# Flammability and Flame retardancy of leather

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## Abstract

Leather is an excellent natural product widely used not only in the footwear industry, but also in the manufacture of more luxury products for upholstered furniture and automotive industry. In the case of the two last applications, fire behaviour is of extreme importance. Leather, when compared to man-made products and textiles used in car and upholstery applications, is safer and also a healthier choice.
In this study leather flammability was compared with that of flame retardant modified leather and artificial leather (based on polyurethane) according to the requirements of upholstered furniture and automotive industries.

## 1.Introduction

The most essential feature of leather is fibrous structure of its tissue. It looks like a three-dimensional network consisting of microscopic-size fibres which, however, are not orderly distributed. Due to small dimensions of pores, tanned leather is characterised by a high permeability for water vapour and other gases and at the same time very low water permeability.
Characteristic fishnet structure of leather tissue can explain many properties of tanned leather such as tear resistance, flexibility, permeability for air, thermal insulation, resistance to water, shape maintenance. Leather shows the above properties at different temperatures and different humidity levels. The above properties are the reason for which leather is widely applied to footwear and clothing industries as well as to manufacturing upholstered seats, e.g. in furniture and automotive industries, particularly in luxury products. In the case of the last two applications, the behaviour of leather in fire conditions is of outmost importance.
In this study, results of flammability measurements of natural leather, applied to the production of upholstered furniture and upholstered seats in the automotive industry, are presented and discussed by taking into consideration the requirements of relevant industrial branches. The study has also included a comparison of the above results with those of flame retardant-modified natural leather and upholstery composites consisting of leather and difficult-to-ignite barrier non-woven [LinFR]300 developed at the Institute of Natural Fibres.

## 2.Experimental

The evaluation of flammability was performed on natural leather with surface mass of 620 g/m$^2$, applied to the manufacture of luxury upholstered seats. Flammability measurements were carried out using three tests for the evaluation of flammability of upholstered materials applied to furniture and means of transport.

- *Road vehicles ISO 3795:1989(E);*

Samples are placed in an U-shaped frame in a horizontal position and subjected to a 15-second exposure to low-energy flame.

- *Textile fabrics-Burning behaviour EN ISO 6940:2004*
  Samples are placed in a rectangular frame in a vertical position. They are exposed for 1 to 20 s contact with flame situated perpendicularly to the sample surface or directly below the sample edge.

- *Cone calorimeter 2 (ISO-5660 – 1:2002 (E)*
  This is the standard device for measuring the rate of heat release from a burning material under a controlled radiant heat source. (Radiant heat is the major cause of fire spread.) The apparatus consists of a conical electric heater (typically 10 - 100 kW/ $m^2$) delivering uniform radiation to the sample situated horizontally, parallel to the source of radiation.

Moreover, leather samples were subject to thermogravimetric analysis (TG) and differential thermal analysis (DTG) on a Setsys 12 instrument (made by *Setaram*). The analyses were carried out in the temperature range from room temperature to 700°C in air flow (30 $cm^3$/min) at linear temperature growth of 10°C/min, using corundum crucibles.
Results of the measurements were compared with those obtained for artificial polyurethane (PU) leather with surface mass of 630 g/$m^2$ that is applied to standard upholstered seats.

## 3. Results and discussion

### *3.1 Flammability of leather*

Tanned leather is resistant to a short-time exposition to temperatures up to 200°C (higher temperatures result in pyrolysis). The exposition to temperatures in the range of 130°C to 170°C for several dozen minutes do not cause structural changes in leather [1]. Resistance to higher temperatures requires appropriate finishing.
In order to determine flammability of natural and artificial leather, measurements were carried out using ISO 3795:1989(E) and EN ISO 6940:2004 methods. Results of these measurements are presented in Tables 1 and 2.

**Table 1.** Leather flammability in compliance with ISO 3795:1989(E)

| Result | Natural leather (for furniture applications) | Artificial PU leather |
|---|---|---|
| Length of sample burnt, mm | 0 | 254 |
| Combustion time, s | 0 | 230 |
| Flammability degree, mm/min | 0 | 66 |
| Other observations | Ignition, glowing, flame going out before the first point of the measurement | glowing: 1850 s causing a slow ashing of the sample |

**Table 2.** Leather flammability in compliance with EN ISO 6940:2004

| Material | Place of the contact with flame | Time of contact with flame, s | Time of sample combustion, s | Observations | |
|---|---|---|---|---|---|
| | | | | Time of glowing, s | Length of burnt, mm |
| Natural leather | Surface (grain) | 18<br>19 | 0<br>0 | 0<br>593 | Local<br>28 |
| | Edge | 5<br>4 | 98<br>0 | Over 600<br>0 | 200 (whole)<br>local |
| Artificial PU leather | Surface | 4<br>3 | 135<br>0 | 403<br>0 | ashing<br>10 |
| | Edge | 1 | 71 | 313 | ashing |

Results obtained by using **ISO 3795:1989(E)** method permit to classify the leather investigated into non-ignitable materials (combustion time: 0 mm/min). On the other hand, artificial PU leather ignites and flame spreads with the rate of 66 mm/min.
Time until which sample is not ignited and does not glow during surface, and edge exposures to flame was determined by **EN ISO 6940:2004** method. In the case of natural leather, the time of surface exposure to flame is 18 s, whereas for artificial leather 3 s (Table 2). When the flame is edge situated, natural leather ignites after 5 s and artificial leather ignites immediately after getting in contact with flame, burns slowly and then glows until the sample undergoes total ashing. Natural leather, when ignited, smoulders slowly, glows for a long time and shrinks.
Results of flammability measurements performed on a cone calorimeter are given in Table 3.

**Tabela 3.** Leather flammability determined using a cone calorimeter in compliance with ISO-5660 – 1:2002 (E)

| Measurement parameters (heat flux of 35 kW/m$^2$) | Dimensional unit | Natural leather | Artificial PU leather |
|---|---|---|---|
| Peak Heat Release Rate [HRR] | kW /m$^2$ | 190.60 | 278.82 |
| Time to Sustained Ignition [TI] | s | 40.11 | 19.28 |
| Total Heat Released [THR] | MJ/m$^2$ | 14.95 | 10.09 |
| Average Heat of Combustion [$HOC_{av.}$] | MJ/kg | 19.87 | 16.72 |
| Average Mass Loss Rate [$MLR_{av.}$] | g / s · m$^2$ | 2.09 | 4.44 |
| Average Specific Extinction Area [$SEA_{av.}$] | m$^2$/kg | 137.66 | 238.32 |
| Average CO emission [$CO_{av}$] | kg/kg | 0.028 | 0.043 |
| Average $CO_2$ emission [$CO_{2av}$] | kg/kg | 2.110 | 2.059 |

In the case of natural leather, heat release rate [HRR] is 190 kW /m$^2$ (on average) and is clearly lower than that observed for artificial leather (Table 3). Time to sustained ignition [TI] in the case of natural leather is 2.1 times longer than that of artificial leather and mass loss rate [MLR] is 2.1 times lower for natural leather, which points to a slow burning of the material. Smoke emission, expressed by specific extinction area [SEA], in the case of natural leather is almost twice as low as that for artificial leather. Natural leather is also safer because of one and a half times lower emission of carbon monoxide.
All three tests have proved that natural leather is relatively resistant to ignition. However, it is also characterised by the ability to glow slowly, which in the case of its application to upholstered furniture, can cause fire after a several-hour stage of latent smouldering. In some cases, combustion can remain at the stage of smouldering, while in the other ones the material can suddenly burst into flames after the phase of smouldering.

When smouldering combustion occurs, the damage is usually limited to the place where it began and losses are relatively low. However, when material burst into flames, then, on the contrary, conditions hazardous to life are generated quickly and such fires can spread rapidly causing serious material losses and casualties. That is why materials of diversified extent of flame retardation should be used for the manufacture of upholstered seats.

### *3.2 Flame retardant treatment of natural leather*

It is well-known that making leather fully resistant to charring and decomposition caused by contact with fire or high temperature is impossible. There is, however, a possibility of providing an increased level of fireproofing by applying appropriate flame retardants.
On the ground of literature information about the application of flame retardants used for textiles to natural leather, we have decided to perform this study basing on the experience of the Institute of Natural Fibres in the field of flame retardation of wool and natural fibres [5].

In the first experiments on the protection of leather, we have chosen flame retardants applied to non water durable and permanent flame retardation of textile raw materials such as boric acid, orthophosphoric acid and three commercial flame retardants for the treatment of natural raw materials based on polyurea – phosphates and borates .
The use of impermanent flame retardants was justified by the fact that leather in upholstered ready products is not subjected to laundering with water during its exploitation. The advantages of these compounds are their low cost and flame-retarding effectiveness. Different formulas of flame retardants used in our experiments for the impregnation of leather (intended to upholstered furniture) of surface mass of 620 g/m$^2$ are listed in Table 4.

**Table 4**: Characterisation of variants of flame retardant formulas

| Sample code | Way of treatment | Impregnant |
|---|---|---|
| 0 | - | Untreated leather |
| 2 | padding | 1M $H_3PO_4$ |
| 3 | | $H_3PO_4$+ 5% $H_3BO_3$ |
| 5 | | 5% $H_3BO_3$ |
| 7 | | Commercial product produced by Devan Chemicals (5% aqueous solution) |
| 11 | spraying from the bottom side | Commercial product based on ammonium polyphosphate and boric acid (10% aqueous solution) |
| 12 | | Commercial product based on INF's product of polycondensation phosphates and borates of urea (10% aqueous solution) |

Flame-retarded leather samples were first air-dried at about 20°C and then drying was continued in a forced air circulation dryer at 35°C. Leather samples, after their treatment and drying, were evaluated from the point of view of changes in their external appearance. On the ground of the evaluation, sample No. 12 was eliminated from further studies because of its considerable stiffening acquired as a result the flame retardant protection.

The effectiveness of the protection was evaluated on the ground of results of flammability tests as well as DTA and TG analyses. Differential thermal analysis curves (Fig. 1) show one endothermic and two exothermic peaks. The first of them at 100° should be ascribed to the removal of water, the second one at about 350°C, that appears as a shoulder on sharply raising curve, may originate from the oxidation of trivalent chromium (present in chrome tanned

leather) to hexavalent chromium [3] and the third peak reflects combustion of leather. Flame retardation according to formula variant No. 7 shifts the maximum of the third peak from 475°C (the case of untreated leather) to 491°C (sample No. 7). Analogous shift in the third peak towards higher temperatures is observed for sample No. 11. In the case of the latter sample, an additional exothermic effect appears at 533°C, which suggests that some components of the material subjected to flame retardation according to formula variant No. 11 respond even more effectively to the flame retardant treatment.

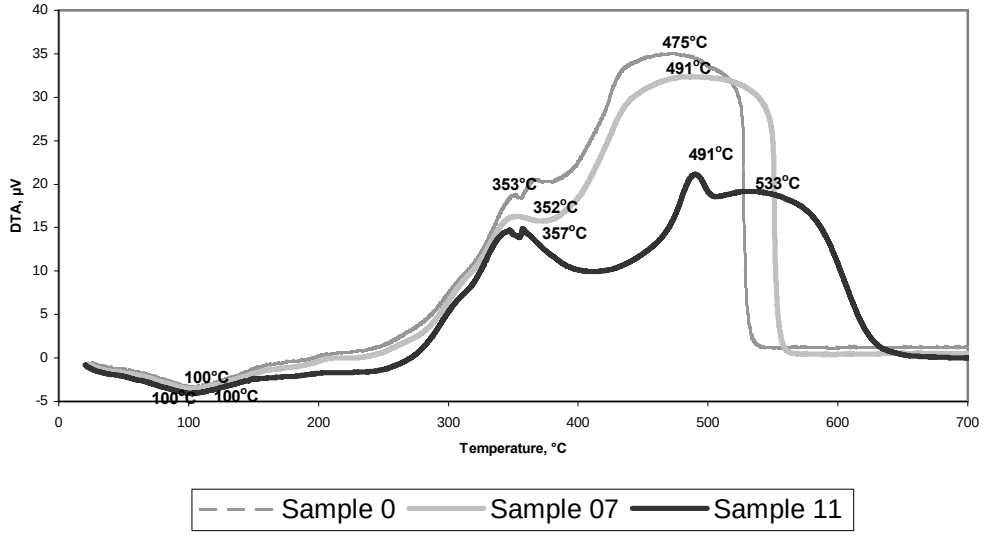


**Fig. 1** Curves of differential thermal analysis (DTA) of untreated leather (sample 0) and flame-retarded leather (samples 7 and 11)

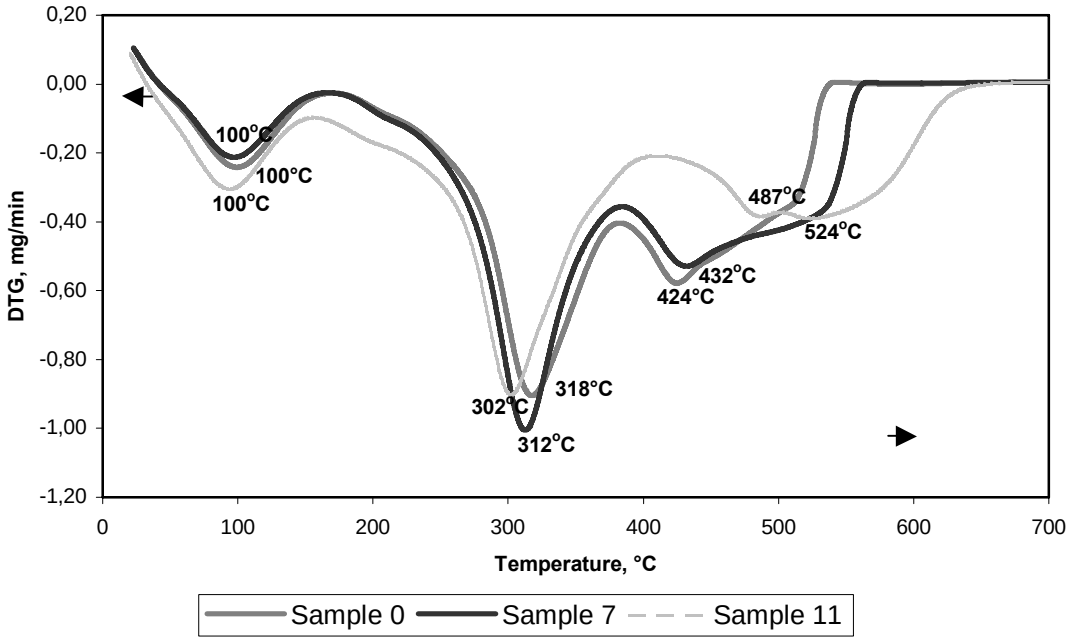


**Fig. 2.** Curves of thermogravimetric analysis of untreated and flame retarded leather

In Fig. 2 results of thermogravimetric analysis are shown as the first derivative (DTG) of TG curves. On the DTG curves, counterparts of all effects observed on DTA curves appear at slightly lower temperatures which results from a difference in the rate of response of detecting devices of differential thermal analysis and thermogravimetric analysis. Despite the mentioned difference in temperatures recorded on DTA and DTG curves, the direction of changes shown by both curves is the same – the employed flame retardants shift the temperature associated with leather combustion to higher values compared to that of untreated leather.
Results of flammability measurements of effective different flame retardant are presented in Tables 5 and 6. For the sake of comparison, results obtained for untreated leather are shown as well.

**Table 5.** Flammability of flame-retarded leather determined on a cone calorimeter in compliance with ISO-5660 - 1:2002 (E)

| **Measurement parameters (heat flux of 35 kW/m$^2$)** | **Dimension** | **Sample number** | | |
|---|---|---|---|---|
| | | **0** | **7** | **11** |
| Peak Heat Release Rate [HRR] | kW /m$^2$ | 190.60 | 182.93 | 152.83 |
| Time to Sustained Ignition [TI] | s | 40.11 | 43.70 | 50.84 |
| Total Heat Released [THR] | MJ/m$^2$ | 14.95 | 11.96 | 12.50 |
| Average Heat of Combustion [$HOC_{av.}$] | MJ/kg | 19.87 | 16.29 | 17.69 |
| Average Mass Loss Rate [$MLR_{av.}$] | g / s · m$^2$ | 2.09 | 2.40 | 4.49 |
| Average Specific Extinction Area [$SEA_{av.}$] | m$^2$/kg | 137.66 | 309.24 | 213.44 |
| Average CO emission [$CO_{av}$] | kg/kg | 0.028 | 0.058 | 0.043 |
| Average $CO_2$ emission [$CO_{2av}$] | kg/kg | 2.11001 | 1.600 | 1.462 |

**Table 6.** Flammability of flame-retarded leather determined in compliance with EN ISO 6940:2004

| **Sample number** | **Place of the contact with flame** | **Time of contact with flame, s** | **Time of sample combustion, s** | **Observations** | |
|---|---|---|---|---|---|
| | | | | **Time of glowing, s** | **Length of burnt, mm** |
| 0 | surface (grain) | 18 | 0 | 0 | 5 |
| | | 19 | 0 | 593 | 28 |
| | edge | 4 | 0 | 0 | 5 |
| 7 | surface | 20 | 0 | 0 | 5 |
| | edge | 8 | 0 | 0 | 5 |
| | | 10 | 4 | 0 | 10 |
| 11 | surface | 20 | 0 | 0 | 5 |
| | edge | 7 | 2 | 0 | 5 |
| | | 8 | 9 | 0 | 10 |

Analysis of flammability characteristics of fire-retarded samples carried out by comparing them with untreated leather has shown that:

- *for sample No. 7*
  a small extension of time to sustained ignition [TI] (by 3 s) occurs, whereas HRR remains on a similar level. The smoke emission, as expressed by specific extinction area [SEA], increases by 125% (Table 5) and time increases by 4 s during edge exposure to flame. Moreover, glowing is eliminated (Table 6).

- *for sample No. 11*
  time to sustained ignition increased by 27 %, heat release rate [HRR] was reduced by 20%, a two-fold growth of mass loss rate was observed, smoke emission increased by 50% (Table 5), time was extended by 3 s during edge exposure to flame and glowing was eliminated (Table 6).

Unfortunately, flame retardants increases the release of carbon monoxide roughly by a factor of 2, although it reduces the emission of carbon dioxide (Table 5).

### *3.3 Flammability of difficult-to ignite upholstery composites based on natural leather and barrier non-woven [Lin FR]300*

In the case of upholstery composites, the application of protective barriers situated between covering and filling materials can be the efficient way of flame retardancy of seats [2]. Such a barrier reduces the susceptibility of filling material present in a piece of furniture to the development and spreading of fire. As a barrier material we have employed in this study a non-woven made of flame-retarded flax fibres, which was developed at the Institute of Natural Fibres [6, 7]. The barrier flax non-woven [LIN FR]300, that is situated in an upholstery composite directly under a covering material, considerably increases moisture sorption and upgrades softness of upholstery system [4].
Results of flammability measurements of upholstery composites, consisting of natural leather or artificial PU leather and barrier flax non-woven [LIN FR]300, are presented in Table 7. Time to sustained ignition of the composites and covering material was shown separately in Fig. 3.

**Table 7.** Flammability of upholstery composites determined by the cone calorimeter method in compliance with ISO-5660 – 1:2002 (E)

| **Measurement parameters (heat flux of 35 kW/m$^2$)** | **Dimension** | **Composite consisting of natural leather + [Lin FR]300** | **Composite consisting of artificial PU leather + [Lin FR]300** |
|---|---|---|---|
| Peak Heat Release Rate [HRR] | kW /m$^2$ | 204.29 | 253.32 |
| Time to Sustained Ignition [TI] | S | 55.82 | 20.77 |
| Total Heat Released [THR] | MJ/m$^2$ | 17.12 | 14.59 |
| Average Heat of Combustion [$HOC_{av.}$] | MJ/kg | 16.10 | 17.14 |
| Average Mass Loss Rate [$MLR_{av.}$] | g / s · m$^2$ | 2.88 | 4.91 |
| Average Specific Extinction Area [$SEA_{av.}$] | m$^2$/kg | 162.82 | 182.96 |

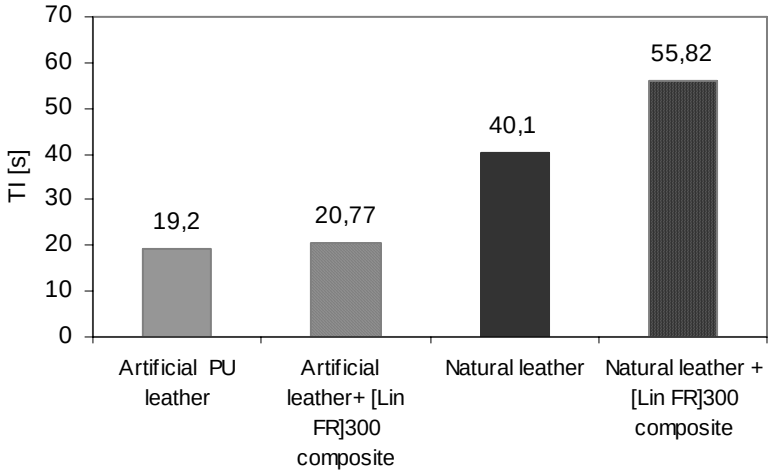


Fig. 3. Comparison of time to sustained ignition (TI) of different materials (heat flux 35 kW/m$^2$)

It results from Table 7 that a more effective composite is that containing natural leather because in the case of this composite, time to sustained ignition is by about 60% longer than that of artificial leather-containing composite. This fact is clearly seen in Fig. 3. Moreover, heat release rate is lower for the composite with natural leather which is, of course, the advantage of the latter composite.

## 4. Summary

1. Flammability studies of natural and artificial leather have shown that natural leather is safer in case of fire because of longer time to ignition (as evaluated by applying three different tests) and two-fold lower emission of carbon monoxide compared to artificial leather.
2. A drawback of natural leather is its tendency to glowing which can cause several-hour long smouldering of an upholstery system. Hence, there is a necessity of applying flame retardants or flame-retarding barriers for the upholstery system.
3. Among fire retardants investigated, the most efficient appeared to be a commercial product based on ammonium polyphosphate and boric acid (formula variant No. 11). It extended time to ignition, reduced total heat released and eliminated glowing of natural leather. Unfortunately, the presence of fire retardants increases optical density of smoke and carbon monoxide emission during combustion.
4. In the case of applying flame-retarding barrier, optical density of smoke, observed during combustion of composites is lower and time to ignition longer. Can flame-retarding barrier effectively stop the development of glowing of upholstery systems? This will be the subject of further studies.

## 5.References


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