants enhances the flame resistance of leather. Out of the 5 products studied here, antimony oxide- halogenated dispersion appears to be the most effective for use in sheepskin.

REFERENCES

- 1. CEFIC-EFRA. European Chemical Industry Council European Flame Retardants Association. http://www.flameretardants.eu/content.
- 2. Building and Fire Research Laboratory. Activities, Accomplishmennts and Recognitions. NIST National Institute of Standards and Technology. http://www.fire.nist.gov.
- 3. Schartel, B.; Hull, T.R.; Development of fire-retarded materials. Interpretation of cone calorimeter data, *Fire and Materials* **31**, 327, 2007.
- 4. Hopkins, Jr D.; Predicting the ignition time and burning rate of thermoplastics in the cone calorimeter, NIST GCR 95 677, National Institute of Standards and Technology, Gaiterburg, US, 1995.
- 5 Tewarson, A.; Flammability parameters of materials: ignition, combustion, and fire propagation, *Journal of Fire Sciences* **12**, 329, 1994.
- 6. Quintiere, J.G.; Fire growth: an overview, *Fire Technology* **33,** 7, 1997.
- Costa, L.; Camino, G.; Bertelli, G.; Borsini, G.; Mechanistic study of the combustion behaviour of polymeric materials in bench-scale tests. I: Comparison between cone calorimeter and traditional tests, *Fire and Materials* 19, 133, 1995.
- 8. Lollar, R.M.; Report of Fire Resistance Subcommitte, *JALCA* **45**, 715, 1950.
- 9. Donmez, K.; Kallenberg, W.E.; Flame resistance of leather, *JALCA* **87**, 1, 1992.
- Zan, H.; Lixin, L.; Yinghong, W.; Yunzhou, L.; Wuyong,
 C.; Performance of flame retardants on leather, *JSLTC* 89, 225, 2005.
- 11. Zan, H.; Lixin, L.; Wuyong, C.; Haibing, G.; Influence of fatliquoring on flammability of leather, *JSLTC* **90**, 155, 2006.
- 12. Wuyong, C.; Chunxia, L.; Ying, G.; Zan, H; Influence of tanning on flammability of leather, *JSLTC* **91**, 159, 2007.
- 13. Kozlowski, R.; Mieleniak, B.; Musyczeck, M.; Fiedorow, R.; Flammability and flame retardancy of leather, Leather International, November 2006, 23-26. http://www.leathermag.com.
- 14. Fire resistance Technologies and testing. New England Tanners Club. 2006. http://www.blcleathertech.com.
- Ohama, Ch. (Nankyo Efnica Co., Ltd., Japan);
 Polyfunctional compositions with good flame retardancy antifogging property. PCT Int. Appl. Patent no WO 2009008239 (2009).
- Jaeger, E.M.; Kim, M. (Ironclad Performance Wear Corp., USA); Fabric with improved heat resistance finish. U.S. Pat. Appl. Publ. Patent n° US 20080242176 (2008).

- 17. Usai, I.; Method of production of a fire-proof leather that does not release smokes and the leather this way obtained. PCT Int.Appl. Patent n° WO 2008105020 (2008).
- Hansel, J.G.; Mauerer, O.; Burgess, D.; Wolf, K.H. (Lanxess Deutschland GmbH, Germany; Trumpler GmbH & Co. KG Chemische Fabrik); Antigreasing fireproof treating of leather. Ger. Offen. Patent n° DE 102006050795 (2008).
- Lim, Y.J. (Limus Co., Ltd., S.Korea); Method for preparing flame retardant composition containing ammonium magnesium phosphate and flameproof process using this composition. Repub. Korea. Patent no KR 751566 (2007).
- Bluecher G.m.b.H., Germany. Fireproof footwear with protective function against toxic substances. Ger. Gebrauchsmusterschrift. Patent n° DE 202005010411 (2006).
- Gaidau, C; Miu, L.; Hentulescu, V.; Lascarov, S.V.; Ionescu, M.; Crudu, M. (Institul National de Cercetare Dezvoltare Textile Pielarie-Filiala Institul de Cercetari Pielarie Incaltaminte, Rom.); Finishing processes for waterproofing and fireproofing of leather. Rom. Patent no RO 2002-200201245 (2005).
- 22. Hack, M. (IBEJI-Investimentos e Servicos, Lda., Port.); Process for fireproofing leather. Port. Pat. Appl. Patent nº PT 102212 (2000).

- 23. Pomrehn, B.; Arnsmann, G.; Pirig, W.D. (Clariant G.m.b.H., Germany); Intumescent flame-retardant coatings. PCT Int. Appl. Patent n° WO 19990603 (1999).
- Wada, K.; Suginuma, S. (Hokuyoo Kk, Japan); Fireretardant natural leather materials and their manufacture. Jpn.Kokai Tokkyo Koho. Patent no JP 06065600 (1994).
- 25. Sharp, R.C.G. (Sandoz Products Ltd., UK); Flameproofing compositions for leather. Brit. UK Pat. Appl. Patent n° GB 2084622 (1982).
- 26. Bourbigot, S.; Jimenez, M.; Dusquesne, S.; Modeling heat barrier efficiency of flame retarded materials. Proceedings of the COMSOL Users Conference 2006 Paris.
- 27. Malgorzata, H.; Methods of testing the flammability of treated woods. COST Action E 37. Sustainibility Through New Technologies for Enhanced Wood Durability. Meeting of working groups, Hamburg, Germany, November 2004.
- 28. Lassen, C., Løkke, S., Andersen, L.I., Brominated flame retardants Substance flow analysis and assessment alternatives. COWI A/S Danish Institute of Fire Technology. Environmental Project nr. 494, 1999.

(Editor Note: Reference web addresses were retained in order to assist in reader pursuit of the regulatory issues discussed.)