**Title**: METHOD FOR THE PROCESSING OF LEATHER

**Abstract**: This invention involves a method for the processing of leather and, in particular, involves a method that has shown to improve or provided completely new post-tanning characteristics of the leather. Said method includes the treatment of the surface of the tanned leather with cold plasma after a suitable and specific outgassing.
DESCRIPTION

"Method for the processing of leather"

The present invention is related to a method for processing leather and, in particular, to a method that has shown to improve or provide completely new post-tanning characteristics of the leather.

At the present time, leathers, after the traditionally used tanning techniques, are subjected to a further series of chemical and mechanical treatments aimed at transforming said leathers into a commercial product, having different characteristics suited to the final use destination.

The practical applicability and commercial value of the leather product are effectively determined by the aesthetic characteristics, the sensation to the touch, and the physical and mechanical characteristics that make this product suitable for the use to which it is intended.

Post-tanning process of the leather generally comprise a variety of phases, including dyeing, fatliquoring, and finishing.

In particular, the dyeing phase includes a series of treatments aimed at lending the tanned leather a certain colour.

The fatliquoring phase allows the fibres making up
the dried leather to be separated after tanning, through the use of products that give the tanned leather softness, flexibility, and feel characteristics of various types of leather.

The finishing in the broadest sense includes chemical operations such as, among others, bleaching, surface degreasing, application of seasons and pigments, varnishing, and mechanical treatments aimed at improving at the aesthetic appearance of the leather. In the more limited sense, finishing intends application of coatings, protection and polishes onto the surface of the leather, whose purpose is to correct any irregularities.

These phases involve the use of considerable quantities of water and especially a wide range of chemical substances. This use not only requires significant consumption of valuable natural resources, but also has an environmental impact due to the presence of the aforementioned chemical agents in the wastewater or their release into the atmosphere.

In addition, these processes can be quite different depending on the type of leather to process, the type of treatments done in previous processing phases, and the type of finished product that needs to be obtained.

In some cases, some characteristics, such as a
certain shade of colour or particular properties (water repellence, oil repellence, among others) cannot be obtained using the methods and chemical products currently on the market today. Others may be obtained, but in achieving these characteristics, irreversible modifications may occur to the properties of the leather, which may have been achieved in previous phases or are intrinsic to the leather, and are as important as the new property (breathability, genuineness, appearance of the grain, among others).

Another problem is associated with static electricity that may be present on the surface of the fibres making up the leather after tanning process.

In detail, the dyeing phase is influenced by the static electricity on the surface of the fibres making up the leather: at the isoelectric point, the collagen in the leather has a very low tendency to combine with the colouring ions since it is electrically neutral. As a result, the farther that the pH in the dyeing bath is from the isoelectrical point, the more rapidly the collagen in the leather will react by combining with colouring ions.

The electrical charge, in turn, depends on the type of tanning process that the leather has been submitted to.
For example, in the case of chrome tanning, it is necessary to carry out a neutralisation or acid-removal phase that tends to eliminate the acid groups created by the treatment by using chrome cationic salts.

Neutralisation brings the pH in the dyeing bath above the isoelectrical point of the leather by forming negative charges prevalent on the surface of the fibres.

Consequently, the affinity the leather has with the dye is reduced, to the disadvantage of a rapid fixation and the uniformity of the colour in the leather.

Furthermore, in the cases where after neutralisation, the leather is subjected to intermediate drying process, it is necessary to send the leather through a re-bathing phase.

The re-bathing phase is difficult to carry out for chrome tanned leathers because during the prior dehydration and drying phases, acid groups replace water groups and bond to the chrome in the form of complexes.

In addition, in leather tanned using cationic chrome salts, the basic groups of the collagen are free and can bind electrovalently with the sulphonic groups of the acid dyes. This type of bond is not very stable and can be further weakened by the attraction between the reagent ions and the permanent dipoles of the water molecules that surround them. These forces of attraction
encourage the solubility of the dyes and are the cause of the insufficient colour fastness of the already combined dye to the water. The dyes that form predominantly electrovalent bonds therefore become unusable due to their poor affinity with the leather.

As regards the quality of the colour, the greenish colour typical of chrome-tanned leather makes it fairly difficult to obtain pastel colours. Light colours are more easily obtained by concealing the chrome by sending the leather through a further stage of processing, known as surface detanning.

While for the aforementioned chrome tanning process, the most like dyes and therefore most used are anionic dyes, for vegetable tanning, which represents a commonly used tanning method with chrome tanning, the presence of negatively charged groups makes cationic dyes more like. The latest, although having elevated covering power, are also very expensive offer poor colour fastness to light, insufficient colour fastness to dry and wet rubbing, and poor solidity against migration.

As regards the finishing phase, a problem that could arise is associated with the absorbing power of the surface of the leather towards the chemical products used (for example, chemicals used in dyeing, protection,
coating, and similar products): if the leather absorbs excessive amounts, it is necessary to limit this tendency in order to obtain a finishing uniform, not crusted, and with a good tightness of grain; if the leather does not absorb enough, it becomes necessary to use more diluted bottoming solutions supplemented by alcohols and surface-active agents that promote adherence of the finishing layers.

At the same time, it is also very important that the leather is as uniform and regular as possible so that the products applied adhere and are distributed evenly over the entire surface.

A process frequently carried out in order to provide greater purity to the tone of the leather is bleaching, which entails lightening the colour and eliminating the oxidised tannins and excess tanning substances from the exterior surfaces.

To do this bleaching process, acids are generally used in traditional technology, including oxalic acid, or, the leather may be immersed in successive alkaline or acidic baths, diluted with intermediate and final rinsing phases in water. In any case, the alkaline solution dissolves the oxidised tannins, while the acidic bath, by lowering the pH, lightens the dark colour acquired by the leather after the alkaline
treatment.

An unfortunate fact is that, due to the residue of the strong free acids that are often left on the leather, the finished leather good may suffer decay of the tanned fibres during storage, with the resulting reduced resistance of the leather.

Another problem arises in a type of leather called "velour", whose finishing treatments include polishing and buffing, which may or may not be followed by a spray on application of a drying oil emulsion to set the colour and prevent colour being lost in the fibre powder that is produced after this final finishing process.

All the suede leather that has been subjected to this treatment releases a small amount of colour if rubbed in dry conditions due to the miniscule particles of dye powder or residual dyed fibres left on the leather even after being scrupulously dusted, brushed and dry paddling.

In addition, there are substantial problems that could arise regardless of the type of tanning process and which are associated with the lack of uniformity in the colouring and the presence of stains and marks.

Among other causes, these inconveniences can also be due to residual undissolved dyes, sediment forming in the liquid dyes or in the dyeing with powder dyes in
reduced baths, or the presence of grease marks and stains due to the uneven absorption of the fatliquoring products.

Generally speaking, plasma use is well known for treating different types of material with a view to obtaining certain structural and functional characteristics.

In this regard, multiple experiments have been conducted whose purpose was assessing the possibility of using plasma as an alternative process to some traditional techniques for treating materials.

In fact, plasma treatment would seem to avoid or at least reduce the need for large quantities of water and chemical compounds that pollute the environment and are toxic to man.

On the other hand, it is important to stress that, at least as regards the field of leather processing, use of plasma alone may not always lead to advantageous results compared to the results obtained using established techniques.

Therefore, we are faced with the pressing need to come up with a method for treating leather that eliminates or at least significantly reduces the use of chemical substances in the aforementioned processing phases and, at the same time, is at least as effective
as the traditional methods.

The problem addressed with the present invention is therefore formulating a method for treating leather that offers characteristics meeting the aforementioned needs and at the same time, obviates the multiple inconveniences presented by the aforementioned leather treatment methods inherent in the traditional techniques.

This problem is resolved by a method for treating leather in accordance with the principal attached claim.

Other characteristics and advantages of the leather processing method described in the present invention are detailed in the ensuing text.

It was very surprising to find that if a leather is subjected to an outgassing phase, the surface of the leather could then be effectively treated with plasma.

Furthermore, another advantage lies in the fact that using plasma treatments, which will be described in the ensuing text, it is possible to lend the leather substantial surface characteristics.

The treatment phase of the leather using plasma can be carried out using all the noble gases, preferably helium, argon, neon and their mixtures with air or oxygen, inert gases such as, for example, nitrogen and their mixtures, fluorinated gases such as, for example,
CF₄, SF₆, CFC, hydrocarbons, CO₂, air, oxygen, silicon compounds, silanes, siloxanes and organosilanes, chlorine compounds, vinyl acrylate monomers, fluorocarbons, as well as corresponding mixtures of said gases, metals and chloromethylsilane.

The plasma used for treating leather in accordance with the discovery is cold plasma, i.e., the temperature of the total mass of gas in the plasma phase is approximately room temperature.

Cold plasma can be produced in vacuum (A) or at atmospheric pressure (B).

(A) In vacuum

In vacuum, cold plasma is produced in chambers containing gas at pressure values varying from 0.1 to 20 mbar.

Plasma can be generated by various electromagnetic sources, i.e. sources at diverse frequencies and different geometry.

The physical and chemical processes that take place on the surface of the leather depend indeed mostly on the parameters of plasma, the pressure of the gas that is used to generate it, and the values of electric potential assumed by the sample with respect to the plasma potential, i.e., the electric fields in the vicinity of the sample. Electric fields produce currents
either of positively or negatively charged species that interact with the sublayer by either bombarding it, or simply electrically charging it. These electric fields can be controlled by biasing the support of the sample (or the sample itself) or by positioning the sample in the ionic sheath that is created in proximity to the antenna, which assumes negative electric potential values of a few hundred volts (from 0 to 800V) in a spatial area of a few millimetres (from 1 to 10 mm).

However, these processes are not strictly dependent on the type of source. In any event, at pressures between 0.1 and 1 mbar, it is preferable to use electromagnetic sources emitted at low frequency and at radio frequency, while at pressures between 10 and 20 mbar, the plasma is generated more easily using a microwave source.

As regards the parameters of plasma, these are set by the so-called discharge parameters, i.e., by the parameters of the source. For example, the electric potential, which for leathers having dimensions between 10 and 400 cm² can vary from 50 to 200W, the geometry of the source that produces the plasma (capacitive, inductive source), the frequencies of the electromagnetic radiation used in producing the plasma, and the residual vacuum inside the chamber where the
treatment is done. In turn, the vacuum is also dependent on the amount of residual humidity and the outgassing of the leather, i.e., the flow of volatile substances that leave the leather and the outgassing of the internal structures that make up the reactor.

The cold plasma that is generated is characterised by parameters such as a density of electrons between $10^8$ and $10^{11}$ cm$^{-3}$ and electronic temperatures from 1 to 15 eV, which represents the average electric energy calculated as $(e k_B T/m)^{1/2}$ ($e=1.9 \times 10^{-19}$ C, $k_B=1.38 \times 10^{-23}$ J/K, $m=9.1 \times 10^{-31}$ kg, $T$ absolute temperature in Kelvin), while the ions and the neutral particles are at a temperature close to room temperature and the density of ions can vary from $10^8$ to $10^{11}$ cm$^{-3}$.

Treatment with the aforementioned type of plasma offers the advantage that the leather does not suffer any heat damage.

Depending on the type of superficial modification process that must be imparted, the position of the leather sample may be varied with respect to the source of the plasma: (a) the sample can be located near the area of diffused plasma mounted on a floating surface; (b) the sample may be mounted on a metallic support that is negatively or positively biased to a few dozen volts in order to encourage the ionic bombarding of its
surface; (c) the sample is positioned on the ionic sheath that is created in proximity to the source of the plasma.

The treatment time of the leather in cold plasma usually does not exceed 20 minutes, and is preferably between 5 and 15 minutes, more preferably, ranges between 6 and 10 minutes.

 Preferably, for the surface treatment of the leather to achieve the water repellent results, the gas that has provided the best performance is SF₆ or mixtures of it with noble gases.

In particular, this type of plasma in vacuum can be used according to discontinuous or continuous methods.

**Discontinuous method**

The discontinuous method requires a first and second phase where, in the first phase, the sample is placed in a chamber that is evacuated at pressures lower than the gas being used. In the case where the gas used is air resident inside the chamber, the evacuation of this air by creating vacuum would occur up to the pressure value at which the plasma treatment is realised.

Instead, in the event that the gas used is not air, the gas used is introduced into the chamber after all the air present in the chamber has been evacuated.
In the second phase, plasma is produced and the treatment is controlled. Plasma can be produced indeed using a number of different electromagnetic sources, i.e., sources of different frequencies. Processing conditions are controlled by measuring the plasma parameters.

Treatment times last less than 15 minutes and the treatment can be repeated several times.

Furthermore, after every treatment, the leather can be left for a considerable amount of time in atmospheres of either air or active or inert gases to then be submitted to another treatment with the same gas or another gas.

Continuous method

In accordance with the continuous method, the system used can be comprised of several chambers, for example a loading and evacuation chamber, a chamber for plasma treatment, and a final evacuation and leather unloading chamber. Once the leather is loaded into the first chamber, it is closed and evacuated at pressure equal to or lesser than treatment pressure so that the outgassing phase of the leather surface can also be accomplished. When this evacuation has been done, the leather is transferred into the treatment chamber where the plasma is generated, which should be at a pressure
higher than or equal to the two adjacent chambers.

In this way, residual gases produced during the evacuation and outgassing phase do not contaminate the atmosphere in which the treatment is completed.

In order to avoid cross-contamination, an alternative solution is to use guards, which are constituted by spaces between the adjacent chambers and function as isolation between the chambers.

In the treatment chamber, the leather is treated.

After the treatment - which lasts less than 15 minutes - the leather is transferred to the evacuation and unloading chamber which is found at a pressure lower than the treatment pressure. Subsequently, the evacuation and unloading chamber is opened and the leather is unloaded.

After the unloading phase, this last chamber is evacuated again and the cycle is repeated.

If the treatments are different, i.e., if different gases or treatment cycles are used, the leather can be treated in a system comprised of several treatment chambers. These chambers are positioned between the loading and evacuation chamber and the evacuation and unloading chamber. Or, in cyclical treatments, the leather can stop in special chambers to then be treated again.
(B) At atmospheric pressure

The cold plasma produced at atmospheric pressure is ideally corona plasma. In this case, the plasma is produced at low frequency at atmospheric pressure between two electrode conductors either one conductor and one dielectric or two conductors covered with dielectric material.

With the aforementioned type of cold plasma at atmospheric pressure, the leather is generally located at a distance of 0.5 cm to 3 centimetres from the electrodes. The sample can move at variable speeds with respect to the plasma source, using movement systems widely used in the sector, so that the treatment time may vary according to need.

In this system, the leather is treated in a continuous way, moving underneath the electrode used to produce the plasma and the treatment time lasts less than one second in order to keep the leather from being damaged.

The power used is approximately 300 W along 20 cm of leather, while the pressure is atmospheric. Before and during treatment, the surface of the leather is cleaned using inert gases.

The sample can be treated either once or several times. Each time, it must be treated for periods of less
than one second, in order to avoid damage.

As mentioned previously, the method for processing the tanned leather includes a phase using cold plasma to treat the surface of the said leather, characterised by the fact that this leather is subjected to a outgassing phase either before or during plasma treatment.

Preferably, in the case of plasma treatment done in vacuum, the outgassing phase is conducted until a flow of residual gas on the surface of the leather is less than $4 \times 10^{-4}$ mbar cm$^3$/sec.

This outgassing phase carries out a sort of cleaning of the gases escaping from the surface of the tanned leather, so that to create the optimal conditions for plasma treatment on the surface of the leather.

When the aforesaid outgassing phase is carried out during the real plasma treatment of the leather, it becomes necessary to make the processing gas flow tangentially to the surface of the leather so that it can be "cleaned" by the same gas.

Vice versa, when the outgassing phase is carried out before plasma treatment, this must be done by generating vacuum conditions.

In particular, the outgassing phase can be done until a residual pressure is obtained that is equal to
or lesser than $10^{-4}$ mbar, preferably equal to or lesser than $10^{-5}$ mbar, more preferably less than $5 \times 10^{-6}$ mbar.

The plasma treatment can be done before any of the other processing phases on the leather, subsequent to the tanning phase.

In some cases, for example, when the surface of the leather must have water repellence features, the treatments normally done can be wholly replaced by the method as described in the present invention.

This technique can be applied to any type of leather and any final use of product and it can be realised with any 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 leather.

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
comprise the following phases either individually, or in any combination:

a) removal of the layers of material closest to the surface of the leather (ETCHING);

b) superficial implantation of atoms or chemical groups (GRAFTING) in which the continuous flow of reactive agents produced in the plasma encourages their adsorption 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 leather without implant the reactive components of the plasma.

Some process and the respective practical examples in the present invention are described in the ensuing text, demonstrating a non-limiting example of the discovery.

These examples have been made experimentally. In any event, adjustments in the treatment to modify it to industrial scale are not beyond the ability of an
industry technician.

I) Process for increasing the wetting of the leather

This process can be carried out with various types of plasma including among these, plasmas of noble gases, inert gases, and preferably, oxygen, air, chlorine, ammonia, fluorinated gases and their mixtures.

In the case where the plasma used was produced in vacuum in which the gas represented is air, the treatment chamber of the leather should be evacuated in order to obtain pressures preferably between 0.1 and 2 mbar.

Note that in the case where other gases are used, the treatment chamber is evacuated in order to obtain pressures lower than the pressure under which the treatment is realised, and consequently, to carry out sufficient outgassing of the surface being treated. Subsequently, the chamber is filled with treatment gas.

When the chamber is filled with the appropriate gas, plasma is generated. In the event that the electromagnetic source is emitted at a radio frequency or low frequency, the pressure is preferably between 0.1 and 10 mbar, the electron temperature of the plasma is between 1 and 15 eV and the electron density is between
10^7 and 10^8 cm^-3. More preferably, the treatment pressure is between 0.2 mbar and 2 mbar, even more preferably between 0.2 and 0.6 mbar.

The said plasma is applied to the surface of the leather for less than 15 minutes, preferably between 3 and 8 minutes and more preferably between 4 and 6 minutes.

This process results in an increase in the wetting of the leather, i.e., the hydrophilic quality of the surface of the leather is improved.

To assess the increase in the wetting, the degradation time of a drop of water was calculated. This represents the time after which a drop of water loses its shape and spreads across the surface of the leather without being absorbed, and the absorption time on the surface of the leather.

When the plasma used is one generated with oxygen or air, the degradation time of a drop of water decreases from one minute, in leathers not outgassed and not treated with plasma, to less than 10 seconds in plasma treated material. Contemporaneously, the absorption time of a drop of water decreases from 10 minutes to less than 1 minute.

The increased hydrophilic quality is temporal limited. Therefore, in the case in which this process is
used before the re-wetting phase or the dyeing phase, it is necessary that the subsequent re-wetting or dyeing phases be done before two weeks have elapsed.

In addition, note that the reduction in the absorption and degradation time of the drop of water is also obtained with a plasma in microwaves at higher pressures, up to 20 mbar, or with a low frequency plasma, or with a corona plasma at atmospheric pressure. In this latter case, the treatment times of the leather are reduced dramatically, decreasing to fractions of a second.

Using corona plasma, it becomes necessary to treat the leather several times in order to obtain the same effect achieved when using plasma in vacuum.

In the case where mixtures of gases containing oxygen, chlorine or \( \text{CO}_2 \) are used, the hydrophilic quality also increases, partly due to the hydrophilic groups implantation on the surface of the leather. These groups are also important for controlling the chemical affinity of the surface of the leather with the dyes or finishing layers, as will be explained in the ensuing text.

Another advantage offered by the method according to the invention lies in the fact that the contact angle decreases by at least 20 degrees.
The contact angle is a parameter used in the sector to evaluate a surface's wettability: the lower the contact angle, the greater the wettability.

In the following paragraphs, some specific examples are given of treatment of leather in the case where the leather must be subsequently subjected to dyeing or finishing phases.

Example 1 (leather to dye)

Type of gas: $\text{SF}_6$ in vacuum
Pressure: 0.1 mbar
Length of the treatment: 10 minutes

Results:
- absorption time of one drop of water: 6.5 minutes
  (10 minutes for leather not treated with plasma)
- degradation time of one drop of water: 2.5 minutes
  (3.0 minutes for leather not treated with plasma)

Example 2 (leather to dye)

Type of gas: air in vacuum
Pressure: 0.4 mbar
Length of the treatment: 5 minutes
Results:
- absorption time of one drop of water: 1.5 minutes
  (10 minutes for leather not treated with plasma)
- degradation time of one drop of water: 0.1 minute
  (3 minutes for leather not treated with plasma)

Example 3 (leather to dye)
Type of gas: oxygen in vacuum
Pressure: 0.4 mbar
Length of the treatment: 5 minutes

Results:
- absorption time of one drop of water: 45 seconds
  (10 minutes for leather not treated with plasma)
- degradation time of one drop of water: immediate
  (3 minutes for leather not treated with plasma)

Example 4 (dyed leather)
Type of gas: SF₆ under vacuum
Pressure: 0.1 mbar
Length of the treatment: 15 minutes

Results:
- absorption time of one drop of water: 6 minutes
(19 minutes for leather not treated with plasma)
- degradation time of one drop of water: 0.75 minute
(6 minutes for leather not treated with plasma)

Example 5 (dyed leather)
Type of gas: oxygen in vacuum
Pressure: 0.4 mbar
Length of the treatment: 5 minutes

Results:
- absorption time of one drop of water: 6 minutes
(19 minutes for leather not treated with plasma)
- degradation time of one drop of water: 0.5 minute
(6 minutes for leather not treated with plasma)

II) Process for increasing and/or controlling the affinity of the surface of the leather to the dyes

As we reported in the introductory section of this description, optimisation of the affinity that the surface of the leather has for the dyes is crucially important.

To this end, the said process in particular aims to activate the surface of the leather by either breaking the chemical bonds and generating the free radicals, or
altering the electrical charge of the surface.

This process can preferably be carried out with a source emitted at radio frequency in vacuum.

The plasma is created with gases such as noble gases, electro-negative gases, among which fluorinated gases such as CF₄ and CFC and preferably SF₆, oxygen, CO₂, air, nitrogen, chlorine, ammonia, and their mixtures, hydrocarbons and their mixtures.

The leather sample is ideally mounted on a moveable support with respect to the source of the plasma, located in a chamber where the vacuum is realised at pressures lower than those used for the plasma treatment, i.e., between 0.1 and 2 mbar. In this way, the surface of the leather to treat can be adequately outgassed. Subsequently the chamber is filled with gas at pressures that may vary from 0.1 to 2 mbar and generate plasma with sources emitted at radio frequency for less than 15 minutes. Preferably, the pressure should range from 0.2 to 0.6 mbar and the treatment times vary from 3 to 8 minutes.

In any case, plasma parameters may vary according to the gas used. Electron temperatures range from 1 to 15 eV, electron densities vary from 10⁷ and 10⁸ cm⁻³ and potentials vary from 0 to 800 V.

With the aforementioned process, it is possible to
advantageously improve the acid de-acidification phase as well as control and optimise the affinity of the leather to the dye to be used, at the same time preventing this dye from excessively or non-uniformly fixing on the surface.

In addition, the aforementioned method increases the solidity of the dye to the leather, thereby improving the fixation and fastness over a longer time with respect to those that are obtained using the methods in the traditional techniques.

It is also possible to insert radicals such as -OH, -COOH or -NH₂ on the surface of the leathers, adapted to bond with various types of dyes, that in the normal operating conditions cannot be used due to the reasons explained in the introductory portion of this description.

III) Process for treating the leathers in order to improve the colour quality.

Another advantage offered by the method described in the present invention, lies in the ability to increase the level of saturation (the quantity of dye absorbed by the leather) and the ability to mount the dye (percentage of dye absorbed in a set amount of time).
In the ensuing text, we are describing two examples for improving the quality of the colour on the leather.

**Example 6**

A method has been devised for improving the colour quality on the so-called "flesh" side of the leather, i.e., the side of the derma originally in contact with connective tissues.

Various types of gas can be used, such as, for example, noble gases, nitrogen, air, fluorinated gases including among these preferably CF₄, SF₆, CFC, ammonia, hydrocarbons, and their mixtures.

The use conditions of the plasma are essentially the ones described in reference to Process II) for increasing and/or controlling the affinity of the surface of the leather to the dyes to use.

**Type of gas:** oxygen in a vacuum

**Pressure:** 0.4 mbar

**Length of the treatment:** 5 minutes

**Results:**
- mounting capacity

Dyeing time in minutes ọ increase in the dye absorbed
Example 7

The method has been devised for improving the colour quality on the so-called "grain" side of the leather, i.e., the side of the derma originally in contact with the epidermis and opposite from the flesh side.

Just as in Example 6, the same types of plasma can also be applied in this example, using the same general treatment conditions as described in the above mentioned Process II).

Type of gas: oxygen in vacuum

Pressure: 0.4 mbar

Length of the treatment: 7 minutes

Results:

- mounting capacity

Dyeing time in minutes % increase in the dye absorbed

33  10

43  10
IV) Process for treating the leather that increases the uniform distribution of the dyes

Another advantage offered by the method described in the present invention lies in the fact that it is possible to obtain excellent uniformity in the distribution of the dyes.

For this purpose, it is best to use gases such as oxygen, air, ammonia, chlorine, and their mixtures used in accordance with the instructions described previously in reference to Process II).

Note that this method prevents the formation of marks and stains on the surface of the leather, caused by excess products that may concentrate unevenly on the leather when the traditional treatment methods are used.

V) Process involved in the treatment of leather that cleans the surface of said material

The method for processing the leather according to the invention can also be used for cleaning the surface of said material.

More specifically, it is possible to remove superficial layers having thicknesses of up to 1 micron.
In these cases, the gases to be used may be, for instance, noble gases, inert gases - ideally nitrogen, oxygen, air, chlorine, ammonia, fluorinated gases and their mixtures.

The plasma can be generated in vacuum or at atmospheric pressure.

This process is preferably carried out with plasma in a vacuum, at pressures between 0.1 and 1 mbar, at an electron temperature of between 1 and 15 eV, electron density from between $10^7$ and $10^8$ cm$^{-3}$, for less than 20 minutes.

Alternatively, when using corona plasmas with air at atmospheric pressure, treatment time is reduced to less than one second.

The aforementioned cleaning can be assessed, for instance, as uniformity and smoothness of the surface of the leather.

A measure of the smoothness of a surface is obtained by measuring the roll-off angle.

The roll-off angle is the angle to which it is necessary to tilt the sample, starting from a horizontal position, to make a drop of water begin to roll.

The roll-off angle decreases from 36° for untreated leather to 20° for leather treated with plasma, and advantageously to less than 10°. Furthermore, the
leather also results hydrophilic in the most cases.

Experiments have shown that better hydrophilic quality is achieved (see Examples 3 and 5) using oxygen plasma at pressures of \( P = 0.4 \) mbar. In particular, the absorption time of a drop of water, as described previously, is less than 10 minutes, and it is preferably equal to or lesser than 6 minutes.

The quantity of surface material removed is always less than 2\% and the surface is surprisingly uniform, smooth, and hydrophilic.

Some examples of this method are given in the ensuing text, complete with comparative data with respect to the traditional techniques.

**Example 8**

- **Type of gas:** \( \text{SF}_6 \)
- **Pressure:** 0.2 mbar
- **Length of the treatment:** 5 minutes

**Results:**

- **Roll-off angle:** 3.8 degrees

(roll-off angle for leather not treated with plasma: 37 degrees)

**Example 9**

- **Type of gas:** air
Pressure: 0.4 mbar
Length of the treatment: 5 minutes

Results:
Roll-off angle: 7.9 degrees
(roll-off angle for leather not treated with plasma: 37 degrees)

Example 10
Type of gas: oxygen
Pressure: 0.4 mbar
Length of the treatment: 5 minutes

Results:
Roll-off angle: 6 degrees
(roll-off angle for leather not treated with plasma: 37 degrees)

Alternatively, using corona plasmas generated with air at atmospheric pressure, the treatment time can be reduced to less than one second and the surface results in being surprisingly uniform, smooth, and, additionally, hydrophilic.

VI) Process for treating the leather in order to
make the material water repellent.

Another use of the method for treating the leather as explained in this discovery lies in obtaining a water repellent effect of the surface of the leather.

In particular, the said process can be realised by using fluorinated gases in general such as, for instance, CF₄, SF₆, NF₃, CFC, composed of silicone, silane, and siloxanes and their mixtures.

In the case where organic fluorides are used, preferably SF₆ or mixtures of this with noble gases, the surface of the leather is bombarded with fluorine radicals that implant to form stable and lasting chemical bonds.

The method for obtaining water repellence is achieved preferably with SF₆ gas or blends of this with noble gases (i.e., gases that enable formation of numerous fluorocarbons) either in vacuum with sources emitted at radio frequency or low frequency or at pressures between 0.1 and 10 mbar, preferably between 0.2 and 2 mbar, more preferably between 0.2 mbar and 0.6 mbar. The electron plasma density should be about 10⁷-10⁸ cm⁻³ while the ion plasma density should have a value of 10¹¹ cm⁻³.

The ionic temperature is between 1-10 eV, preferably between 3 and 8 eV, more preferably between 4
eV and 7 eV. The treatment time is less than 10 minutes, preferably between 3 and 8 minutes, more preferably between 4 and 6 minutes.

The method for affording water repellence to a leather according to this invention will be described below, including some practical examples of realisation.

The method

In a plasma reactor, at radio frequency or low frequency, the treatment of the leather can be carried out as follows.

The leather sample is mounted on a moveable support and positioned in a chamber that is evacuated at pressures lower than the processing gas, i.e., lower than the processing pressure. Subsequently, the chamber containing the sample fills up with gas and the plasma is generated with a source emitted at radio frequency or low frequency. The treatment of the leather lasts less than 10 minutes.

The water repellent effect with fluorinated gases on the leather does not depend on the source generating the plasma and can be obtained with either microwave sources or with corona plasmas at high pressures that contain numerous fluorine radicals. However, the effectiveness and stability of the effect on the leather
improves when a fluorinated gas containing SF₆ is used for the process.

Example 11 (ANILINE leather)

Type of gas: SF₆.
Pressure: 0.3 mbar
Length of the treatment: 6 minutes

Results:
- absorption time of one drop of water (200 microlitres) > 100 minutes
  (19 minutes for leather not treated with plasma)
- degradation of the drop: absent
  (6 minutes for leather not treated with plasma)
- roll-off angle for plasma treated leather: 27 degrees
  (roll-off angle for untreated leather: 38 degrees)
- contact angle for plasma treated leather: 120 degrees
  (contact angle for untreated leather: < 90 degrees)

Example 12 (SUEDE)

Treatment is the same process presented in example
Pressure: 0.3 mbar
Length of the treatment: 15 minutes

Results:
- absorption time of one drop of water: 9 minutes
  (20 seconds for leather not treated with plasma)
- degradation of the drop: 3 minutes
  (8 seconds for leather not treated with plasma)
- roll-off angle for plasma treated leather: 19 degrees
  (roll-off angle for untreated leather: 47 degrees)
- contact angle for plasma treated leather: 120 degrees
  (contact angle for untreated leather: 90 degrees)

In any case, the marks left by drops of water are visibly reduced as the swellings of the surface.

This process is useful in order to make leather water repellent without altering the organoleptic properties obtained with prior treatments while also guaranteeing the breatheability.

Furthermore, thanks to the versatile nature of the process, it can be applied not only to make the grain side of the leather water repellent, but also for suede
treatment whose exposed-fibre structure and elevated absorption power makes it difficult to achieve water repellence and a good colour fastness to the drop of water with traditional technology.

If the treatments described in Examples 11 and 12 are repeated several times, the leather is also endowed with an oil repellent quality.

VII) Other process for treating leather in accordance with the discovery

Numerous other properties can be imparted to the leather by using the method in accordance with the present invention.

For example, it is possible to achieve a flame resistant property by using the method described previously using mixtures of gas with phosphorus during the finishing phases. Alternatively, it is possible to prepare the surface of the leather in accordance with Process II) and successively apply a surface layer of flame-resistant products according to the usual finishing methods.

Anti-bacterial properties can be obtained preferably by using either inert gases with metals, noble gases with metals, ammonia, or mixtures with nitrogen.
In a similar way, the anti-static quality of the leather can be improved by using especially plasma with metals or chloromethylsilane.

In addition, deposits of organic and inorganic materials on the surface of the leather can be obtained with cold plasma in a vacuum generated with acrylates, vinyl monomers, fluorocarbons, silanes, siloxanes, organosilanes, saturated hydrocarbons and their mixtures.

The layers deposited can be of varying thicknesses: with treatments lasting just a few minutes, deposits of a few dozen nm (10-50 nm) are made, for longer treatments, deposits thicker than a micron are achieved.

The stability of the deposit depends on the degree of adhesion to the surface of the leather and therefore on the sublayer subjected to treatment.

The plasma can contemporaneously activate the surface during the depositing process or it can make the deposit phase precede activation or carry out cyclical processes.

Some special effects can be obtained by creating areas that are more or less hydrophilic and similar to the dye, in order to create patterns on the surface of the leather, or metallic areas.

These effects can be obtained using a cold plasma
by activating the surface locally or by depositing material with a localised plasma, for example, using a plasma brush from a narrow source (either cylindrical or spherical) mounted on a moveable support that moves across the leather.

Leathers treated according to the method described in the present invention can be used advantageously in order to produce any manner of leather article, for example leather for leather goods, apparel, automobile upholstery, furniture and footwear.

The previous paragraphs give an idea as to how this method of treating leather, comprising application of a plasma on the surface of the said leather according to the present invention, can meet all the needs mentioned in the premises of this description and at the same time, overcome the inconveniences presented by the traditionally used treatment methods. Obviously, a technician expert in this field, in order to meet contingent or specific needs, can make numerous modifications and variations to the method described above, all of which fall under the broader scope of the invention as defined by the following Claims.
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CLAIMS

1. Method for the processing of leather in post-tanning process, comprising a phase of treatment with cold plasma on the surface of said leather, characterised in that said leather is submitted to an outgassing phase before or during the treatment with plasma.

2. Method according to Claim 1, in which the said cold plasma is obtained from gases selected from the group consisting of noble gases, air, oxygen, inert gases, fluorinated gases, hydrocarbons, CO₂, silicon compounds, silanes, siloxanes and organosilanes, chlorine compounds, vinyl acrylate monomers, fluorocarbons, and corresponding mixtures of said gases, and gases with metals and chloromethylsilane.

3. Method according to Claims 1 or 2, in which said noble gases are selected from helium, argon, neon, and their mixtures, said inert gas is nitrogen and said fluorinated gases are selected from CF₄, SF₆ and CFC or their mixtures.

4. Method according to Claims 1, 2 or 3, in which the plasma is produced in vacuum or at atmospheric pressure.

5. Method according to any one of the Claims from 1 to 4, in which said phase of outgassing is conducted in
vacuum.

6. Method according to any one of the Claims from 1 to 4, in which said outgassing phase is conducted by applying a gaseous flow tangentially to the surface to treat of said leather.

7. Method according to any one of the Claims from 1 to 6, in which said outgassing phase is carried out until a residual flow of gas lower than $4 \times 10^{-4}$ mbar per cm$^3$/sec is obtained from the surface of the leather.

8. Method according to any one of the Claims from 1 to 7, comprising the following phases in succession:
   - positioning the leather to treat inside an evacuation chamber;
   - treating said leather in a vacuum for enough time to attain said outgassing;
   - filling the said evacuation chamber with a gas, according to Claim 2 or 3;
   - generating the plasma in vacuum;
   - treating the surface of said leather with said plasma for less than 20 minutes.

9. Method according to any one of the Claims from 1 to 4, comprising the following phases in succession:
   - positioning the leather to treat inside an evacuation chamber;
   - evacuation of said chamber;
- introducing a gas according to Claim 2 or 3 in the said evacuation chamber tangentially to the surface of the said leather in such a way as to attain the said outgassing;

- generating the plasma in a vacuum;

- treating the surface of said leather with the said plasma for less than 20 minutes.

10. Method according to any one of the Claims from 1 to 9, in which the plasma is produced at a pressure ranging from 0.1 mbar to 20 mbar, at an electron temperature ranging from 1 eV to 15 eV and for processing periods of less than 20 minutes.

11. Method according to any one of the Claims from 1 to 9, in which plasma is produced with SF₆ at a pressure between 0.1 and 10 mbar, an electron temperature between 1 and 10 eV and for periods of less than 10 minutes.

12. Method according to any one of the Claims from 1 to 11, in which the plasma in a vacuum is used with either the discontinuous or continuous method.

13. Method according to any one of the Claims from 1 to 4, in which the plasma is a corona-type plasma produced at atmospheric pressure for a period of less than one second.

14. Method for treating leather according to any of
the Claims from 1 to 13, in which said application of plasma comprises the following phases either individually or in any combination:

a) removal of the layers of material closest to the surface of the said leather (ETCHING);

b) implantation on the surface of said leather of atoms or chemical groups (GRAFTING) in which the continuous flow of reactive agents produced in the plasma encourages their adsorption inside the leather to treat, encouraging implantation of functional groups on the surface of same;

c) deposit of thin layers of metal or polymers on the surface of said leather;

d) activation of the surface of said leather by breaking chemical bonds and generating free radicals on the surface;

e) spontaneous formation of new bonds on the surface of said leather without implant the reactive components of the plasma.

15. Process for increasing the wetting of the leather by using the method according to any one of the Claims from 1 to 14.

16. Process according to Claim 15, in which said leather is treated with a plasma at pressures ranging from 0.1 to 10 mbar, electron temperatures ranging from
1 to 15 eV, and for a period of less than 15 minutes.

17. Process as referred to Claim 15 or 16 in which the treatment pressure of the plasma is between 0.2 and 2 mbar, preferably between 0.2 and 0.6 mbar, the electron temperature is between 1 and 15 eV, and the treatment time lasts from 3 and 8 minutes, preferably from 4 to 6 minutes.

18. Process according to Claim 15, 16, or 17 in which when the gas used is SF₆, the plasma is generated with radio frequency at a pressure of 0.1 mbar, with an electron temperature of 4.5 eV., said plasma being applied to the surface of the leather for a period less than or equal to 10 minutes.

19. Process according to Claim 15, 16, or 17 in which when the gas used is oxygen or air, the plasma is generated with radio frequency at a pressure of 0.4 mbar, and electron temperature of 4.5 eV., said plasma being applied to the surface of the leather for a period of 5 minutes.

20. Process for increasing and/or controlling the affinity of the surface of the leather to the dyes and/or their quality on the "flesh" side and/or "grain" of said surface by using the method according to any one of the Claims from 1 to 14.

21. Process according to Claim 20, in which said
leather is treated with plasma at pressures ranging from 0.1 to 2 mbar, an electron temperature of between 1 and 15 eV, and for a period of time less than 15 minutes.

22. Process for removing/cleaning superficial layers of a leather using the method according to any one of the Claims from 1 to 14.

23. Process according to Claim 22, in which said leather is treated with plasma at pressures ranging from 0.1 to 1 mbar, an electron temperature of between 1 and 15 eV, and for a period of time less than 20 minutes.

24. Process according to Claim 22 or 23 in which when the gas used is SF₆, the treatment pressure of the plasma is 0.2 mbar and the treatment time is 5 minutes.

25. Process for making the surface of the leather water repellent using the method according to any one of the Claims from 1 to 14.

26. Process according to Claim 25, in which said leather is treated with plasma at a pressure ranging from 0.1 to 10 mbar, an electron temperature of between 1 and 10 eV, and for a period of time less than 10 minutes.

27. Process according to Claim 25 or 26, in which the treatment pressure of plasma is between 0.2 and 2 mbar, preferably between 0.6 and 0.6 mbar, at electron temperatures of between 3 and 8 eV, and treatment times...
lasting 3 and 8 minutes, preferably between 4 and 6 minutes.

28. Process for making the surface of the leather flame-resistant using the method according to any one of the Claims from 1 to 14.

29. Process for making the surface of the leather anti-bacterial using the method according to any one of the Claims from 1 to 14.

30. Process for depositing inorganic or organic materials on the surface of the leather using the method according to any one of the Claims from 1 to 14.

31. Process for creating areas on the surface of the leather having different hydrophilic qualities and different affinities to dyes, using the method as described in any one of the Claims from 1 to 14.

32. Leather obtainable in accordance with the method or process as in any one of the Claims from 1 to 31.

33. Hydrophilic leather characterised in that the degradation time of a drop of water on the surface of the said leather is less than 1 minute, whereas the time of absorption of the said drop of water on the surface is less than 10 minutes.

34. "Aniline" leather characterised in that the absorption time of a drop of water of 200 µl on the
surface is greater than 100 minutes.

35. "Suede", leather characterised in that the absorption time of a drop of water of 200 µl on the surface is 9 minutes.

36. Leather characterised in that the percentage of dye absorbed by the surface of the leather on the "flesh" side around 40% in 31 minutes.

37. Leather characterised in that the percentage of dye absorbed by the surface of the leather on the "grain" side is 10% in 33 minutes.

38. Leather characterised in that the roll-off angle of a drop of water of 200 µl deposited on its surface is less than 36°, preferably less than 20°.

39. Leather characterised in that the contact angle of a drop of water of 200 µl is up to 120°.

40. Leather comprising layers of organic or inorganic material deposited on its surface, characterised in that the thickness of the layers ranges from 10 to 50 nm.

41. Articles in leather comprising the leather in accordance with the Claims 32 or 37.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 7 C14C/00 C14C11/00

According to International Patent Classification (IPC) or to both national classification and IPC.

**B. FIELDS SEARCHED**
Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C14C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>1, 2, 4, 6, 12, 14, 22, 25, 29, 30, 32, 40, 41</td>
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X further documents are listed in the continuation of box C.

X Patent family members are listed in annex.

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Date of actual completion of the international search
26 August 2002

Date of mailing of the international search report
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