for leather,
for you

GSC GROUP

THE DYNAMICS OF LEATHER COMBUSTION

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Part I

Leather is a combustible material and must be treated with appropriate flame retardant products in order to give passive protection in fire prevention.

Fireproof leather offers the obvious advantage of always having an element available that can reduce the speed of fire propagation so that the flames do not touch other combustible materials. This increases the time allowed for evacuation before the fire spreads.

Slowing the spread of a fire means having a low participation in combustion but also a rapid cooling time so as not to contribute to the overheating of the environment. The level of passive safety can also include minimal formation of dense and toxic fumes to promote visibility and breathability.

Fire Regulation and Reaction Tests

Each country has fire regulations for each type of application field, whether in the aeronautical, naval, railway, technical clothing or furnishing sector. Methods applied and parameters to be matched can be quite different if no harmonized standars are used.

Given the breadth of the topic, reference will be made to the few most widely requested and more space will be given to understanding the combustion mechanism.

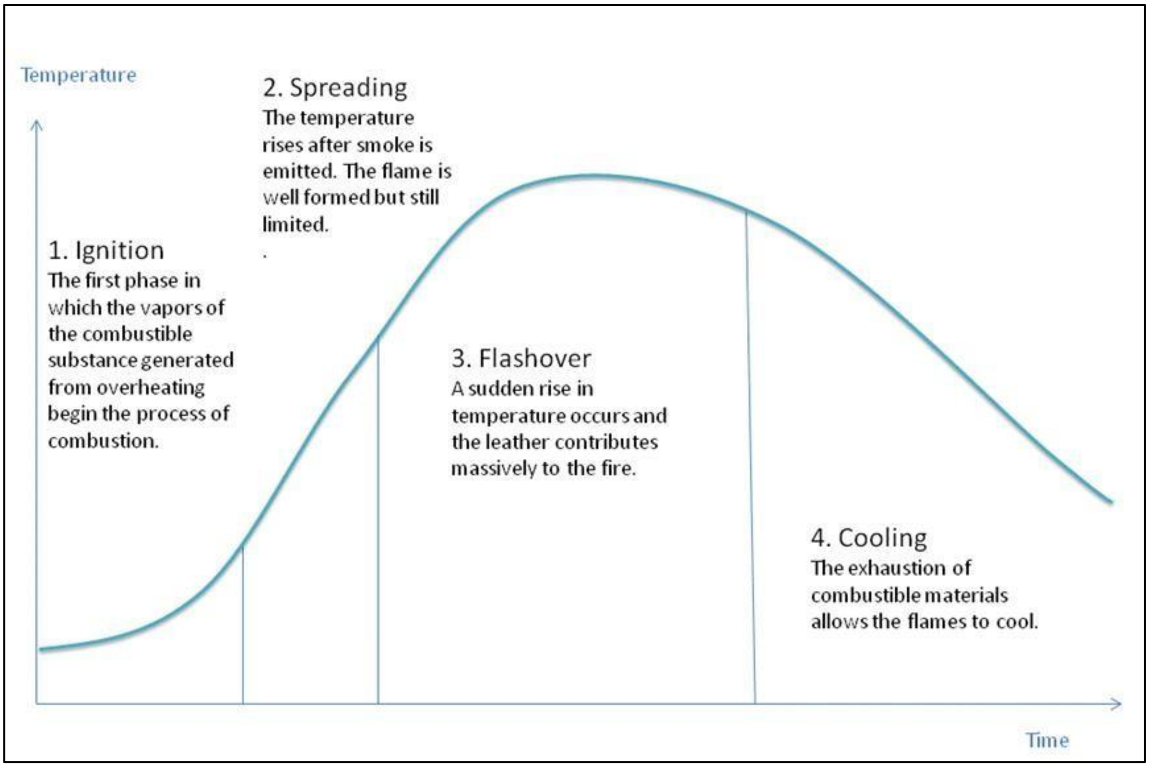
In order for the leather to meet the regulation requirements, flame retardants must be selected that are suitable for the preparation of the leather for the test and for the dynamics of combustion during the test.

A good example is the UNI EN 91/75 standard for the 1IM classification and the BS 5852 - source 1- standard which are very similar in carrying out the test, however, without considering the different ignition sources that will have an effect proportional to their aggressiveness, only the UNI EN 91/75 provides an initial wash of the specimen which aims to remove any deposited treatments and anything not fixed on the support. It follows that the use of flame retardants that can be washed out prejudices the result of the test according to Italian law.

How Fire Reacts to Leather

Let us now try to highlight what contributes to the behaviour of fire on leather in order to meet the correct performance criteria. Depending on the application sectors and the type of environment in which the leather is used, the tolerance of measured parameters can vary greatly (for example, in both aircraft and trains, the development of smoke can be taken into account but in the first case tolerance is much lower).

As a premise, we have fragmented the course of combustion in four phases:



Let's now consider which parameters to keep under observation during leather combustion and the factors that influence them (considering a generic finished leather):

Fire Resistance

Fatliquors provide the greatest amount of fuel vapour, and particularly those with mineral oils. In order for the fireproof leather system to work, it must be balanced:

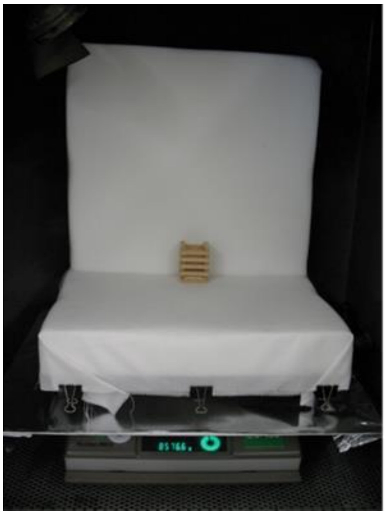
the flame retardants used must be available in the immediate vicinity of the flame and must degrade around the temperature in which combustion takes place.

. An example of an unbalanced system where the flame is far from the fireproofing agents is when there is a simultaneous high presence of mineral oils and a very thick finishing layer.

Overheating generates gases on the flesh side, which is more permeable than the finishing side. In the case of a vertical test conducted on leather, the flame acquires a large volume that remains distant from the flame retardants and as a result they offer a limited contrast. In this case the criteria of reduced post-combustion time and reduced destruction of the material are at risk. On the one hand the flame mainly feeds on the back of the specimen with gases expelled, and on the other, being durable and in light contact with the leather, it manages to carbonize it at a temperature without giving rise to a real combustion that degrades the flame retardants.

An example of an unbalanced system in which the combustion temperature is too low to degrade the flame retardants is observed when a small flame that brings little destruction but is very persistent is fed over the oil that oozes from the surface of the leather. It is a candle effect by which the wick burns with slow destruction fed by the vapours of the overheated wax. In both cases flame retardants fail to intervene correctly and risk not complying with the standard performance requirements.

We report another experiment in which the dynamics of combustion must be adequate for the test method. In the case of applications for furnishings, according to UNI EN 91/75 and BS 5852, the use of padding is foreseen. This adds a variable which complicates things. The filling foam, even if it is fire-retardant, releases combustible gases. If the fire-retardant leather is destroyed only a little it helps to keep the gases imprisoned and this condition maintains the flame inside the pillow. The latter is consumed more quickly and, once its thickness is consumed, it does not satisfy one of the requirements required by law. The leather must be destroyed to the extent that it allows the outflow and dilution of the gases on the outside to avoid excessive consumption of the padding.



Post incandescence

The persistence of embers in the leather as a result of combustion is a parameter that is not considered in the aeronautical sector but is instead very important in the public spaces sector.

It is well known that embers are a problem to consider if fire-retardant leathers are produced from mineral tanned hides, while organic tanning agents do not present this phenomenon. This is due to the absence of metals for which the stabilization of collagen is different as well as the chemistry of combustion. With the presence of metals, combustion results in more solid residue which is compacted by absorbing more heat and offering more resistance to destruction. In the absence of metals, organic substances have better combustion and are destroyed more quickly with the advantage of dispersing heat more quickly. However, it must be taken into account that a wet-white leather must be more lubricated than a wet-blue leather. For now, we just say that where the fatliquors are deposited in the dermis and their type are factors that contribute to combustion.

Dripping

During combustion, some portions of molten material can become detached, with the risk of spreading the fire front. This phenomenon does not usually occur with leathers, unless they are treated with oils or waxes to produce burnished and pull-up articles. Waxes, particularly, melt and burn, and therefore may migrate in liquid form before being consumed. In this type of leather, it is very difficult to reconcile the aesthetically pleasing effect obtained with oils and waxes with the performance requirements imposed by the fire regulations. Even a cigarette resting on an armchair covered with this material could constitute a risk of ignition. On the other hand, being treated with a flame retardant would compromise the essential characteristics of these pleasantly natural articles. To date, the only solution to offer an acceptable compromise between aesthetics and performance is a bonded resin and wax finish applied to a fireproof crust. This type of finish is also suitable for non-fireproof leathers in the case of minor cigarette-induced ignition, while in more severe cases it does not contribute to combustion and does not disturb the effect of the flame retardants used during the retanning process.

Deciding to face a test for fireproof leather is certainly helpful to understand the dynamics of combustion. We have reported some experiments that will be implemented in the future in order to get a more complete overview and to choose the type of processing best adapted to the purpose.

Part II

Fume toxicity

Smoke is a collection of tiny particles in solid, liquid and gaseous form, not sufficiently destroyed by the thermal reaction. According to statistics, its inhalation is the main cause of death in fires.

Although it may contain a large number of chemicals that contribute to continuous reactions, only a limited number of the main products of combustion are included in the tests conducted in the aeronautical and railway sectors. Some test variations can be specifically requested by the manufacturers of aircraft and trains, as well as the non-use of certain substances upstream. Typically, these are:

- **Carbon dioxide:** the better the system's combustion, the greater its proportion in fumes. It is present in far greater quantities than other gases.
- **Carbon monoxide:** it forms due to the incomplete combustion of hydrocarbons.
- **Hydrogen sulfide:** it forms through the combustion of sulphur; it is a constituent part of leather, but may also be present as a residue of dehairing.
- **Sulphur dioxide:** it forms in the presence of sulphur when more oxygen is available for combustion.
- **Hydrogen cyanide:** it is formed, for example, by acrylic resins, following combustion with poor aeration.
- **Hydrochloric acid:** it is formed by the chlorine contained in retanning or fireproofing products.
- **Hydrobromic acid:** it is formed by the bromine generally contained in fire retardants.
- **Nitrogen oxides:** they are formed by the nitrogen contained, for example, in melamine resins as well as by the nitrogen present in the air.

The way in which combustion occurs determines the final composition of the fumes. The variables involved are temperature, the type of fuel (the leather and all the products it contains) and the percentage of oxygen available.

In general, for the aeronautical and railway sectors, the toxicity of leather's combustion fumes is not considered a worrying obstacle. The empirical values detected are widely below the limits imposed.

Fume density

The ability to emit low-density fumes is the most complex feature to impart to leather, due to the fact that it is always linked to another flame resistance requirement, i.e. either low destruction or low heat development.

We know that the warmer the flame, the faster pyrolysis takes place, and that the better the combustion, the lower the smoke density.

Complete combustion forms water vapour and carbon dioxide, the products of maximum oxidation, with a much more transparent gaseous phase. The material that does not sublimate remains in the ashes, which are therefore composed of the residual minerals and carbon. In the case of wet-blue leather, there is usually more material in the solid carbonized portion than in a wet-white leather - and therefore, also hexavalent chromium. In the final phase of the combustion reaction, carbon dioxide is still released. Since it cannot be further degraded, it does not give rise to fire, but it can keep the embers incandescent if a high temperature is maintained and there is contact with oxygen. It is advisable to keep the hot coals to a minimum because they could cause pyrolysis of the leather in adjacent areas, increasing the unburned particulate in the gas phase.

In the combustion chamber where the leather specimen is tested, the amount of air available is fixed. Combustion proceeds in different ways with a higher or lower than stoichiometric air-fuel ratio. In the former case, we have partial combustion with less heat, more unburnt particles released, and a long, yellow, smoky flame. In the second case, with lower fuel than air, we have better combustion, with a short, bluish flame.

To produce a leather that will pass the fumes test, therefore, it is possible to act on the other parameters listed below, seeking the right compromise between the leather's resistance and its reaction to fire.

Leather mass

The greater the amount of material to burn, the greater the potential smoke. The unevenness of the leather's surface should be taken into account (open areas vs closed areas requiring different products in order to render the organoleptic characteristics more uniform), as well as its cross section (compared to thicker leather, thinner leather has a proportionally thicker papillary layer than its reticular layer). The deposit of retanning products in these two cases is somewhat different. From a practical point of view, it is useful to know that although thin leather burns faster and may favour the formation of low-density fumes, on the other hand it could generate too much heat or even destruction. The advantage in terms of fumes should be managed by selecting the most suitable fire retardant, which must offer strong resistance. In this context, it is recommended to use a product that adheres, in order to achieve more constant results.

This is because thin leather does not retain the same proportion of fire retardant if this does not adhere completely. It is important to be aware that the finish will always make either a little or a very favourable contribution to combustion, but never a negative one. The dynamics ultimately depend on the density and the thermal properties of the leather, obtained through tanning, retanning and mechanical operations.

Type of retanning products used

A priori, it is better to avoid or limit the use of smoke-producing products such as resins or phosphorus-based flame retardants. A relatively low combustion temperature could be generated, making these products readily manifest their attitude. They are inadvisable in applications in the aeronautical sector, whereas for the railway sector, where smoke tolerance is higher and higher resistance to destruction is required, they can benefit the retanning process. As for the finish, it is worth exploiting the lack of resistance to fire, provided it is not too thick and the crust fireproofing is very high: during the initial ignition phase, it could give off black smoke.

- **Product distribution in the substrate**

To provide an example, if you apply fire retardant before the fatliquor, the fuel will be more exposed than the fire retardant. Its vapours will spread and contribute to the combustion before being able to react with the flame retardant, also due to the fact that the latter is generally slower to degrade. This situation is accentuated if the leather is squeezed by setting-out and vacuum dried, a process that pushes outwards the fatliquors. This phenomenon can be exploited for the purposes of better combustion.

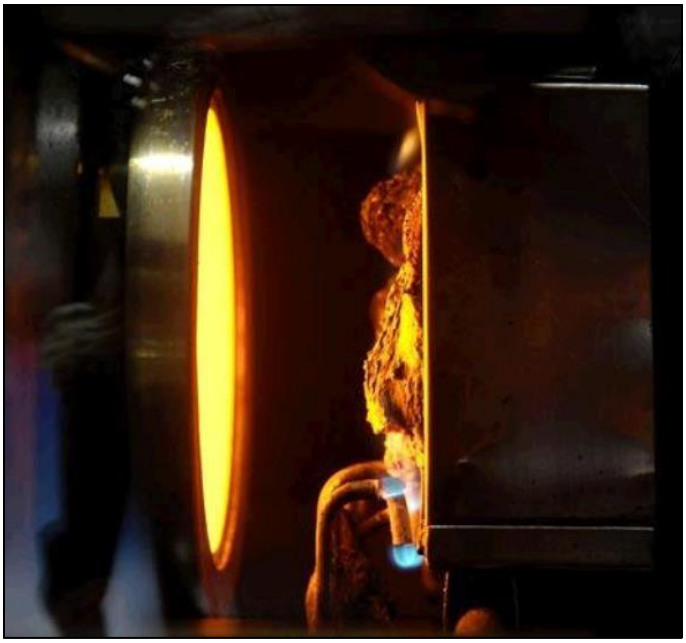
- **Physical state or structure of the leather**

Compact leather contains less air than spongy leather. Toggling frame drying not only leaves less fatliquor on the surface of the leather compared to vacuum drying; its combustion is also richer in oxygen.
All the mechanical operations that contribute to modify the structure of the leather, such as the compression of fibres due to embossing or their opening due to milling, are to be taken into strict account. If the leather takes in more air, there will be more comburent for the reaction.

In reality, combustion can proceed in a more or less linear way, depending on the heat source and on the physical and thermal properties of the leather.

The method for analysing fumes adopted by the aeronautical sector envisages two different ignition conditions: flaming and non-flaming, in other words the addition or otherwise of small flames to the constant jet of hot air from a radiant oven. To understand the difference they entail, let us think of materials with which we are much more familiar, such as plastic and wood. In general, plastic generates little smoke with non-flaming and a lot of smoke with flaming, i.e. with an open flame. On the contrary, wood, which is more porous and richer in oxygen, generates less smoke when subjected to flaming and much more when subjected to non-flaming due to its insulating power.

Leather can be processed in such a way as to maintain good shape stability during the test, so that the final result is a reliable indicator of its behaviour. Conversely, it may deform upon moving away from the heat source. This would be counter-productive and would result in worse combustion. It can even become detached from the test substrate, withdrawing completely from the heat source. This can occur with a very extreme test, but on the basis of the adopted Sandard, such behaviour can give a paradoxically positive result if it is repeatable.



Setting aside extreme cases, the dynamics of leather combustion can be summarized as follows. At the time of applying the flame, it heats up considerably in the area concerned, therefore degrading quickly and with little smoke formation. In the meantime, the areas above are exposed to a lower temperature, which however is sufficient to make the flammable gases evaporate. At a certain point the resulting flashover occurs, with a substantial increase in fire volume and a sudden increase in the heat emitted. The propagation continues in the upper layers, where it invests a larger surface and therefore the smoke starts to be much more substantial. In this phase, the fire reaction characteristics of fire retardants and their quantity determine the success or failure of the test.

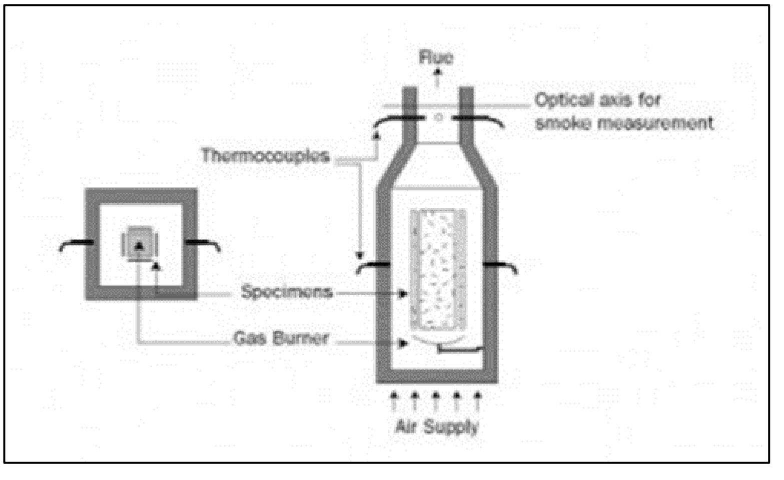
What role does the relative humidity of leather play?

The presence of moisture in the leather slows the absorption of heat and, in theory, tends to increase thermal conductivity. This favours faster internal energy diffusion compared to dehydrated leather. In the absence of moisture, pyrolysis takes place more quickly and combustion is facilitated. This characteristic can be useful in ignition tests, where fire source application times are short. Furthermore, water vapour does not affect fume opacity. This small expedient, however, is not a decisive factor in more aggressive and complex tests.

Heat release

In the aeronautical sector, the FAR 25.853 Standard contemplates the emission of heat generated by combustion. During a certain period of time, the average energy produced is required to be lower than a specific value, and throughout the duration of the test no peak should occur in excess of that same value. Basically, the combustion of leather is required to take place slowly and as constantly as possible, limiting flashover to the greatest possible degree. It is worth noting that, based on empirical tests, the contribution of the finishing layer alone can reach 10% of all the energy emitted, while the remaining 90% is generated by the source of ignition plus the propagation of the flame on the crust. Striking a balance is rather difficult.
The temperature measurement can be applied directly to the combustion smoke. This is the case of Germany's strict DIN 4102 Standard for B1 classification. Partial combustion generates dense gases which can ignite at a later time and at a higher level due to the new oxygen caused by the heat or an increase in the temperature generated by the underlying combustion; therefore, their formation is not desirable.

The combustion must be as complete as possible with a high temperature and a short flame. The reduced fire load allows for better heat dispersion in a relatively larger volume of air, so that when the smoke reaches the flue where the measurement takes place, it may have a sufficiently low temperature.

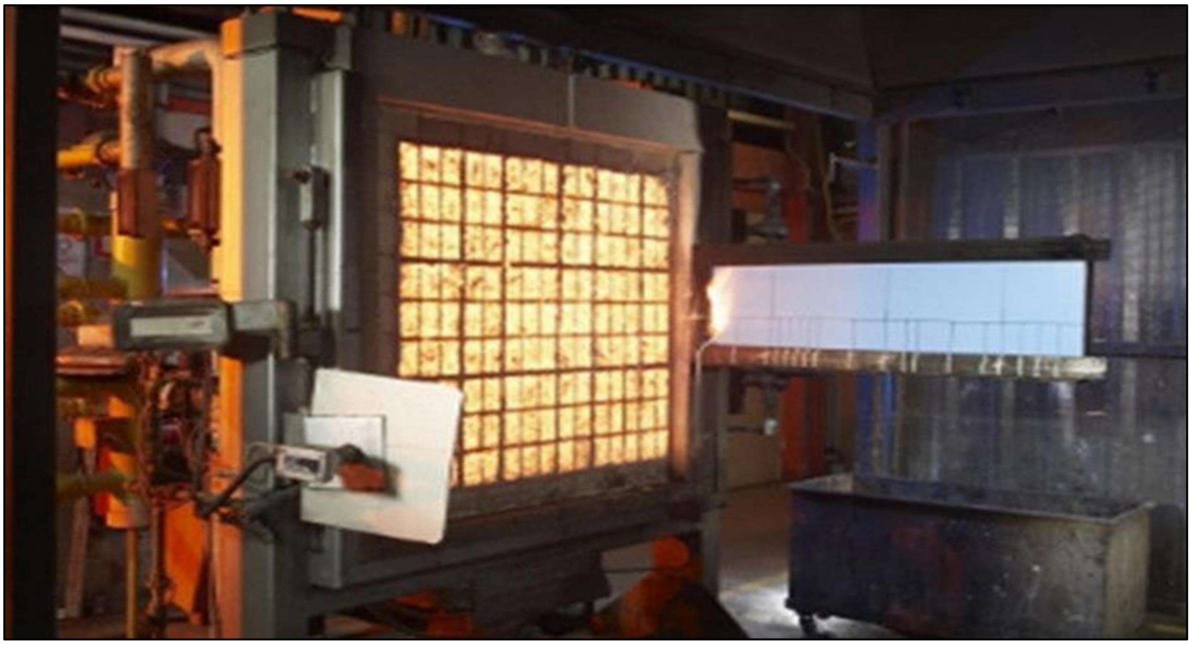


Once again, striking the right balance is difficult. Using flame retardants with only one type of reaction to fire is not sufficient to achieve the desired effect. In other words, it is necessary to combine several types of fire retardants and benefit from a synergistic effect. Given the variety of retanning processes, it is not possible to predict the result as there are too many unquantifiable variables: not least, the formulation of the fatliquors and polymers normally used to confer the desired organoleptic characteristics.

Combining multiple materials

For upholstered furniture intended for public spaces or for means of transport, where the most restrictive safety regulations generally apply, it is important to use fireproof foams. Subjected to flame, these polyurethane materials are destroyed without combustion, only emitting gases. The absence of flame is due to the fact that the gases disperse quickly, and the temperature lowers rapidly. These foams can be of various densities, providing more or less resistance to destruction. The use of a more economical, non-fireproof foam can result in complete destruction of the sofa, and the formation of a large volume of fire.

In the case of very strict tests, it is necessary to place a barrier between the foam and the upholstery. The purpose of the barrier is to isolate the foam from the flame. However, as the temperature rises due to continuous exposure to the heat source, the more gas is produced. Upon reaching a certain threshold, it is possible to see large amounts of fumes filtering outwards as a result of considerable accumulation on the inside. This can result in the leather unexpectedly starting to burn, with destruction happening too quickly to be able to complete the test successfully.



Assembling a piece of furniture suitable for these extreme tests is rather complicated as it depends on the correct combination of three different elements. It should not be assumed that the sum of three materials, each with excellent individual performance levels, will automatically generate a positive result. In any case, the essential work is performed by the barrier. If we consider wall panels in which the leather adheres to a non-combustible material, the difference in fire resistance is clearly evident. Since there is insufficient comburent, the reaction is very slow.

The UNI 45545-2 standard envisages two methods for assembling the foam, barrier and leather, in which only the middle layer changes. The first method relates to the prevailing use of a middle layer in technical fabric, whereas in the second method this is replaced by aluminium foil. In the second case, the aim is to assess the characteristics of the upholstery alone, as aluminium foil does not possess the necessary mechanical requirements for actual use in real life. In this case, when totally isolated from gases, the leather will exert greater reaction resistance. The resistance value is deduced from the heat emitted during thermal degradation, which will be lower than in the event of using technical fabric.

How fire retardants work

It is worth remembering that fire retardants can: subtract fuel from the reaction, forming a protective carbon barrier that separates it from the flame; vitrify around the substrate, raising its combustion temperature; dilute the comburent with inert gases or water vapour; or subtract oxygen from the reaction. To obtain the best possible combustion with adequate resistance to destruction, the quantities and type of fire retardant can only be balanced empirically.

To be avoided

Imperfect adhesion of the finishing film can cause air to infiltrate into the gap between the crust and coating, feeding the fire on the grain side. This is a disadvantage in the finishing phase and can occur when the crust is very hygroscopic due to the use of certain flame retardants, disturbing the crosslinking of the film. Other precautions must be taken to manage this type of fire retardant.

If we are not careful, leather "saturated" with fireproofing products that are hard to burn, will burn like a pile of straw when its porosity is increased by a perforating embossing. This is an extreme example, but it highlights the fact that there is a limit to the deformation of the natural appearance of leather for these types of technical articles. Returning for a moment to a more traditional use, it should be noted that leather that is left too empty due to a lean re-tanning process or to natural sponginess of the raw hide, will also tend to incorporate more oxygen, with the inevitable consequences.

For questions or advice, please do not hesitate to contact:

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