

COLD PLASMA TREATMENT (CPT) FOR NEW HIGH QUALITY WATER REPELLENT LEATHERS

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October 2004

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Tanning industry products must meet world-wide and user's requirements, who demands high quality leathers both for fashion and performance characteristics as waterproof or water repellent leathers.

Chemical technologies have made good results in the last years, but the hydrophobising process is expensive and the results are not satisfactory and often the organoleptic characteristics are modified.

These problems have led to design a new system based on an innovative, environment-friendly and chemical free hydrophobising system based on the use of cold plasma technology.

The CPT is applied for:

- a wider range of types of water-oil repellent and resistant to water spot leathers thanks to the possibility of applying this versatile treatment to all types of leather;
- an improvement in the quality of currently produced finished leathers because the treatment do not affect the organoleptic properties of leathers;
- elimination of the consumption of traditional chemical products for superficial hydrophobisation treatment, eliminating the air pollution currently associated with this type of superficial treatment;
- improvement of working conditions thanks to a safer chemical free new process.

2. DESCRIPTION OF THE INSTALLATION

This installation is composed by three vacuum chambers which are linked together and have the following functions:

1. introduction chamber (IC);
2. plasma chamber (PC);
3. end chamber (EC).

The **IC** has horizontal cylindrical shape with internal diameter of 1000 mm and its overall length 920; it is placed on a blue painted iron loom.

At the end of the shell-plating two hemielliptical doors open an elastic hinges. Viton seals provide the thightness less 1.10^{-8} mbar/l.sec.

On the external shell-plating flanges of several sizes, in order to allow the access in the chamber of the sensors and feedthroughs needed to make the installation work, are welded.

The pumping system installed on the IC is optimized to have water pump high speed;the following components are mounted :

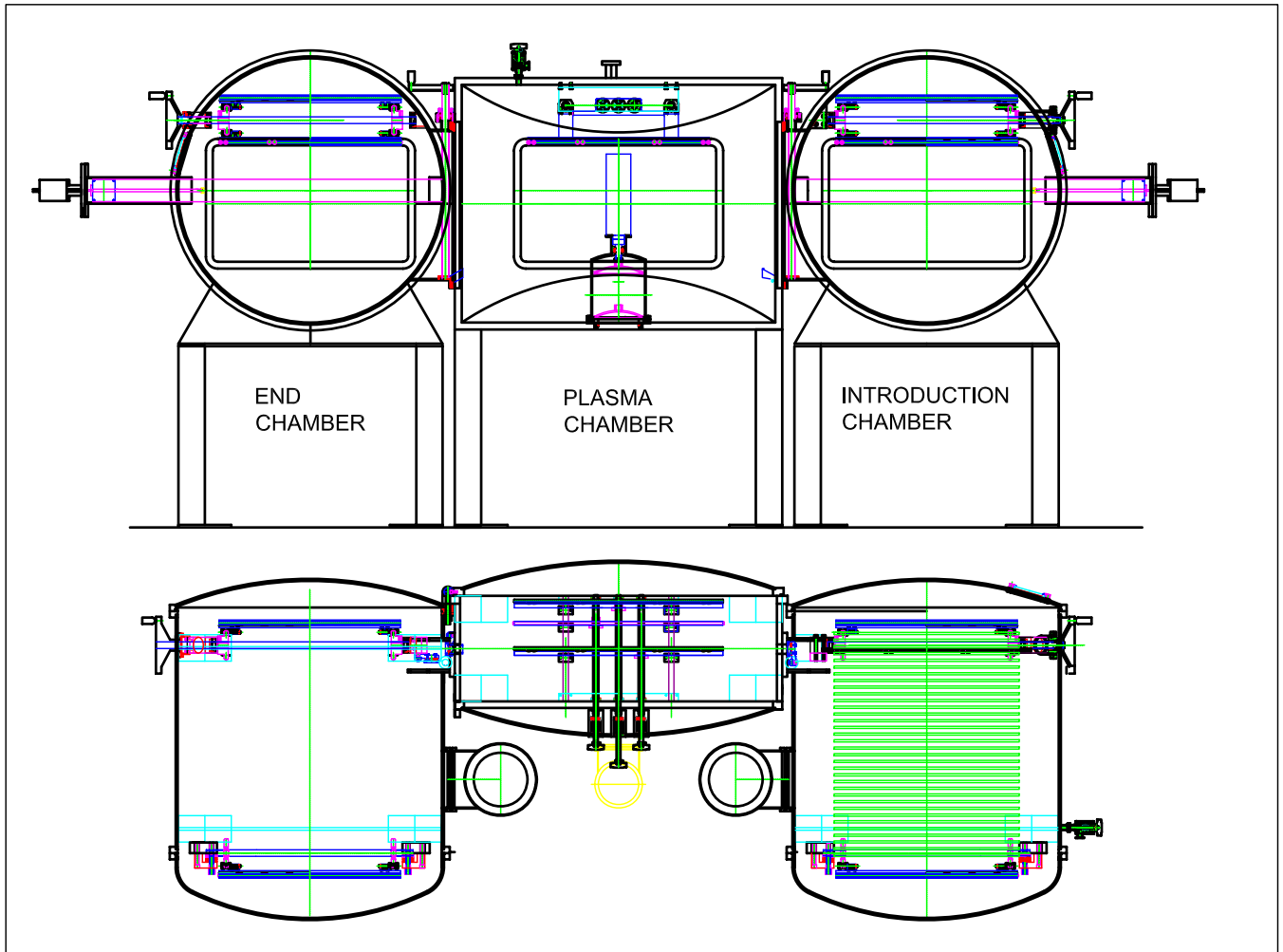


Fig 1 -Sketch of general layout of PLASMA LEATHER

- Primary pump;
- 100 m³/h mechanical pump;
- 300 m³/h roots;
- 1500 l/s Turbo-molecular pump;
- 1500l/s cryopumps with LN2 panel (30 000 l/s water pumping speed);
- Vacuum gauges.

The manipulation of leathers inside the chamber is possible with a coupling chain-pinion that allows shifting the leathers through a handle placed near the entrance of the IC.

On the chamber some flanges with tempered glass viewports are provided, allowing users to check at any time the process inside the chamber.

The IC, as well as the EC, can contain 32 looms at the same time for each process. These chambers have been planned to hold easily an increasing number of looms, with the introduction of a reservoir above the plant and another one below the plant.

The **PC** is linked to the IC by a rectangular flange, and the inter-face between the two chambers is made possible using an airtight door, which is manually opened for leather sample transfert.

The shifting of the hides from one chamber to the other is allowed by a magnetic manipulator, which hooks the loom and places it in the PC.

The PC has a rectangular shape and its bulk is 1240x950, about 700 mm depth, and is also positioned on a painted iron loom. A rectangular door allows to open the chamber. This chamber is provided with the following devices:

- 82 m³/h mechanical pump;
- 1000 liters/sec. Turbo-molecular pump ;
- Vacuum gauges;
- Mass Flow Controller (MFC) for process gases;
- Electrical feedthroughs;
- Insulated liquid feedthroughs;
- RF Cooled antenna for plasma matching.

The **EC** has got the same size as the pre-treatment chamber; here again a sample-holder manipulation system is provided, through the coupling chain/cog-wheel. We also find a flange of rectangular section, that will inter-face the treatment chamber. In front of the door there is another magnetic manipulator, which carries the sample-holder from the PC to the EC.

This EC is provided with the following devices:

- 35 m³/h mechanical pump;
- 1000 l/s turbo-molecular pump;
- Vacuum gauges.



Fig 2 Pumping group of intrduction chamber

3. PROCESS

3.1 The introduction chamber (IC) has a high sized vacuum pumping system designed for outgassing the leather as fast as possible before the plasma treatment. Roughly a 30.000 l/s should be considered. Depending of the types, quantity and the pre-treatment of the leathers, the time to reach $2 \cdot 10^{-5}$ mbar is variable from 5-6 h to 24 h.

To recover vacuum to $5 \cdot 10^{-6}$ mbar requires about 8 h more.

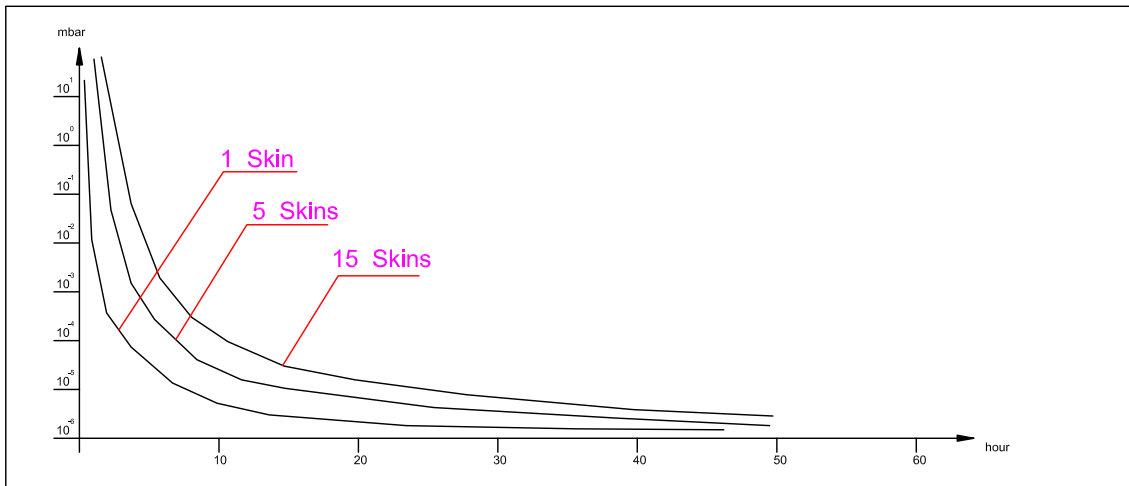


Fig 3 -Outgassing diagram of skins in vacuum chamber (IC)

Up to 32 looms of 800x500 mm sizes are set in the transport chaine of IC. The looms charge is made through the back door of IC.

Manually operated, outgassed leather is alligned to the rectangular valve laterally opened to treatment chamber for transfert. Using the magnetic manipulator positioned at the entrance of the chamber, the operator hitches the loom and let it slides into the PC. The operations are managed looking through the viewports located here and there on the chambers.

3.2 Plasma chamber is equipped with a 900 l/s turbomolecular pump to reach 10^{-6} mbar so to equilibrate the vacuum during the connection with the IC.

4. PLASMA PROCESSING

Plasma processing is well known for treating different types of material with a view to obtaining certain structural and functional characteristics. The method for processing the tanned hide, characterised by the fact that this hide is subjected to a outgassing phase either before of during plasma treatment. This outgassing phase carries out a sort of cleaning by the gases escaping from the surface of the tanned hide or skin, and creates the optimal conditions for plasma treatment on the surface of the hide. In particulr, the outgassing phase can be done until a residual pressure is obtained that is equal to or less than 10^{-4} mbar, better if equal to or less than 10^{-5} mbar, and ideal if less than $5 \cdot 10^{-6}$ mbar.

The plasma treatment is realised with a cold plasma reactor in order to improve and modify the surface characteristics without altering the massive characteristics obtained during the previous processing phases, nor the characteristic intrinsic to the hide or skin.

More specifically, in a cold plasma environment, the physical and mechanical characteristics and volume performance remain unvaried. Effects of the plasma treatment are limited essentially to area of contact, constituted by the surface of the material and the result of the process involves layer depths that may vary from 1 nanometer to 1 micrometer.

In general, regardless of the way in which the plasma is generated, the plasma treatment can preferably include the following phases either individually, or in any combination:

a) removal of the layers of material closest to the surface of the hide or skin (ETCHING);

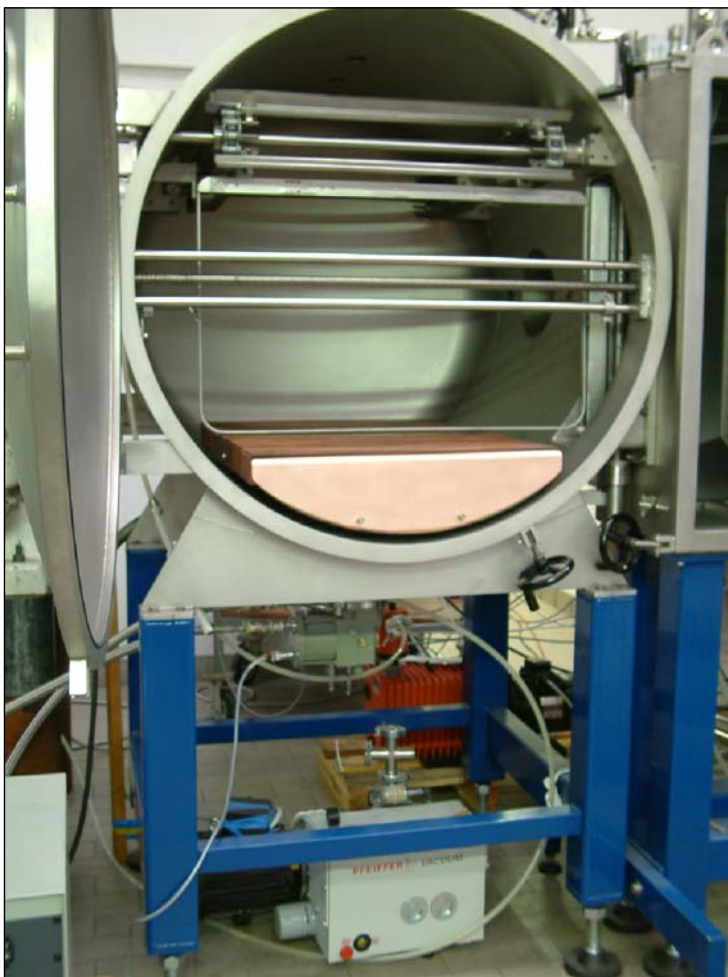


Fig 4 -The loom transfer and cryogenic panel

- b) Superficial implantation of atoms or chemical groups (GRAFTING) in which the continuous flow of reactive agents produced in the plasma encourages their absorption inside the material being treated, encouraging implantation of functional groups on its surface;
- c) deposit of thin layers of metal or polymers on the surface of the material;
- d) activation of the surface by breaking the chemical bonds and generating free radicals on the surface;
- e) spontaneous formation of new bonds on the surface of the hide or skin without implant the reactive components of the plasma.



Fig.5 Angle valves and turbo groups



Fig.5 In vacuum grafting plasma

In particular, the said procedure can be realised by using fluorinated gases and composed of siloxanes. In the case where flourides are used the surface of the hide or skin is bombarded with single fluorine radicals that graft to form stable and lasting chemical bonds. In the case of organoxyline gases the plasma breaks the gas in silica-like compounds whose diffuse on the surface forming a deposition of a thin layer. In the optimisation study the experiments are performed using both fluorine gas and organoxyline gas.