"New plasma application technologies for leather finishing"

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ABSTRACT

The availability of plasma application technologies no longer limited to operating in low pressure conditions, but operating at atmospheric pressure has allowed to significantly expand the range of treatable materials. As regards the applicability of atmospheric plasma on leather, this work deals with the increase of the adhesion properties of leather to the surface finishing layers in order to increase the mechanical and fastness performance. The ability of a surface to come into contact with liquid molecules, determined by the balance between cohesion forces and adhesion forces, can be increased by opening the bonds present on the surface, in this way the latter becomes more reactive towards the material to be adhered, or by inducing surface crosslinking, in which the attractive forces between the substrates can be increased thanks to the modification of the hydrophilic component of the surface. The atmospheric plasma DBD (Dielectric-barrier discharge) type, with its ability to amplify the adhesion properties of the treated materials, has been exploited to selectively treat the interfacial area, making it possible to increase the adhesion values of the finishing films on leather, as well as dry and wet rubbing fastness, compared to the usual spray or roll coating treatments, maintaining thin layer compliant with the required standards and with improved organoleptic properties with more pleasant and natural film.

Keywords: surface finishing, plasma, improve adhesive properties, leather coating

Introduction

Surface modification techniques which can transform conventional materials into highly valuable end products have become industrially important for a wide range of applications. In recent years, great advances have been achieved in developing surface treatments to modify the chemical and physical properties of polymer surface without affecting bulk properties. The plasma technique is probably the most versatile surface treatment technique. Plasma is a gaseous mixture of electrons, radicals, ions and excited molecular states which are created by collisions between high energy electrons and ground state atoms or molecules. The high energy particles in plasma can interact with the polymer surface by both chemical and physical processes, which are known to improve the adhesive properties, induce cross-linking and chemical functionalization of the polymer surface.[17] Gases such as argon, oxygen, nitrogen, fluorine, carbon dioxide and water can produce the unique surface properties required by various applications. For example, fluorine plasma treatment can decrease the surface energy and improve the chemical inertness of a polymer, whereas cross-linking at the polymer surface can be introduced by inert gas plasma.[18] In addition, plasma treatment is usually confined to the first few nanometers depth beneath the polymer surface and therefore does not affect the bulk properties.[17-19] Other advantages of plasma treatment are that this technique is environmental-friendly and easy to implement. In this study oxygen plasma treatment was employed to modify the surface of the leather to increase some performance by increasing the adhesion between the coating films. The changes in adhesion strength and surface mechanical resistances such as color fastness to rubbing and abrasion resistance of the treated coating were investigated. The aim of this study was to find a simple and efficient way to enhance the fastness leather coating without sacrificing crucial mechanical properties.

In particular, through a series of experimental tests it has been possible to verify the increase in adhesion capacity of the leather to be subjected to finishing or lamination (foil transfer), where it has been possible to give evidence that certain atmospheric plasma pre-treatments are able to significantly amplify the bond at the crust-finishing interface.

Materials and method

Plasma treatment

The tests were carried out using laboratory equipment capable of processing leather samples measuring 2 cm x 30 cm. The system consists of a Dielectric Barrier Discharge (DBD)-type discharge device, involving a pair of ceramic electrodes opposed to a silicone-(PDSO) coated discharge cylinder. The atmospheric plasma laboratory machine (compressed air supply) works by treating a leather, bound to the 150 mm diameter silicone cylinder that acts as a dielectric. The working speed, represents the rotation speed of the cylinder, can vary from 10 to 30 m/min. The high-frequency generator has a maximum power of 1.5 kW and can also work in pulsed as well as continuous mode. The device is equipped with two ceramic-coated discharge electrodes. In addition, there is an extraction hood system for any exhaust gases and the control panel equipped with a PLC with operator panel for setting process parameters: cylinder speed, electrode power and the number of revolutions of the cylinder which represent the number of treatments that can be carried out. The device calculates the power output per surface area as a function of speed and number of revolutions and the working power applied, effectively obtaining the applied power measured in W•min/m^2. Another parameter that can be varied is the distance of the cylinder and the electrodes, which in all the experiments carried out in this work was 3.0 mm for each electrode. For example, with a linear roller speed: 10 m/min; a plasma power applied: 750 W 50 roller revolutions; there is a specific energy on a sample of 15 kW•min/m^2.

Application of Finishing

Samples of crust leather (chrome-tanned and retanned for upholstery uses) were cut to the dimensions of 21,2 cm x 21,2 cm, corresponding to the surface area of 1/2 square foot, to be able to properly fasten them to the plasma roller. The method of preparation and execution of the tests for spray-finished samples is as follows:

1. Application of Polyurethane/Acrylic + dye base coat: 12÷13 g/sq ft
2. Drying
3. Printing (hot press)
4. Second dye base coat application 3 g/sq ft
5. Drying
6. Fixative (6% isocyanate crosslinker to be added at the time of use) = 3 g/sq ft
7. Drying

Plasma application was used on no buffed crust leather (P1) or after the base coat, before fixative (P2).

A sample is prepared for reference and one with the application of plasma with optimal specific energy corresponding to 15000 W/m2min. The samples are left to cross-link for 24 h at room temperature and then the values of adhesion of the finish and fastness to wet rubbing are determined.

Hot foil transfer, also known as hot stamping or foil stamping, is a process that utilizes a heated roll and pressure to transfer the metallic (or other prints) hot foil film onto a surface. The heat melts the adhesive on the hot foil film, which then adheres to the leather surface, fig 1 and fig,2

For the lab trials, samples of crust leather (chrome-tanned leather with leather goods retanned) were prepared cut in the dimensions of 21.2 cm x 21.2 cm, corresponding to the surface area of 1/2 square foot. The so-called standard samples were processed with foil transfer methodology, while those subjects to innovative modification were pre-treated with plasma with optimal specific energy corresponding to 15000 W/m^2 , then immediately transferred to the foil transfer machine, left, in the end, to cool for 24 h before adhesion strength tests. The materials and application technologies were supplied by the company FAMAC. Srl of Arzignano (VI) Italy

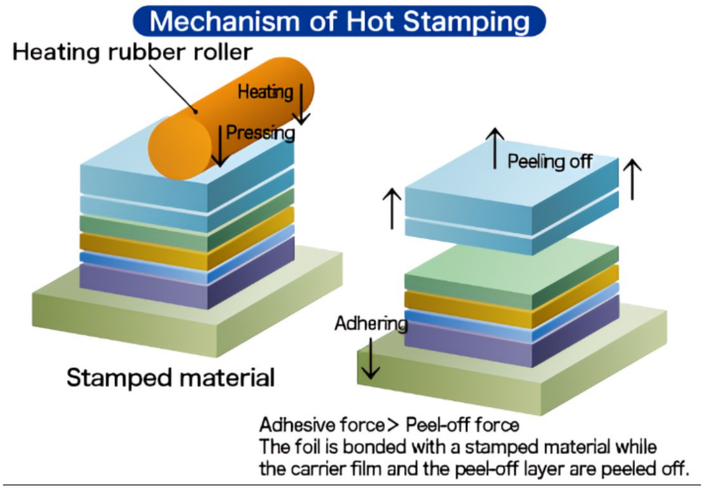

Fig.1 [4]

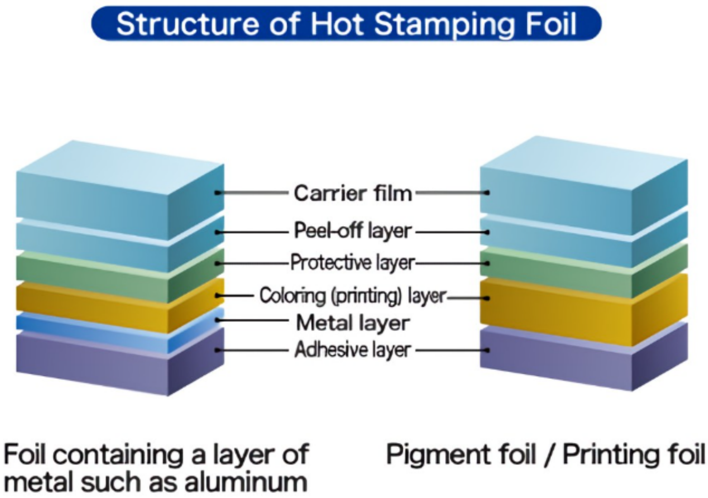

Fig.2 [4]

Measurement of physical Testing

The performance tests of the coatings were determined through the official methods:

Wet rubbing fastness (UNI EN ISO 11640 / IUF 450)

Finishing adhesion (UNI EN ISO 11644)

Results and Discussion

The plasma technique is probably the most innovative and versatile nanosurface treatment technique. Consisting of a gaseous mixture of electrons, radicals, ions and molecules in the excited state resulting from a set of inelastic collisions between high-energy electrons and atoms and molecules in the ground state, this state of matter has the property of interacting with the surface of tanned leather through both chemical and physical processes. The result of these interactions results in increased hydrophilicity both in the adhesion properties to a possible finishing polymer or in the induction of cross-linking and chemical functionalization of the polymer surface. For example, by using an inert gas it is possible to induce cross-linking phenomena that will affect only a surface layer limited to a few nanometers, while the internal area of the film would remain unchanged, as well as the general properties of the polymer mass.

By means of a system of generation of plasma in the atmosphere, i.e. both at pressure and in the chemical composition of the gases used "atmospheric", increases in the adhesion of the finish coating and resistance to wet rubbing were observed.

Spray finishing

Exposure of the leather to be sprayed to plasma pre-treatment with different energy inputs (15÷90 kW/m^2•min) and in two different ways: plasma applied initially in the no buffed crust (P1) or before the fixative (P2). P1 or P2 spray finishing was carried out immediately (up to a maximum of 10 minutes after exposure to plasma) by standard products for furniture or leather goods; while physical performance tests were performed after rest of at least 24 hours.

The specific plasma energy values applied were, respectively: 15000, 30000, 60000 and 90000 W/m2min.

Table 1 shows the wet rubbing values (UNI EN ISO 11640) with 800 wet cycles and P1 type application

Sample	Rating (Grey Scale)
Reference no plasma	4 gs @ 800 Wet
P1 15k	5 gs @ 800 Wet
P1 30k	4/5 gs @ 800 Wet
P1 60k	3 gs @ 800 Wet
P1 90k	3/4 gs @ 800 Wet

Table 1; legend: P1 xk = plasma treatment at x specific energy in kW/m^2; gs = grayscale

Tests with samples subjected to wet rub fastness test at different wet cycles: 150, 250 and 500, with the results shown in table 2

Sample	Rating (Grey Scale)
Reference no plasma	3 gs @ 150 Wet
P1 15k	5 gs @ 500 Wet
P1 30k	2/3 gs @ 250 Wet

Table 2

Fig 3 standard samples, P1 15k and P1 30k subjected to the wet rubbing test as an example

These tests demonstrated a positive effect on wet rubbing resistance only if the plasma was applied at an energy of 15 kW/m2min, while it had a negative performance effect at higher energies.

The adhesion tests of the finish (UNI EN ISO 11644) were verified on leather specimens treated with different plasma energies and in different phases of spray finishing, i.e. initially on the crust (P1) and before the final fixative (P2)

Sample	N/10mm (*measurement after 48 h)*
Reference no plasma	7,2
P1 15k	10,8
P1+P2 15k	10,8
P1 30k	11,9
P1+P2 30k	13 N

Table 3 (measurement after 48 h)

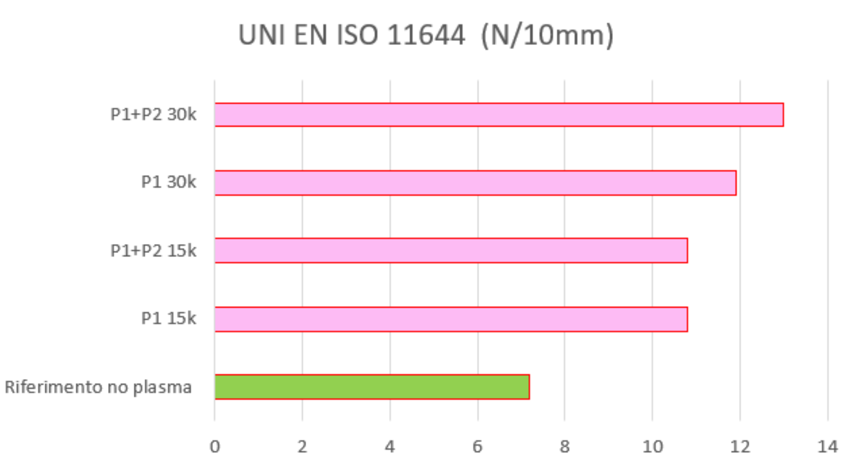

Fig 4 explanatory graph of the values in table 3

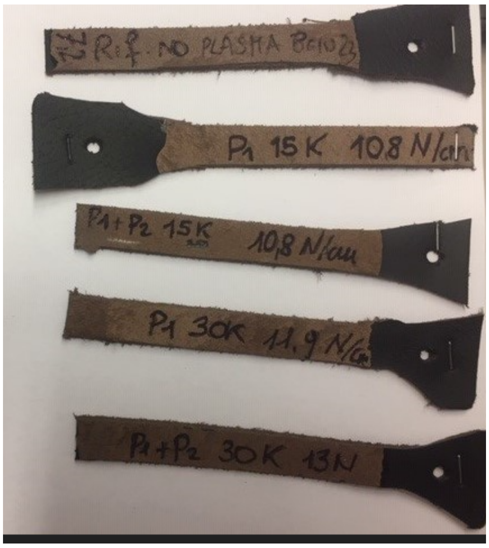

Fig 5 images of the samples subjected to resistance tests.

Subsequently, leather samples were tested in P1 mode with different energy and different rest times (48 h or 24 days). The results are explained in table and graph 4.

• Sample	N/10mm after 48h	N/10mm after 24 days
Reference no plasma	7,4	9,0
P1 15k	15	14,9
P1 30k	12,9	11,5
P1 60k	12,5	10,0
P1 90k	10.5 N	12,0

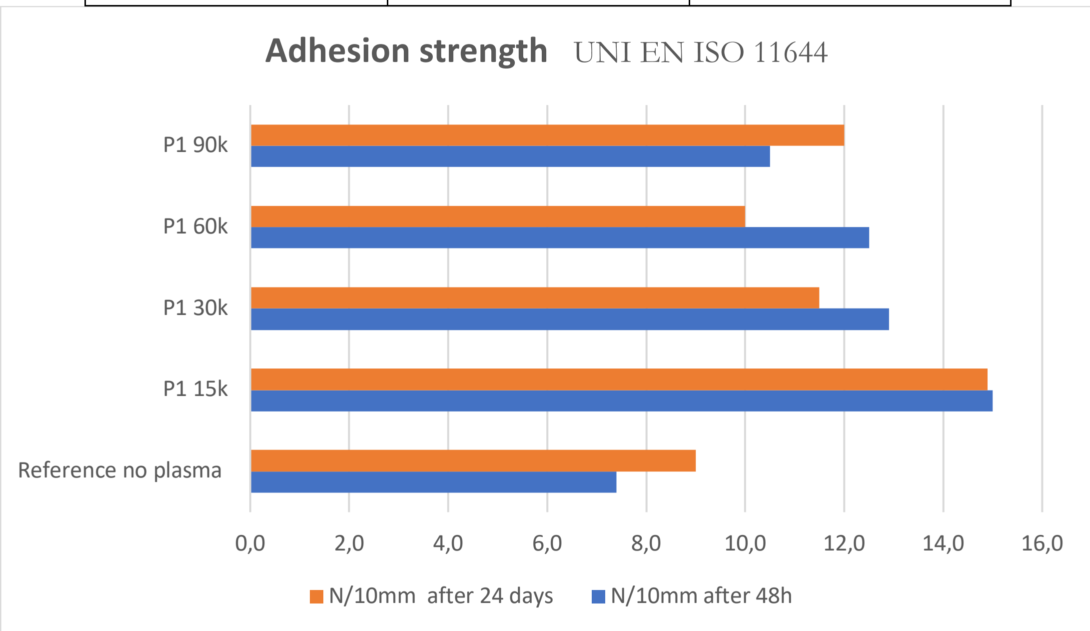

Table and graph 4

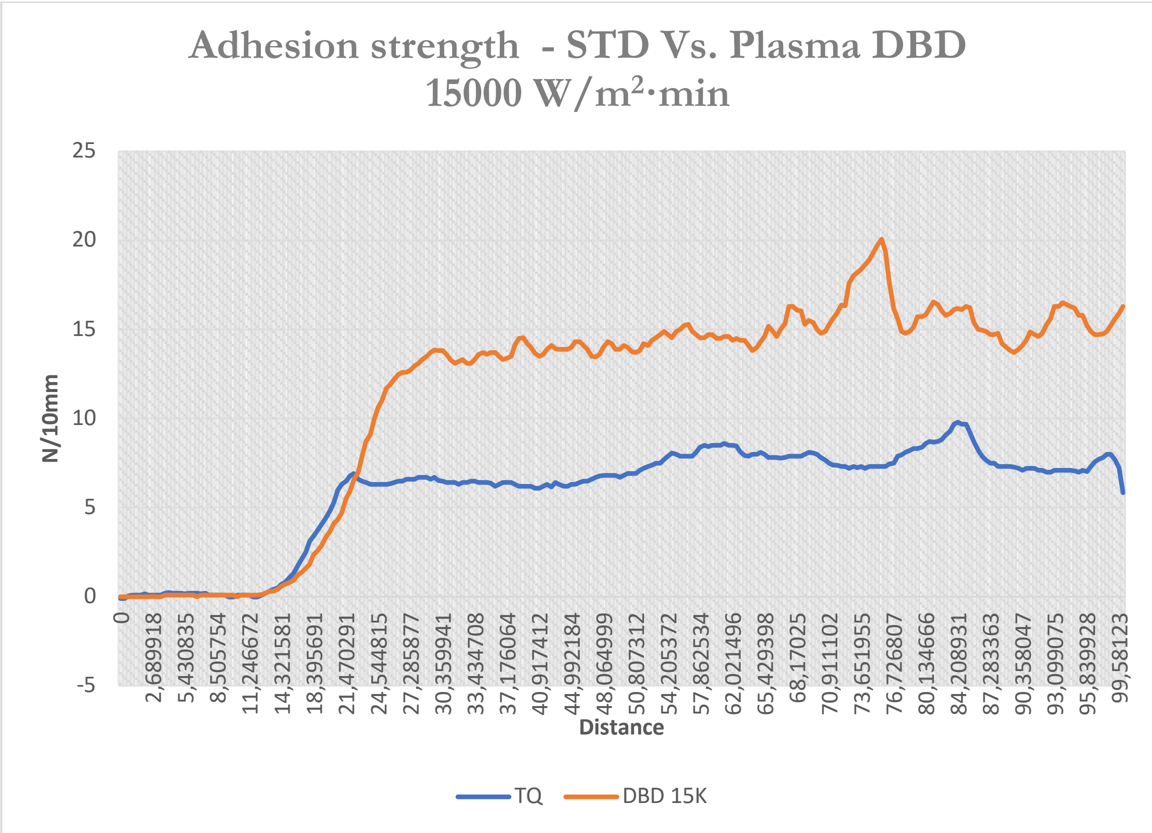

Fig 6 trend of the dynamometer stress of two samples under examination by way of example

As regards the increase in adhesion of plasma-treated leathers to finishing coatings, an increase in the strength values necessary to remove coatings can be deduced from up to 40 to 70% for specimens activated at 15 kW/m2min, compared to the standard with traditional finishing. The most efficient system to obtain higher performance seems to be those with P1 plasma treatment on crust with 15 k W/m^2, even if a more expensive treatment, such as the concomitance of P1 and P2 before the final fixative with energy of 30k W/m2min has shown high adhesion values.

Modification of adhesion properties on leather finished with *foil transfer system*

Thanks to the exploitation of its atmospheric plasma pilot generator, it has been possible to verify the increase in adhesion capacity of crust leather even for finishing through lamination (foil transfer).

Even in the case of foil transfer finishing applications, plasma demonstrates competitive advantages on coating performance thanks to the activation of the heat-reactivating adhesive and allowing an increase in cohesion with the leather fibers. In the experiment, 2 samples of leathers for leather goods in full grain (brown crust B and black crust C) and buffed leather (brown crust B and black crust C) were treated.

The average adhesion values in N over 10 mm are expressed in Table 5 where the increase in performance for all samples pretreated with plasma is clear.

Sample	STD (N/10mm)	Plasma DBD (N/10mm)	Delta %
FULL GRAIN B	5,1	7,1	+39,2%
FULL GRAIN C	4,65	6,6	+41,9%
BUFFED B	4,15	7,5	+79,5%
BUFFED C	3,2	5,7	+78,1%

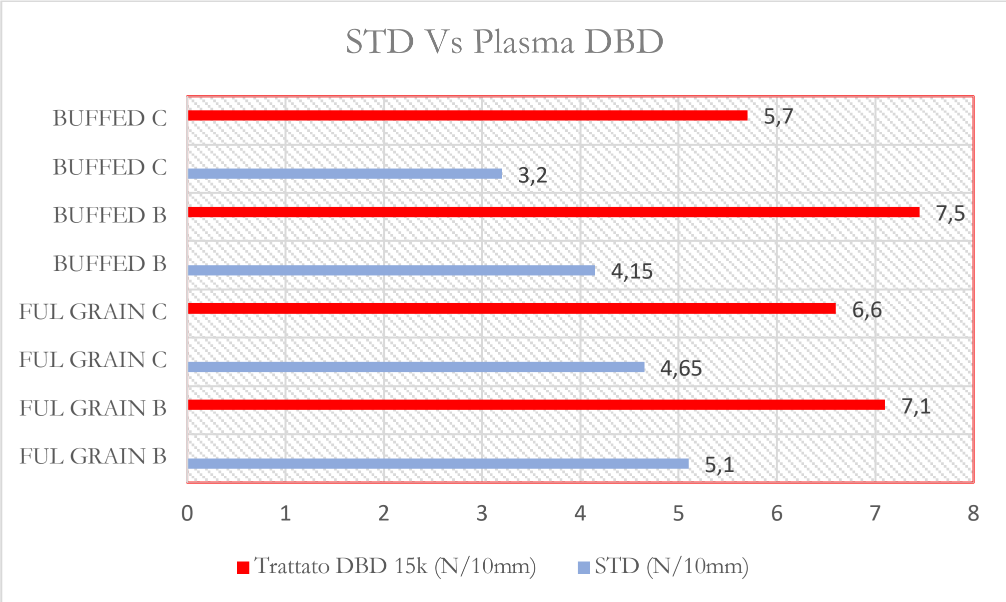

Table and graph 5

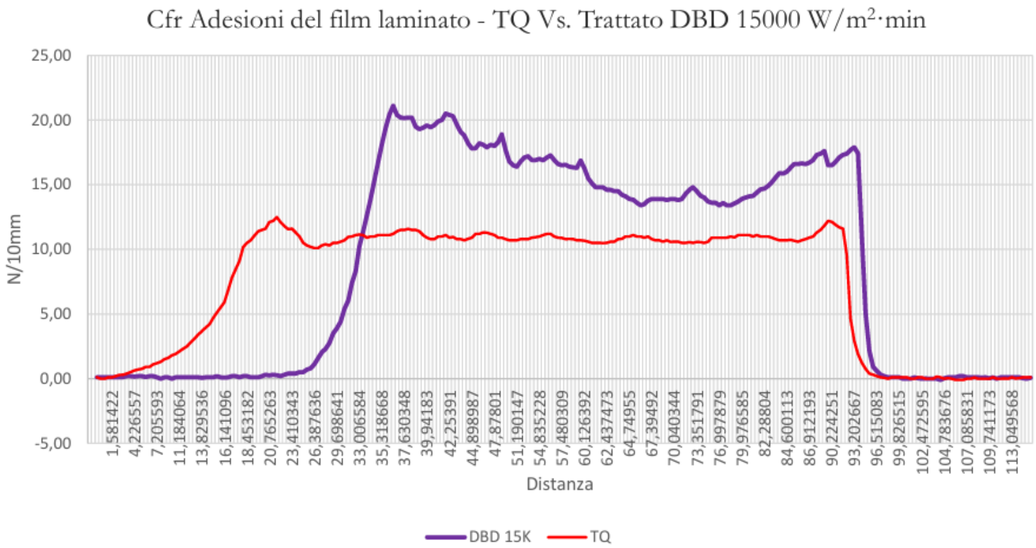

Fig. 7 trend of the dynamometer stress of two samples under examination by way of example

Conclusion

The availability of plasma application technologies no longer constrained to operate in low pressure conditions, but operating at atmospheric pressure has made it possible to significantly expand the range of materials that can be treated. As regards the applicability of atmospheric plasma on leather, the surface activation of crust leather to be finished both in the most usual spray mode and through foil transfer technology to increase the adhesion and anchorage of polymeric films to the first collagen layer of crust leather have been explored. The implemented performance of the finished leathers was measured through wet and dry rubbing smoothness and finishing adhesion. The research has shown above all an increase in the adhesion of leather treated with plasma with 15 kW/m2min of applied energy, towards finishing coatings; i.e. an implementation of the force values necessary to remove coatings from 40 to 70% compared to the standards finished in usual and standard conditions. Treatment with plasma at atmospheric pressure in oxygen lends itself to surface modifications capable of facilitating the adhesion mechanism of polymeric films to the collagen layer of leathers to be finished, without causing degradation of the general properties of the leather product. The technique is also very interesting from an ecological point of view, both for the absence of chemical and mechanical additives, such as grinding and low energy expenditure.

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