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(54) Method for working polymeric and inorganic materials with plasma

(57) The present invention relates to a method for the working of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara. In particular, it relates to a method comprising at least one treatment stage with cold plasma, realised using a source of plasma that originates particles that are substantially neutral, wherein said plasma is produced at a pressure approximately the same as the atmospheric pressure, and said plasma source originating substantially neutral particles is obtained through pulsed plasma.

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Description

[0001] The present invention relates to a method for working various types of materials such as woven fabrics, non-woven fabrics, yarns, natural fibres, polymeric and inorganic fibres (in other words, fibres produced from polymeric material such as PET, cotton, wool and similar products, as well as fibres produced from inorganic materials such as carbon, glass and similar products), alcantara (polymer microfibre) glasses and films of any type, and other similar products. In particular, the present invention refers to a method for working said materials including a treatment stage using plasma.

[0002] The aforesaid method permits the modification of the physical and chemical properties of the materials described above.

[0003] As far as woven fabrics, non-woven fabrics and yarns in general are concerned, under present conditions their practical applicability and their commercial value are determined by the appearance, tactile impression, and the physical and mechanical characteristics that make the aforesaid materials suitable for the use for which they are destined.

[0004] The methods that are generally employed to obtain these characteristics include several stages for woven fabrics, non-woven fabrics and yarns, among which in particular, the stages for dyeing, printing and finishing treatment. In particular, the dyeing stage, and the printing stage for woven and non-woven fabrics and yarns are composed of a sequence of processes suitable to provide the material with an established colour.

[0005] Through the use of chemical products or physical-mechanical processing, the finishing stage provides the woven and non-woven fabrics with various characteristics such as softness, hand, water and oil-repellent properties, as well as certain colouring and lustrous effects. Widely speaking, the finishing stage comprises chemical operations that, among others, include the application of sizing and pigments, painting and mechanical treatments aimed at improving the appearance. More in particular, finishing refers to the application of covering layers, protection, and coatings on the material surface. This treatment can be applied during any one of the working stages.

[0006] The aforesaid processing stages involve the use of large quantities of water and above all, chemical agents of different natures. As well as the considerable resource consumption, these processes also have a an impact on the environment due to the discharging of said chemicals in the sewerage or into the atmosphere.

[0007] In general, plasma is well known for processing different types of materials in order to obtain special structural and functional characteristics. In this context, numerous experiments have been conducted to assess the possibility of using plasma for treating materials as an alternative to some of the treatments described above. In fact, plasma treatment would make a large contribution towards avoiding, or at least reducing the use of large quantities of water as well as substances that create pollution and that are toxic for humans.

[0008] In particular, it has been seen that fluorocarbons, silicones, silanes and siloxanes, can be used in plasma form, and under these conditions they polymerise to form a film on the surface of the aforesaid materials to create waterproofing characteristics. These polymeric films are adsorbed by the surface of said materials but not necessarily chemically bonded.

[0009] As a result, after treatment such as washing with water and solvent, or after some mechanical action, these films can be easily separated from the surface of the materials thus loosing their waterproofing properties.

[0010] This has led to a strong need for providing a method for processing woven, and non-woven fabrics, yarns, materials, films in general and similar products, that will prevent or at least reduce the use of chemical substances considerably during the aforesaid material processing stages. It must also be emphasised that the use of plasma according to current methods does not often provide advantageous results compared to those obtained using traditional methods.

[0011] The basic problem that the present invention aims to resolve is to invent a method that will provide functional surface properties of a different nature that offer characteristics to eliminate the numerous problems created by the methods traditionally employed in treating these materials.

[0012] This problem is resolved with a working method using plasma on the aforesaid materials according to the appended main claim.

[0013] Further characteristics and advantages of this method according to the present invention will be provided in the description below.

[0014] In the following description, the term "materials" refers to any one of the materials described previously, namely woven and non-woven fabrics, yarns, polymeric and inorganic fibres as defined previously, glass and film.

[0015] The plasma used for processing materials according to the present invention is cold plasma, in other words, the temperature of the total gas mass during the plasma stage is the same level as the environmental temperature.

[0016] It has been noted that the aforesaid materials used in industrial processing emit various types of gas from their surface, (in other words: degassing) when placed in contact with plasma or when placed in low-pressure chambers. In particular, it has been noted that more energetic impact, like the charges produced by plasma provokes a degassing reaction on the surface of water and residue gases from the surfaces or bulk of the material; this degassing is mainly caused as a result of chemical etching (breaking of bonds on the surface, caused by plasma and the degassing of volatile substances, or gases) or as a result of variations in the surface energy, or by the effect of heating on the material surface.

[0017] After a large number of experiments it was surprising to note that the said gas emission or transpiration interferes considerably with plasma processing.

[0018] As a result, according to the present invention, the method for working materials comprises at least one stage of cold plasma treatment wherein, during said plasma treatment stage, the emission of gas from the surface of said materials is controlled each time according to the type of material and the particular processing conditions to ensure that it does not influence the plasma processing to an important degree.

[0019] According to a first embodiment of the invention, said method comprises a gas removal stage in sequential order or simultaneously, to remove the gases adsorbed on the surfaces of said materials, and a plasma processing stage on said surface. In particular, the removal stage can be performed by subjecting the substrate to vacuum conditions to the level where the pressure obtained is lower than or equal to 10^{-2} mbar on cm^3/sec inside the processing chamber, preferably lower than 10^{-4} mbar cm^3/sec, and even more preferably lower than $5x10^{-5}$ mbar cm^3/sec. In other words, this does not depend on the device used for the removal under extreme vacuum, for example, it does not depend on the size of the vacuum chamber or the type of pump use to produce the vacuum to whatever level employed, when the pressure registered inside the treatment chamber reaches said values, then it is considered that the gases adsorbed by the substrate surface have been sufficiently removed to be able to guarantee successive efficient plasma treatment.

[0020] Alternatively said gas removal stage can be realised by making the treatment gas flow during plasma application at a tangent to the surface to be processed to "wash" the surface, or remove the gases adsorbed by the surfaces. In fact tangent gas flow, since applied with the molecules and charge as explained previously, will remove the gas from the surface of the materials to be processed, blowing them away. In this manner, the length of time the degassed gases remain on the surface is reduced considerably and the surface is able to interact with the plasma much more efficiently.

[0021] According to a further embodiment of this invention, the gas emission from the surfaces of said materials, in other words, the degassing phenomenon, can be controlled by using a plasma source that originates substantially neutral particles.

[0022] The neutral particles have a contrary effect compared to the charged particles described above. In fact, thanks to the considerable absence of charge, these particles do not remove the gases adsorbed by the surfaces of the materials to be processed, but prevent, or at least reduce their detachment so that they cannot affect the plasma process negatively. An example of this further embodiment of the invention is the use of a power-modulated plasma. For example, by modulating the amplitude of the power at the source it is possible to switch the plasma on and off in order to minimize the flow of charged particles on the substrate surface. In other words, by producing plasma for short periods with a duration between 10ms and 10ms, then eliminating the plasma for periods lasting between 10ms and 1s, it is possible to maximize the production of the charges that produce chemical etching, and as a result, degassing. In fact, during the stages where plasma is applied, the charged species and the neutral species are present, including the radicals, while during the absence of the plasma, the charged particles recombine to neutralise each other almost immediately. On the contrary, the neutral particles survive for longer periods of time (recombination times are longer). This method is important for limiting the degassing phenomenon considerably and above all when it is necessary to realise processes that involve radicals rather than charged types.

[0023] On operating according to any one of the methods just described it was surprising to note that it is possible to obtain better and more efficient processing results, and in any case, that are more advantageous from an economical point of view, compared to those that exist in state of the art methods, and it is even possible to obtain important new properties, especially properties that are long-lasting or permanent, with reproducible processing.

[0024] The plasma treatment stage on materials can be realised with all noble gases, preferably helium, argon, neon, and their blends with air or oxygen or hydrogen, inert gases such as nitrogen and its blends, fluorated gases chosen from the fluorocarbon group, and especially CF_4 and CFC, WF_6. XeF_2, on condition that SF_6 is not included, since it is already known and included in the patent application PCT/IT02/00335, hydrocarbons, CO_2, hydrogen, silicon, silane, siloxane and organosiloxane compounds, chlorine, acrylate, vinylic monomer, styrene, and chloromethylsilane compounds, metals including corresponding blends or polymers. Moreover, the process can be realised also using aforesaid gases in liquid solution, on condition that the respective vapour pressures are greater than the plasma production pressure. In particular, it is possible to prepare a liquid solution in a suitable container, in which said gases are dissolved using well-known techniques, and to connect said container to the processing chamber so that the gases dissolved in said solution can be released inside said chamber when their vapour pressure exceeds the pressure at which plasma is produced.

[0025] Alternatively, when the liquid solution has a vapour pressure lower than the plasma production pressure (for example at atmospheric pressure), then the solution is vaporised in aerosol form.

[0026] The plasma used for material processing according to the present invention, is cold plasma, in other words, the temperature of the total gas mass is the same as the environmental temperature (room temperature).

[0027] Cold plasma can be produced at pressures between 10^{-4} mbar and 100 mbar, in other words, under vacuum as defined in the present description, or at pressures over 100 mbar and under or equal to 2 atm, or substantially at atmospheric pressure as defined in the present description. The plasma can be generated with various electromagnetic sources, that is, sources with different frequencies and geometries. The power emitted by the sources can be modulated in amplitude and/or in frequency in order to control, for example to minimise or maximise, the local density of charged species on the surface of the sample, and therefore to select the type of treatment to be applied according to necessity or preference, and at the same time, to control the degassing phenomenon of the material surfaces.

[0028] The physical-chemical processes that occur on the surfaces of the material depend not only on the degassing, but also on the plasma parameters and the electrical potential values assumed by the sample compared to the plasma potential, or the electrical fields in the proximity of the sample. The electric fields produce positive or negative electric charges that interact with the substrate bombarding it, or simply charging it electrically. These electric fields can be controlled by polarising the sample support, (or the sample itself) or by placing the sample in the ionic sheathe created in proximity to the antenna, which assumes negative electric potential values equal to several hundred volts (from 0 to 800 V) in a spatial area of a few millimetres (from 1 to 10 mm). This method is preferably adopted to produce physical and chemical etching aimed at cleaning the surface, removing any deposit, modifying superficial roughness, and activating the surface.

[0029] In any case, the variations in plasma parameters mentioned above can be effectuated by any technician with knowledge of the art, once the operative conditions and the desired results have been established.

[0030] Vice versa when the processes need to be realised with neutral species, to produce grafting or deposits, rather than using special charges, the source power is modulated in amplitude in order to pulse the plasma in short periods and to minimise the charge flows compared to those of the neutral species. Moreover, this last process is particularly advantageous in cases where it is necessary to minimise degassing as far as possible, as described above.

[0031] On the contrary, said processes do not depend strictly on the type of source. However, at pressures ranging between 10^{-4} mbar and 1 mbar it is preferable to use low frequency electromagnetic and radio frequency sources while at pressures from 10 up to 100 mbar plasma is generated more easily with a microwave source. The plasmas at pressures around atmospheric pressure are generated at low frequency or with microwaves or with ultraviolet rays, or with continuous discharge.

[0032] As far as plasma parameters are concerned, these are imposed by the aforesaid discharge parameters, in other words, the source parameters which, for example, have an electrical power ranging 0.1 W/cm^2 and 50 W/cm^2, the geometry of the source that produces the plasma, (capacitive, inductive source) the frequency of the electromagnetic radiation employed to produce the plasma and the residual vacuum inside the chamber where the processing is conducted. In turn, the vacuum level also depends on the residual humidity and the material degassing, or in other words, the flow of the volatile substances that are released by the materials and degassing of the internal structures that make up the reactor. With regard to this aspect before the plasma processing, it is preferable to proceed with a stage that includes the pre-drying of the material followed by degassing of the material under vacuum. Successively, plasma production should preferably occur in pulsed mode, in order to reduce even further the degassed flows caused by the plasma species bombarding on the surface.

[0033] Moreover, in particularly preferable conditions, the gas flows must be at a tangent to the substrate to "wash" the surface of all gases degassed during the process.

[0034] For example, in certain cases, when thick and/or spongy materials need to be processed, it is also advantageous to maintain the substrate at a temperature under 70°C, preferably less than or equal to environmental temperature to create a temperature and pressure difference between the plasma and the substrate, or in other words, a difference between the pressures of the substrate and the plasma in order to facilitate the flow orientation towards the substrate when processing is to be applied, or vice versa, away from the substrate when it is necessary to facilitate the degassing before plasma processing.

[0035] The cold plasma that is generated is characterised by parameters such as a density of electrons ranging between 10^8 cm^{-3} and 10^{13} cm^{-3} and electronic temperatures from 0.04 eV to 15 eV , that is an average calculated thermal energy such as (ekBT/m)1/2 (e=1,9'10-19 C, kB=1,38'10-23 J/K , m= 9,1'10-31 kg, T absolute temperature in Kelvin), while the ions and the neutral particles are at more or less environmental temperature and the ionic density can vary from 10^8 cm^{-3} to 10^{13} cm^{-3} .

[0036] The treatment with the said type of plasma permits an added advantage in that the materials do not suffer from thermal damage.

[0037] According to the type of surface modification process desired, the position of the sample can be varied compared to the plasma source: (a) the sample can be placed in the area of diffused plasma mounted on a floating support; (b) the sample is mounted on a metal support that is polarised up to several decades of negative or positive volts (up to 100 V) to facilitate the ionic bombarding on the surface; (c) the sample is positioned in the ionic sheathe that is created near the plasma source; (d) the sample is moved constantly to render the processing more homogeneous.

[0038] The time lapse that materials are subjected to cold plasma processing normally never exceeds 20 minutes, preferably less than 15 minutes, and even more preferably, less than 5 minutes.

[0039] In general, the said process is realised under vacuum or at atmospheric pressure.

(A) Under vacuum.

[0040] Under vacuum, the cold plasma is produced in a chamber containing gas at a variable pressure between 10^{-4} mbar and 100 mbar. In particular, said type of plasma under vacuum can be employed according to discontinuous, continuous, or semi-continuous methods as well as roll-to-roll methods.

Discontinuous method.

[0041] The discontinuous method envisages a first and second stage wherein during the first stage, the sample is placed in a chamber that is then evacuated to a pressure lower than the working gas. In the case where this gas is the air that exists inside the chamber, said air must be evacuated to create a vacuum until a pressure value is attained that is suitable for plasma processing. On the other hand, in the case where the gas is not air, after the air inside the said chamber has been substantially evacuated, the working gas is introduced into the chamber. This stage is essential if pure gas is to be obtained inside the process chamber, and in order to produce good degassing levels on the substrate, as will be specified further on, before the application of the following plasma stage.

[0042] During the second stage the plasma is produced and the plasma processing occurs. In certain cases the method also includes a third processing stage wherein, immediately after, or during the plasma process, the sample is made to interact with gases of various types, such as polymeric or polymer gases in gaseous state.

[0043] Alternatively, degassing can occur by sending a flow of gas at a tangent onto the sample and/or pulsing the plasma. In particular, the flow action with pulsed plasma provokes an excellent synergy effect as far as results are concerned.

[0044] Plasma can be produced with various electromagnetic sources, that is, with sources that have different frequencies. The process working conditions are controlled by measuring the plasma parameters and the physical-chemical properties of the samples.

[0045] Processing times are shorter than 20 minutes and processing can be repeated several times. Moreover, after each process the materials can be left for a certain time in an atmosphere composed of air or inert or active gas, and then can be subjected to further processing with the same or a different gas.

Semi-continuous method.

[0046] Generally the semi-continuous method is preferable for limited material quantities, that is, manufactured pieces or materials, fibres used in sectors of specific applications. According to the semi-continuous method, an installation composed of several chambers can be used, for example: one chamber for loading and evacuation, the following chamber for plasma processing, and the last for evacuation and material unloading. The chambers can be connected through open ducts or isolated using vacuum valves. Once the material has been loaded into the first chamber, in rolls or pieces, said chamber is closed and evacuated to a pressure lower than or equal to processing pressure, in order to be able to obtain also degassing on the material surface, degassing that is of primary importance. This stage also permits a type of surface cleaning process above all when dry gases are applied, meaning inert gases completely free of any humidity.

[0047] When the evacuation is complete, the material is transferred to the processing chamber which has a pressure that is higher than or equal to the adjacent chamber, where plasma is applied. In this manner, the environment where processing occurs is not contaminated by residual gases produced during the evacuation stage and material degassing.

[0048] Alternatively, to avoid said contamination, partitions can be installed in the form of walls between the adjacent chambers, that act to isolate one chamber from another.

[0049] It should also be emphasised that the degassing problem can be advantageously resolved by pulsing the plasma and/or making the gas flow onto the surface and/or processing with dry gas in the previous chamber where the plasma process occurs.

[0050] The material is processed in the plasma chamber and after processing that lasts less than 20 minutes, it is transferred into the evacuation and unloading chamber that has a lower pressure level than the processing chamber. Here the material can be maintained in an atmosphere of a gas that is different from air once again. Successively, the evacuation and unloading chamber is opened and the material is unloaded.

[0051] After the unloading stage, this last chamber is evacuated again, and the cycle is repeated.

[0052] If treatments are different, that is, using different gases, or if treatment is performed in cycles, the material can be treated either in a single chamber, or in a system composed of several processing chambers. These chambers are located in the intermediate position between the loading and evacuation chamber and the unloading and evacuation chamber. Otherwise, in the case of cyclic treatment, the material can remain in special chambers and then treated again. This method can be applied for fibres used in textile sectors, for material pieces, and manufactured pieces as described above. It must be emphasised that during treatment in the plasma chamber manufactured items or fibres can be moved constantly to ensure homogenous treatment results.

Continuous method.

[0053] The continuous method can be performed using various systems as described below.

Roll-to-roll system.

[0054] The roll-to-roll system is preferably applied to wound materials. This refers to systems composed of an unwinding and rewinding system inside a processing chamber insulated form the environment. The roll-to-roll treatment is carried out at low pressure chamber, wherein the material is unwound and pulled through the plasma for processing, and then rewound inside the vacuum chamber. This system is composed of a vacuum chamber that can be evacuated thanks to a pumping system in which it is possible to maintain a gas flow to the desired pressure. In the front region of the vacuum chamber, it is possible to produce an electrical discharge and generate plasma, using an antenna as a source, supplied by a transmission system, such as radio frequency for example, or microwave, or simply using static or low frequency electrical fields. The plasma production systems are similar to those described previously.

Continuous air-vacuum-air system.

[0055] The continuous process can be performed in a processing chamber wherein the materials are pulled through said chamber in continuous mode through seals that improve the hermetic condition between environmental pressure and the vacuum inside the chamber. In this configuration, the material enters and exits through the seals and the process occurs in continuous mode. A vacuum installation of this type must include several pumping chambers to obtain the vacuum necessary. This technique can be applied to any one of the aforesaid materials and for any kind of employment destination, and can be used with any type of cold plasma reactor, with the aim of improving or modifying surface characteristics without altering the bulk characteristics obtained using previous processing, and without altering the intrinsic natural characteristics of the materials themselves.

[0056] Independently of the system adopted, in cold plasma environments, the physical, mechanical and volume performance characteristics remain unchanged. In fact, the effect of plasma processing is limited essentially to the contact area composed of the material surface and the result of the process in relation to the depth that can vary from 1 nanometre to 1 micrometer.

(B) At atmospheric pressure.

[0057] Cold plasma produced at atmospheric pressure can be preferably of crown type. In this case, the plasma is produced at low frequency, that is at a frequency ranging between 1 and 200 kHz, at a pressure more or less at atmospheric pressure as specified previously, between two conductor electrodes or between one conductor and one dielectric type, or between two dielectric types, that is, two dielectric coated conductors.

[0058] With the aforesaid type of cold plasma produced with gases such as air, inert gases and noble gases, including blends with the aforesaid gases, the materials and the relative fibres are placed at a distance from the electrodes that varies preferably between 0,2 cm and 3 centimetres. The sample can be moved in relation to the source using a system such as the aforesaid roll-to-roll system at variable speeds, just as the processing time can be varied according to necessity. With this system, the materials and the relative fibres are treated in continuous mode moving under the electrode used to produce the plasma and the processing time is shorter than the second method because the power of the crown system is stronger than that produced at low pressure and this could lead to the materials and the relative fibres becoming damaged. The power employed can range from 300 W for a length of 20 cm of material, while the pressure is close to atmospheric pressure that is in the range specified previously. Before or during the processing stage the material surface is cleaned (and degassed) with inert gas or dry air, or is subjected to a preliminary drying process.

[0059] In typical conditions, the material speed ranges between 1 m/minute and 100 m/minute, power ranges between 50 W and 2 kW, frequency ranges 1kHz and 200 kHz.

[0060] Moreover, the crown dose (defined as D= nP/v/ES, where n is the processing number, P is the electrical power, v is the substrate speed, Es is the discharge length) generally ranges between 1 and 30 W minute/m^2 while the treatment time for a single treatment ranges between 1/100 s and 5/10 s.

[0061] The material can be processed once or several times, but each time for a period less than a second in order to avoid the aforesaid damage. After or during processing the materials can be bombarded with gases of different natures that is different from air. In this case the crown processing is performed in a chamber at controlled atmosphere and the gas is sent in a flow near the electrodes or by the electrode itself.

[0062] As mentioned previously, the processing method used on the materials and relative fibres is composed of at least one stage of cold plasma processing wherein, during said plasma processing stage the gas emission from the surface of the said materials and relative fibres occurs each time according to the type of material and the particular treatment conditions, controlled in a manner so that it does not have a strong impact on the plasma process.

[0063] The aforesaid gas emission control can be obtained by subjecting the sample to be treated to extreme vacuum conditions before the plasma stage. In particular, the degassing flow can be controlled by applying pressure that is equal to or lower than 10^{-2} mbar, preferably equal to or lower than 10^{-4} mbar, and even more preferably equal to or lower than $5x10^{-5}$ mbar.

[0064] Alternatively, in the case where extreme vacuum conditions are not desired, (for example because the material could be damaged, or in order to reduce processing times, or in order to operate in a more economical reactor), it is possible to control the degassing phenomenon during the actual processing of the materials and the relative fibres with plasma, by adopting the following methods:

a) by sending a flow of process gas at a tangent to the material surface and the relative fibres so that they can be "washed" by the same gas, and/or
b) by modulating the plasma source, as explained above, in order to minimise the degassing phenomenon of the sample as far as possible.

With these two methods used alternatively or together, it is possible to process the materials without necessarily having to control the degassing phenomenon using vacuum pressures under 10^{-4} mbar. Therefore these two methods are advantageous compared to the use of a system that works under extreme vacuum conditions, since the pumping system would be calculated in any case for vacuum levels of 10^{-2}-10^{-3} mbar instead of those under 10^{-4} mbar, with considerable cost saving.

[0065] In certain cases, for example when waterproofing, oil-repellent and water-wetting properties are required on the surface of the materials and the relative fibres, the treatments performed with state of the art techniques can be even replaced completely with the method described in this invention.

[0066] In any case, plasma treatment is realised before any of the other working stages on the materials following the drying or exsiccation stages, while, for fibres, the treatment is applied before and after the stages that involve the use of water or other solvents. This technique can be applied to any type of material and relative fibre, as well as for any employment destination and can be realised with any type of cold plasma reactor, with the aim of improving or modifying the surface characteristics without altering the bulk characteristics obtained through previous processing, and without altering the intrinsic natural characteristics of the materials and the relative fibres.

[0067] More specifically, in cold plasma environments, the physical, mechanical and volume performance characteristics remain unchanged. In fact, the effect of plasma processing is limited essentially to the contact area formed by the surface of the material and the result of the process in relation to the depth that varies between 1 nanometre and 1 micrometer.

[0068] In general, the plasma treatment stage can preferably include the following stages either singularly, or in any combination whatsoever:

a) removal of the layers of material closest to the surface (ETCHING);
b) surface insertion and grafting of atoms or chemical groups (GRAFTING) in which continuous flowing of reactive components produced in the plasma facilitate their adsorption inside the surface of the material to be processed facilitating the insertion of functional groups on the surface in question, or in other words, forming chemical bonds between the reactive components in the plasma and those belonging to the surfaces;
c) deposit of very fine film, for example metal, polymer, organic and inorganic material film on material surfaces;
d) activating surfaces through the breaking up of chemical bonding and the generating of free radicals on surfaces to be used successively to form chemical bonds, among which, co-valent bonds with molecules of various types, including organic molecules;
e) forming of new bonds on the surface of said materials without the transfer of plasma reactive components (cross-linking)
f) radical activation of the non-activated carbonhydrogen bond on fibres and the consequential reaction with organic molecules or polymers.

[0069] The material treatment method comprises a stage of plasma application on material surfaces to improve current properties or to provide new properties. In particular, the advantages of the method according to the present invention in relation to traditional surface processing can be summarised as follows:

- realising surfaces with innovative and exclusive properties, or improvement of said properties;
- realising said treatments using a method with low environmental impact:
- a quantity of additional chemical products lower than those used in conventional processes; in fact, this process involves only a few surface layers at molecular level for a depth of a few decades of nanometres as far as a maximum

of a few microns;
- an advantage from an energetic point of view; This is a dry process, and therefore does not require the use of water or energy to evaporate the water and/or other possible solvents;
- ecological advantage; this process does not produce waste or emissions, it makes fibre recycling easier because the quantity of chemical additives is negligible, and moreover, it reduces water consumption since it is a dry process that reduces the water cycle.

[0070] Below are some processes and relative examples of embodiments of the present invention provided purely as information and to be considered by no means limitative. These examples of plasma application have been performed experimentally. In any case, variations to raise processing to industrial scale are within the capacity of any technician skilled in the art in this sector.

I) Process to obtain an increase in wetting capacity and hydrophility in materials and fibres through cold plasma working.

[0071] It is possible to obtain an increase in wetting capacity of materials, that is, to reduce the angle of contact, and it is also possible to increase hydrophility, or water absorption through the use of this process. Various types of plasma can be used for said processing, including plasma of noble gas, inert gas, and preferably oxygen, air, chlorine, ammonia, aforesaid fluorated gas, hydrogen, nitrogen, argon, helium, neon, and their blends, and monomers of various types. In the case where plasma produced under vacuum is employed where the gas is represented by air, the processing chamber of the material is evacuated in a manner to obtain a pressure between 0,1 and 2 mbar.

[0072] It should be noted that in cases where other gases are employed, the processing chamber is evacuated to obtain pressure lower than the pressure used for treatment, and consequently, this provides an adequate degassing control. Successively, the chamber is filled with gas and the plasma is generated, for example using a radio frequency electromagnetic source, with a pressure level ranging between 0.01 and 20 mbar, preferably between 0.1 and 2 mbar, and even more preferably between 0.2 mbar and 0.8 mbar and an electronic temperature ranging between 0.1 eV and 20 eV, preferably between 1 eV and 15 eV, and even more preferably between 2 eV and 10 eV.

[0073] The power employed per surface unit ranges between 0.1 W/cm^2 and 50 W/cm^2, preferably 1 W/cm^2 and 10 W/cm^2.

[0074] The plasma is applied on the material surface for time lapses shorter than 15 minutes, preferably shorter than 10 minutes, and even more preferably between 30 seconds and 5 minutes.

[0075] In order to assess the hydrophilic increase, the degradation time of a drop of water is calculated, that is the time after a drop of water of 20 μl looses its shape, expanding and spreading on the material surface without becoming absorbed, followed by the absorption time on the material surface.

[0076] When the plasma employed is an air or oxygen based plasma, the degradation time of a drop of water passes from 1 minute, for example, in the case of non plasma-treated materials, to less than a second in the case of treatment according to this invention. Moreover, the absorption time for a drop of water changes from 5 minutes to less than a second.

[0077] The same effect is obtained using nitrogen, argon, helium, neon, and more generally with inert and noble gases.

[0078] The duration of the hydrophilic effect in certain cases can be limited in time. Therefore, in the case where said process is used before the dyeing or coating stage, it may be necessary that the following re-wetting or dyeing or coating stages be performed within the successive two weeks. In this case plasma processing is applied to increase hydrophilic and wetting capacity, and can increase or even replace conventional mercerisation methods generally performed using chemical substances containing chlorine or ammonia, or bleaching products such as hydrogen peroxide. Moreover, it should be noted that the reduction in absorption and degradation time of the water drop can also be obtained with microwave plasma at higher pressure as high as 200 mbar, or using a low frequency plasma, or yet again, using crown plasma at atmospheric pressure. In this last case, processing times are reduced considerably until they reach a period of less than a few seconds. As a result, it may be necessary to process the material several times to obtain the same effect obtained using plasma under vacuum.

[0079] In cases where gases are used composed of blends containing oxygen, chlorine, or CO2, the hydrophilic increase results as even greater thanks to the grafting of hydrophilic groups on the material surface. The latter is also very important for controlling the chemical affinity of the material surface for colorants and finishing layers, as will be explained further on. In any case, installations with either atmospheric or low pressure can be used.

[0080] A further advantage provided by plasma processing lies in the fact that the angle of contact is reduced considerably. In particular, the angle of contact is a parameter used in this sector to calculate the wettability level of a surface: the lesser the value, the greater the wettability level (refer to table I). Table I contains certain results on the hydrophilic content obtained with atmospheric pressure plasma.

TABLE I - CROWN PLASMA PROCESSING

Class	Gas	Ass NT minutes	Deg NT minutes	Cont NT degrees	Roll Off NT degrees
Raw cotton	air	100	60	122°	>50°
PET	air	11	7	109°	36°
Film-polip	air	infinite	none	90°	29°
Aluminium Film	air	infinite	none	90°	60°

Class	Ass T minutes	Deg T minutes	Cont T degrees	Roll Off T degrees	Speed in m/minute
Raw cotton	immediate	immediate	-	-	1m/minute
PET	immediate	immediate	-	-	1m/minute
Film-polip	none	-	<30°	-	1m/minute
Aluminium Film	none	-	<30°	<40°	1m/minute

[0081] Below are certain specific examples of material processing for cases where the materials need to be subject to dyeing, finishing or other finishing treatments at a later stage.

Example 1

[0082]

Material: textile materials for printing that have already been through the printing process but have not yet been subject to impregnation and colour fixing obtained with high pressure and temperature vaporisation.
Type of gas: air
Pressure: atmospheric with crown plasma
Distance between sample and electrodes: 2 mm
Processing speed: 1m/minute

Results:

[0083] Water drop absorption time less than a second (2 minutes for non-treated material according to the invention). Immediate degradation time for a water drop (30 seconds for non-treated material according to the invention). Moreover the drop spreads on the surface immediately. The fabric was later subject to impregnation and fixing in vaporisation: Fabric colouring is improved and results as more homogeneous, denser and brighter.

Example 2 - Treatments of PET fabric using plasma in a vacuum.

[0084] In Table II is a list of the treatment obtained using radio frequency plasma on PET fabrics before the colouring stage. It should be noted that it is possible to obtain permanent hydrophilic properties by increasing the processing time and/or polarising the sample (polar.) at negative potentials

TABLE II

Pressure in mbar	Power in watt	Distance in cm	PROCESS TIME minutes	Polar. Volts	Absorption time in sec	Absorption time * in sec
0.4	10 0	5	1	0	<1	39
0.4	10 0	5	10	0	<1	60
0.4	10 0	5	10	0	<1	60
0.4	10 0	5	10	+30	2	170
0.4	10 0	5	10	-30	<1	<1
* Absorption time after 15 days.						

[0085] Moreover, the water drop spread immediately on the treated sample over a larger surface, approximately three time the size of the space occupied by a drop on non-treated fabric.

Example 3

[0086] Materials processed with plasma under vacuum.

TABLE III SHOWING PLASMA PROCESSED SAMPLES.

Class	**Sample**	**T.assorb (s)**	**T.deg (s)**	**Contact angle**	**Roll-off angle**	**Treatment time (min)**	**Note**
Silk	SO1	Immediate	Immediate			5	O2
Cotton	F3 (F6)	Imm.	Imm.			3 (4)	Air (O2)
Pet	ET5 (A7)	Imm.	Imm.			10 (1)	Air (O2)
Raw Pet	AG2	Imm.	Imm.			1	O2
Viscosa	V5	Imm.	Imm.			1	Air
Viscosa +PA	TR2	Imm.	Imm.			3	Air
Wool	GA2	Imm.	Imm.			3	Air
Raw wool	LN1	Imm.	Imm.			4	Air
Wool+PA	FO1	Imm.	Imm.			3	Air
Lyocell	BI1	Imm.	Imm.			5	Air
Film PE	PEL1	-	-	~0°	7°	3	Air
Glass		-	-	~0°	6°	5	Air
Film PP	PPL1	-	-	~0°	9	3	Air
Film PS	PSL1	-	-	~0°	8°	3	Air
Film Copolim	COL1	-	-	~0°		3	Air

(continued)

Class	Sample	T.assorb (s)	T.deg (s)	Contact angle	Roll-off angle	Treatment time (min)	Note
Carbon fibre	FC1	Imm.	Imm.			5	Air
Fibre glass	FV1	Imm.	Imm.			5	Air
Kevlar	AR1	Imm.	Imm.			5	Air
Imm. = immediate							

Below the comparative TABLE IV shows the values for non-processed samples.

TABLE SHOWING NON PROCESSED SAMPLES.

Class	Sample	T.assorb (s)	T.deg (s)	Contact angle	Roll-off Angle
Silk	NT	5	Imm.	30°	-
Cotton	NT	3	Imm.	32°	-
Pet	NT	660	420	109°	36°
Raw Pet	NT	Infini to	3600	132°	37°
Viscosa	NT	3	Imm.	30	-
Viscosa +PA	NT	120	5	-	41°
Wool	NT	Infini to	Infini to	>90°	-
Raw wool	NT	10	5	-	-
Wool+PA	NT	3600	3600	>90°	22°
Lyocell	NT	Imm.	Imm.	-	35°
Film PE	NT	-	-	109°	29°
Glass	NT	-	-	~30°	21°
Film PP	NT	-	-	100°	16°
Film PS	NT	-	-	-	15°
Film Copolim	NT	-	-	-	22°
Carbon fibre	NT	60	3	-	15°
Glass fibre	NT	Imm.	Imm.	-	-
Kevlar	NT	Imm.	Imm.	-	-

II) Process for increasing and/or controlling the affinity of the surface of materials and fibres in relation to resins and colorants.

[0087] As described in the introduction to the present description, it is very important to optimise the affinity of material surface in relation to resins (resin adhesiveness) and colorants. In order to obtain this, plasma treatment according to the present invention activates the material surface by breaking the chemical bonds and by generating free radicals, modifying the roughness of the surface.

[0088] A material sample is processed with both plasma produced from a radio frequency source under vacuum, as well as plasma at atmospheric pressure.

[0089] Plasma is created with gases, for example electronegative gases, oxygen, CO_2, air, and with chlorine, hydrogen, ammonia, inert gases, noble gases, inert gases and their blends.

[0090] Preferably the sample is mounted on a mobile support positioned in the chamber where a vacuum is created to produce a pressure level lower than that used for plasma processing, which is less than 20 mbar. Then the chamber is filled with gas at a pressure that can vary from 0,01 mbar to 20 mbar, preferably between 0.1 and 10 mbar, even more preferably between 0.2 and 3 mbar and the plasma is generated with a radio frequency source for a period less than

10 minutes, more preferably for a period between 30 seconds and 5 minutes.

[0091] As far as power is concerned, the values specified previously are also applicable in this process.

[0092] Alternatively, crown plasma can be used with processing at atmospheric pressure with a gas such as air, noble gas, or inert gas for a period less than a second, and repeated up to a maximum number of 20 times.

[0093] With the process that has just been described, it is possible to advantageously facilitate the adhesiveness to resins and metals, as well as to control and optimise the material affinity with the colorants required, and at the same time preventing that said colorants become fixed on the surface in an undesired and non-homogeneous manner.

[0094] As far as the increase in adhesiveness is concerned, this is also due to a change in the morphology of the surface: in fact the adhesion surface for resins can increase three times after plasma processing.

[0095] Moreover, the aforesaid method provides an increase in colour solidity on the material, that is - it provides better fixing and stability for a far longer period compared to the levels obtained with current state of the art methods.

[0096] It is also possible to graft functional groups on the surface, such as alcohols (OH for example) carbonyls (for example CO) carboxylics (COOH for example), ammines($-NH_2$) suited for bonding with various types of colorants. A further advantage provided by material processing using plasma according to the present invention, lies in the fact that it is possible to obtain excellent distribution uniformity for resins and coating deposits of various types.

[0097] Below are the results concerning colouring of textile materials such as cotton and PET after plasma processing. Because of the high level of crystallinity and the absence of reactive groups, current dyeing methods for polyesters are performed in rather drastic conditions (T>100°C) and/or with the aid of chemical volume increase ("carriers") that facilitate the penetration of the colouring molecule inside the fibre. The aforementioned characteristics permit the use of a single class of colorants at industrial level, so-called dispersed colorants, that act according to a basically physical dispersion mechanism composed of two stages, one dyeing bath colorant diffusion that acts on the external surface of the fibre, and an internal diffusion from the surface inwards towards the amorphous areas of the fibre. The plasma process is able to influence the first stage of this process, by both increasing surface affinity to colorants (by using reactive gas plasma, such as air) and by increasing the penetration speed of the solution into the fibres (improving the hydrophilic properties), as well as by increasing the absorbency capacity of the colorant on the surface (increasing the extension through increased micro-roughness, and through etching phenomenon induced by the plasma).

[0098] Dyeing was effectuated as described previously, at the Experimental Silk Station. In the dispersed colorant class, the chosen colours were Palanil Navy Blue (C.I.94, dispersed in lg/l concentration in the presence of 10ml/l of acetic acid with a bath ratio of 1:300) and Palanil Yellow (C.I.64, dispersed in lg/l concentration in the presence of 10ml/l of acetic acid with a bath ratio of 1:300) with opposing properties as far as diffusion speed was concerned. Dyeing was performed using a dye bath containing an excessive amount of colorant. In this manner, samples treated with plasma under different types of condition, as well as non-treated samples were placed in the same dye bath, to prevent competitive effects among the various samples. This method permits direct assessment of dyeing capacity improvement induced by plasma processing. Standard dyeing processing was performed leaving the samples in the dye (concentration C=0.1% and bath ratio Rb 1:300) for 1 hour at a temperature of 98°. The samples were left to dry in the air and were then washed (with standard soap 0.5 g/l at 50° for 45') to remove any excess, non-fixed colorant. A series of tests were performed varying the dyeing parameters: results demonstrate that the increase in dyeing capacity does not depend on the concentration (C=0.05-1%) or the duration of the dyeing process (t=30'-2h). In this case the sample was processed in a configuration with a cylindrical antenna in air plasma: these conditions correspond to a pressure level of P=0.4 mbar, power RF (with the former adaptation method) W=200 W, treatment time t=1' , with the sample positioned at a distance of D=5 cm from the antenna, and maintaining voltage of V=-20 V compared to the vacuum chamber that acts as a mass electrode. The standard dyeing process with Palanil Navy Blue demonstrated a K/S increase (K/S = (1-R) ^2/ (2R), where R refers to the reflectivity at a determined wave length. This is proportional to the concentration of the colorant on the fibre by 50-75%. Increases of this type correspond to dyeing capacity increases up to 40% of the K/S value measured in dyes at T=130°. Further improvement can be obtained using a cyclic process (a sample treated three times for t=30" produces a better increase in dyeing capacity compared to a sample treated only once for t=2').

TABLE V PET - DYEING CAPACITY

Pressure in mbar	Powerin watt	Distance in cm	PROCESS TIME minutes	Polar. Volt	K/S % increase
0.4	155	5	2	30	99%
0.4	155	13	2	0	75%
0.1	160	6	2	0	82%
0.2	125	11	2	0	103%
0.4	160	5	10	0	99%

[0099] These are the results on processed cotton.

[0100] As far as cotton fabric is concerned the choice of dyeing procedure was more difficult given the considerable diversity in techniques and in the classes of colorants used at industrial level. It was decided to work with reactive type colorants (in particular Levafix Bright Red and Levafix Turquoise Blue) (bright Red E-BA Bayer, Turquoise Blue E-G Bayer) rather than direct type. Dyeing was effectuated both at environmental temperature (20°) and in the dye bath (50°-80°). The samples were then left to dry in the air, or were subject to pressing or padding. Before analysis all the samples were washed (with standard soap without bleaching agents ISO 105 C01C05) 0.5 g/l at 40° for 1h) to remove any non-fixed colour. In this case as well, a series of tests were performed varying the dyeing parameters to control the extent to which the dyeing capacity increase results depend on the concentration (C=0.05-1%), the bath ratio (Rb=1:10- 1: 200), the duration of the dyeing process (t=10'-2h) and the type of colorant employed.

[0101] At environmental temperature with pressing and stocking in air, there is a general improvement in dyeing capacity. In particular, there is an increase in the colorant rise speed (+15%) and in the final quantity of colorant that rises on the fabric under saturation conditions (+30%).

III) Process for cleaning the surface of materials and fibres.

[0102] This method can be applied to facilitate material recycling, for example, for facilitating the removal of resin or chemical film from material surfaces or colorants.

[0103] The method for processing the aforesaid materials and fibres used in the specific sectors in question including the application of plasma according to this invention can also be used to clean material and fibre surfaces. In particular, it is possible to remove surface layers with a thickness up to 10 micron. In this case gases such as noble gases, and inert gases can be used, preferably nitrogen, oxygen, air, chlorine, ammonia, hydrogen, fluorated gases and their blends.

[0104] The plasma employed can be vacuum or atmospheric pressure type.

[0105] According to a preferred embodiment, the aforesaid surface cleaning on materials can be realised using plasma under vacuum at a pressure 10^{-4} mbar and 20 mbar, for a period less than 20 minutes, preferably less than 10 minutes, and even more preferably for a period between 30 seconds and 5 minutes. Like the process described previously, in this case as well, the power employed corresponds with that specified in the general part of the present description.

[0106] Alternatively, by using crown plasma with air or noble gas, or a blend of air and noble gas at a pressure level similar to atmospheric pressure, the processing time is reduced to the extent of only a few seconds and with a surprisingly uniform and hydrophilic surface.

[0107] The quantity of material removed is performed in a controlled manner and is under 20% of the total weight.

[0108] In this process, cleaning is realised by bombarding the surface with active species and therefore the processes involved are above all those of physical and chemical etching. These processes also facilitate material wettability and therefore also facilitate any successive traction wetting stages or removal of protective film, including during conventional recycling.

[0109] This method can be used in any case for also removing resin from material surfaces.

[0110] In this case, where physical etching needs to be produced, or in other words, the removal of nanometric layers or portions (between 1 nm and 10 mm) of surface, the charged particles must be accelerated towards the sample, for both positive and negative ions. To obtain this, the sample must be polarised at positive or negative potentials in relation to the plasma potential.

IV) Process for making materials and relative fibres water-repellent.

[0111] A further use for the material process with cold plasma application according to the invention lies in the fact that it is possible to obtain a water-repellent effect on material surfaces and the relative fibres.

[0112] In particular, plasma processing can be effectuated using fluorated gas in general, such as fluorocarbons, including for example, CF_4, CFC, or NF_3 and WF_6, silicon, silane and siloxane compounds, organosilanes such as hexamethyl-disiloxanes, hydrocarbons, styrenes, and their blends.

[0113] It has been seen that fluorocarbons and silicon, silane and siloxane compounds can be deposited to form a film on material surfaces to create the said water-repellent effect. These polymer films, that can vary in thickness between 1nm and 10 microns, can be removed from the material surface and the fibres with the loss of the water-repellent properties. Therefore for these deposits, the thickness and their adhesion to the surface must be optimised. This varies from sample to sample because it depends on the roughness and capillarity of the sample. It is also important to have a stable clean surface in order to obtain good deposit adhesion, that is, a surface where the degassing has been particularly well controlled and simultaneously activated.

[0114] With this aim in mind, a preliminary process using plasma activation with noble or inert gas, or with hydrogen is performed for certain highly hydrophilic samples.

[0115] On the other hand where fluorated gases such as NF_3, WF_6 and their blends with hydrogen or noble gases are used, the material surface is bombarded with fluorine radicals that are grafted to form stable long lasting bonds, but without forming a film.

[0116] In cases where organosilanes such as hexamethyl-disiloxanes are used, a film of a SiO_2 type with variable thickness can be formed.

[0117] The method preferably used to obtain water-repellent properties is with fluorocarbons, that is with a gas that permits the forming of numerous fluoro-carbon bonds, and with organosilanes and their blends. Pressure ranges between 0,1 and 10 mbar, preferably between 0.2 mbar and 5 mbar, more preferably between 0.2 mbar and 3 mbar. The electronic plasma is approximately 10^8 cm^{-3} while the density of ionic plasma reaches a value of 10^{11} cm^{-3} .

[0118] Processing time is less than 15 minutes, preferably less than 10 minutes and even more preferably less than 5 minutes, and the power corresponds with that already specified previously.

[0119] When CF^4 is used, the residual pressure is preferably between $3x10^{-6}$ mbar and $5x10^{-5}$ mbar. The distance between the sample and the antenna can be between 5 cm and 7.5 cm. When organosilanes are used, the residual pressure is between $2x10^{-3}$ mbar and $8x10^{-3}$ mbar and the distance between the sample and the antenna is between 3 cm and 6 cm.

[0120] The material sample can also be mounted on a mobile support and positioned in a chamber that is evacuated to a pressure lower than that used for process gas, that is - less than treatment pressure. Following this stage, the chamber containing the sample is filled with gas and the plasma is generated with a radio frequency or low frequency source.

[0121] The water-repellent effect on materials and fibres does not depend on the source with which the plasma is realised, and can be obtained using radio frequency, microwave, or low frequency sources or crown plasma with pressure at approximately atmospheric pressure that contain numerous fluorine radicals or radicals from organosilanes. However the efficiency and the duration of the effect on the surface improve when the gas used for processing is a fluorated gas that contains CF_4 and its blends, hexamethyldisiloxane and its blends, preferably with oxygen or air.

[0122] Moreover, thanks to the versatile character of the process, this can be applied to make the surfaces of the aforesaid materials water repellent. In fact the high absorbency capacity makes it difficult to obtain the same water resistant results together with water drop colour solidity, using traditional technology.

[0123] At a later stage, after performing a flow control on the gas produced by surface degassing, the water-repellent effect becomes permanent.

[0124] Certain preferred embodiment examples for obtaining water repellent properties on different materials according to the present invention, will be described in detail below.

Examples with organosilanes

[0125] The pressure used for processing samples with pure hexamethyldisiloxane ranges from P=0.1 mbar to P=10.0 mbar, preferably between P=0.4 mbar and P=5 mbar, more preferably between P=0.6 mbar and P=3mbar; the plasma processing times are shorter than 10 minutes, preferably less than 5 minutes, and even more preferably less than 3 minutes; power ranges between 0.1 W/cm^2 and 20 W/cm^2, preferably between 1 W/cm^2 and 10 W/cm^2, even more preferably between $1W/cm^2$ and 5 W/cm^2. For each type of material, plasma processing with organosilanes and their blends with oxygen demonstrate 20 μl water drop absorption times as longer than 100 minutes (100 minutes is the time necessary for the complete evaporation of the whole water drop, so therefore the water drop evaporates) compared to absorption times that vary between 0 seconds (for absorbent materials) and a few minutes.

[0126] The roll-off angle is reduced up to 10°. There are no traces of ring marks or surface swellings left by the water drop. The reduction of the roll-off angle means that drops of water can slide off the surface far more easily. This process is useful for making materials and fibres water-repellent without varying the organoleptic properties obtained through previous processing, while guaranteeing long duration at the same time.

[0127] Deposits on the surface are lower than μm, with organosilanes, preferably 10nm and 100nm. Moreover, permeability tests on gases demonstrate that water vapour and oxygen permeability are reduced, for example on plastic films used for packaging.

[0128] Certain specific examples are described below. Oil repellent capacity was also assessed on samples using test-kit standards.

[0129] Using CF_4 gas and the same conditions described in the example n° 2 above, oil repellent levels are approximately ¾ . Organosilanes provide grade 1 oil repellent levels.

[0130] The applications of the aforesaid processing include materials and fibres which for example, can be used for solid and liquid foods, for woven and non-woven fabrics, technical fabrics (such as glass fibre or carbon fibre fabrics, blended fabrics) glass, metals, alcantara and relative fibres.

Table VI for processing materials with CF4 under vacuum.

Class	gas	Ass NT seconds	Deg NT seconds	Contact NT degrees	Roll Off NT degrees
Cotton	CF4	<1	<1	32°	>50°
Silk	CF4	<1	<1	30°	-
PET	CF4	150	7	109°	36°
Viscosa/ linen	CF4	10	2	30°	>40°
Kevlar	CF4	<1	<1	-	-
Mixed cotton/PA	CF4	90	30	>90°	37°
Film-polip	CF4	inf	-	-	29°
Glass fibre	CF4	2	<1	-	-
Carbon fibre	CF4	30	5	-	41°
Alcantara	CF4	10	3	-	-

Ass refers to "the absorption time for a drop of 20 micro litres of waters", Cont indicates "the angle of contact", NT indicates "Non treated", Deg indicates "degradation time for a drop of 20 micro litres of water", Roll Off indicates the Roll Off angle, Time indicates "the time lapse the sample is exposed to the plasma, or, the plasma processing time", Inf indicates "infinite" or drop evaporation.

Class	Ass T seconds	Deg T seconds	Cont T degrees	Roll Off T degrees	Time sec	Pressure N_2 eq. mbar
Cotton	infinite	None	142°	9°	60	0,6
Silk	inf	None	125°	10°	60	0,6
PET	inf	None	150°	8°	60	0,6
Viscosa/linen	inf	None	-	14°	120	0,6
Kevlar*	inf	None	-	18°	120	0,5
Mixed cotton/Pa	inf	None	>>90°	-	180	0,6
Film-polip	inf	None	>130°	21°	180	0,6
Glass fibre	inf	None	>>90°	27°	120	0,6
Carbon fibre**	inf	None	>129°	22°	120	0,6
Alcantara	inf	none	>130°	23°	120	0,6
*The water repellent effect decreases until it is saturated after 15 days at a level equal to an absorption time of 15 minutes; ** the water repellent effect decreases until it is saturated after 15 days at a level equal to an absorption time of 10 minutes.						

[0131] The effect on glass fibre decreases in time attaining absorption time of approximately 1 minute after a period of 15 days. For all the other samples the effect is permanent.

[0132] Below, Table VII shows the results obtained on certain materials with organosilane blends (with oxygen).

TABLE VII

Class	Ass NT minutes	Deg NT Minutes	Cont NT degrees
Cotton	0,1	0,01	32°
Silk	0,05	0,01	30°
PET	11	7	109°

Class	Ass T minutes	Deg T minutes	Cont T Degrees	Tempo secs	Pressione N_2 eq. mbar
Cotton	inf	None	140°	180	1
Silk	inf	None	125°	180	1
PET	inf	None	150°	180	1

VI) Process of grafting and deposit of polymers, organic and inorganic materials, and metals on material surfaces.

[0133] The applications of said process also include the generation of a surface barrier film on water repellent, flame-proof, anti-static, and biocompatible surfaces. Moreover there are other characteristics designed for use in other sectors such as waterproofing materials after dyeing, resistance to oxidising agents, protective coatings, metalising, printing improvement through material modification before printing, product protection against sunlight and UV radiation, polarising with monomers, barrier films against vapours or gas, synthetic polymer grafting on cellulose, and biodegradable deposits.

[0134] A large number of other properties can be applied to the materials specified in the introduction to the present description using the method according to the present invention.

[0135] The methods used to obtain a deposit or grafting are described individually or in any type of combination as follows:

- production of a plasma of the substance that one wishes to deposit (for example, see process IV);
- activation of the surface with a gas plasma, inert gas for example, (process II) and followed by the creation of interaction between the substrate with the substance in gaseous stage, with or without plasma in the same container chamber;
- effectuating the cycles that follow methods a) or b) with a pulsed source: in this manner the surface is activated (method a) by the charge from the substance, (method b) with inert gas) and immediately after the plasma is switched off, the substrate interacts with the activated substance (in method a)), or not activated (in method b));
- activation of the plasma surface according to process II, and deposit operation using conventional methods.

[0136] At the same time, the plasma can activate the surface during the deposit process (method a)), or the deposit stage can be preceded by the activation stage as described in process II) realising cyclic processes (method c)) in which the sample is subject to plasma activation, and immediately after or during the activation, the surface is bombarded with gas, whose molecules (monomer or radical, for example) are grafted and/or deposited on the surface itself. For example it is possible to obtain flame-proof properties using directly any method whatsoever described above with gases mixed with phosphorous (method a) or b) or c). Alternatively, it is possible to prepare the material and fibre surface using method 2) and then successively, to apply a surface flameproof layer according to standard finishing methods (method d)).

[0137] In a similar manner the anti-static properties of materials can be improved, by using metal plasma in particular, or chloromethylsilane, or hydrocarbons such as methane.

[0138] It is possible to realise barrier film for food product protection against the light and UV radiation. For example, Parma Ham tends to oxidise certain amminoacids that contribute to the particular flavour and aroma under sunlight and in the presence of oxygen, vice versa by using a barrier film against radiation and oxygen on the film generally used for food packaging, it is possible to reduce or prevent oxidising.

[0139] Similarly barrier films are realised for organic substances of various types, useful, for example in all food packaging containing liquids, such as cartons for fruit juice, wine, and milk; this packaging must not release any of the organic substances of which they are composed.

[0140] Moreover, organic and inorganic deposits on material surfaces can be obtained using cold plasma containing acrylates, vinylic monomers, fluorocarbons, silanes, siloxanes, organosilanes, saturated hydrocarbons and their blends (method a)). Alternatively the surface can be activated according to process II) and polymers of various types and chemical substances of various kinds can be successively deposited during the gaseous stage under vacuum, several of these being already used in conventional processing (method b) or c)). The liquid substances at standard pressure can be used in gaseous stage under vacuum, as long as the vapour pressure is approximately the same as or higher than that in the vacuum chamber.

[0141] Preferably pressures vary from 0,1mbar to 20 mbar, more preferably from 0.2 mbar 5 mbar, and even more preferably between 0.3 mbar and 3 mbar.

[0142] The layers can vary in thickness: for treatment that lasts only a few minutes, deposits of only a few decades of nm are used, for treatment that lasts several decades of minutes, deposits can attain a thickness of over a micron. Deposits can be used to modify the optical properties of materials, for example, to realise absorbent or reflective surfaces. In fact, the deposits are characterised by refraction indexes that can be controlled as necessary, and chosen according to the optical filtering that is required.

[0143] Certain special effects can be realised through the creation of areas that have a greater or lesser hydrophilic capacity and affinity to dyes for the creation of patterns and designs on materials or metalised areas for special visual effects, for example on fabrics for wearing apparel. These effects can be obtained using cold plasma activating the surface locally, or by depositing material with localised plasma, for example using a plasma brush realised through a limited source (cylindrical or spherical) mounted on a mobile support, that can be moved as required.

[0144] The processes described above can also be obtained with crown discharge, using methods a) b) or c) or d), at atmospheric pressure that contains blends of the aforesaid gases with noble or inert gases or air. For example, in a noble gas, inert gas or air atmosphere, it is possible during (method a)) or after crown processing (method b) or c)) to send a flow or organosilane, such as hexamethyldisiloxane, directly from the electrodes or in areas close to them, during the gaseous stage onto the substrate or fibre surface so that it is deposited and/or grafted on the surface. This last method is important for depositing and/or grafting groups of various natures on surfaces, including hydrophobic and hydrophilic groups, and/or that have a close affinity with certain substances, and/or with specific properties such as anti-bacteria, anti-mildew, anti-static, flame-proof, biocompatible, barrier films, and EM radiation protection film. Lastly, deposits can be made successively, using conventional and nonconventional types, during the gaseous, liquid or solid stage such as that used in method d)).

[0145] As can be understood from the description above, the processing method of the aforesaid materials including the application of a plasma on the surface of said materials according to the invention, provides the possibility of satisfying the requirements listed in the introduction to the present description, and to overcome the problems that exist with current state of the art processing methods at the same time.

[0146] The present invention further discloses the following embodiments:

[0147] Embodiment 1. Method for the working of woven and non-woven fabrics, yarns, natural, polymeric, and inorganic fibres and films, alcantara and glass, including in successive order or simultaneously, a stage wherein the gases adsorbed on the surface of said woven and non-woven fabrics, yarns, natural, polymeric, and inorganic fibres and films, alcantara and glass are removed, by at least one plasma processing stage on said surface.

[0148] Embodiment 2. Method for the working of woven and non-woven fabrics, yarns, natural, polymeric, and inorganic fibres and films, alcantara and glass, comprising at least one treatment stage with cold plasma, realised using a source of plasma that originates particles that are substantially neutral.

[0149] Embodiment 3. Method according to Embodiment 1 wherein said removal stage is performed under extreme vacuum in order to obtain a pressure lower than or equal to 10^{-2} mbar on cm^3/sec inside the processing chamber.

[0150] Embodiment 4. Method according to Embodiment 1 wherein said removal stage is performed by sending a flow of treatment gas at a tangent to the surface to be treated.

[0151] Embodiment 5. Method according to Embodiment 3 wherein said pressure is lower than 10^{-4} mbar on cm^3/sec, preferably lower than $5x10^{-5}$ mbar on cm^3/sec.

[0152] Embodiment 6. Method according to Embodiment 2 wherein said plasma source that originates substantially neutral particles, is obtained through pulsed plasma.

[0153] Embodiment 7. Method according to Embodiment 6 wherein said source is power modulated in a manner to produce plasma for a period ranging between 10 μs and 10 ms interrupted at intervals by the switching off of said source for periods of time ranging between 10 μs and 1 s.

[0154] Embodiment 8. Method according to any one of the Embodiments from 1 to 7 wherein said cold plasma is obtained from gases chosen from the group consisting of noble gases, air, oxygen, inert gases, fluorated gases chosen from the group of fluorocarbons, on condition that said gas is not SF_6, hydrocarbons, CO_2, hydrogen, silicon, silane siloxane and organosilane compounds, chlorine, acrylate, vinylic monomers, styrenes and metals as well as blends of said gases.

[0155] Embodiment 9. Method according to Embodiment 8 wherein said noble gases are chosen from helium, argon, neon, and their blends with air, oxygen or hydrogen, said inert gas being nitrogen, said fluorated gases being chosen among CF_4, WF_6, XeF_2 and CFC or their blends, and said silanes being organomethylsilanes, and more specifically hexamethyldisilane.

[0156] Embodiment 10. Method according to any one of the previous Embodiments from 1 to 9 wherein the plasma treatment stage includes the use of polymers in gaseous and liquid stage.

[0157] Embodiment 11. Method according to any one of the previous Embodiments from 1 to 10 wherein the plasma is generated using electromagnetic sources and wherein the antenna creates a spatial area around itself between 1 and 10 mm forming an ionic sheath having electric power values between 0 and 800 Volt.

[0158] Embodiment 12. Method according to any one of the previous Embodiments from 1 to 11 wherein the said plasma is produced under vacuum or at a pressure approximately the same as atmospheric pressure, namely between 100 mbar and 2 atm.

[0159] Embodiment 13. Method according to Embodiment 12 wherein the plasma under vacuum is produced at a pressure ranging from 10^{-4} mbar and lower than 100 mbar.

[0160] Embodiment 14. Method according to Embodiment 12 or 13, wherein, when the electromagnetic source is at low frequency or radio-frequency, the plasma pressures are between 10^{-4} and 1 mbar.

[0161] Embodiment 15. Method according to Embodiment 12 or 13, wherein the plasma is generated using a microwave source at a pressure between 10 mbar and 200 mbar.

[0162] Embodiment 16. Method according to any one of the previous Embodiments from 1 to 15 wherein the electrical power of the plasma ranges between 0.1 W/cm^2 and 50 W/cm^2.

[0163] Embodiment 17. Method according to any one of the previous Embodiments from 1 to 16 comprising a pre-exsiccation stage of the materials to be treated before the gas removal stage.

[0164] Embodiment 18. Method according to any one of the previous Embodiments from 1 to 17, wherein the woven, and non-woven fabrics, yarns, natural and polymeric fibres and inorganic fibres and films are maintained at a temperature lower than 70°C, preferably lower than or equal to environmental temperature, during said plasma treatment.

[0165] Embodiment 19. Method according to any one of the previous Embodiments from 1 to 18, wherein the plasma under vacuum is used according to the discontinuous, continuous, semi-continuous or roll-to-roll method.

[0166] Embodiment 20. Method according to Embodiment 12, wherein the plasma is a crown plasma produced at atmospheric pressure, with power ranging 50 W and 2 kW, frequency ranging between 1 kHz and 200 kHz, having crown doses ranging between 1 and 30 W minute/m^2 and individual treatment times between 1/100 seconds and 5/10 seconds.

[0167] Embodiment 21. Method according to any one of the previous Embodiments from 1 to 20, wherein said plasma process is realised before any one of the other working stages on the woven and non-woven fabrics, yarns, natural and polymeric fibres and inorganic fibres and films following the drying stage, and before and after the stages that involve the use of water or other solvents.

[0168] Embodiment 22. Method according to any one of the previous Embodiments from 1 to 21, wherein the plasma is produced at an electronic temperature ranging between 0.04 eV and 15 eV.

[0169] Embodiment 23. Method according to any one of the previous Embodiments from 1 to 22, wherein said plasma application comprises the following stages, either individually or in any combination whatsoever:

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

b) surface insertion and grafting of atoms or chemical groups (GRAFTING) wherein the continuous flow of reactive components produced in the plasma facilitates their adsorption inside the surface of the material to be treated, facilitating the grafting of functional groups on the surface in question, in other words, realising chemical bonds between the reactive components in the plasma and those belonging to the surface in question;

c) deposit of a fine film, for example of a metal, polymer, biopolymer, organic or inorganic material on the surface of the material;

d) activation of the surface through the breaking of the chemical bonds, and the generation of free radicals on the surface to be used successively to form chemical bonds, among which, covalent bonds having molecules of various types, including organic molecules;

e) formation of new bonds on the surface of said materials without the application of reactive components of the plasma (cross-linking);

f) radical activation of the non-activated carbonhydrogen bond on the fibres and the consequential reaction with biodegradable organic molecules or polymers.

[0170] Embodiment 24. Method according to any one of the Embodiments 1, 3, 5 and from 8 to 23, wherein the removal of the gases adsorbed on the surfaces of said materials occurs under extreme vacuum and flowing the gas at a tangent to the surface of said materials.

[0171] Embodiment 25. Method according to any one of the Embodiments 1, 2, 3 and from 5 to 23, wherein the removal of the gases adsorbed on the surfaces of said materials occurs under extreme vacuum and using a plasma source that originates substantially neutral particles.

[0172] Embodiment 26. Method according to any one of the Embodiments 24 or 25 wherein the removal of the gases adsorbed on the surfaces of said materials occurs under extreme vacuum using a plasma source that originates substantially neutral particles that are made to flow at a tangent to said surface.

[0173] Embodiment 27. Process to increase the wettability and hydrophilic capacity of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara using the method according to any one of the Embodiments from 1 to 26.

[0174] Embodiment 28. Process according to Embodiment 27, wherein the woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara are processed with plasma at a pressure level ranging between 0.01 and 20 mbar, at an electronic temperature ranging 0.1 and 20 eV for a period of time less than 15 minutes, and with power ranging between 0.1 W/cm^2 and 50 W/cm^2.

[0175] Embodiment 29. Process according to Embodiments 27 or 28 wherein the plasma processing pressure level ranges between 0.1 and 2 mbar, preferably between 0.2 and 0.8 mbar, the electronic temperature ranging between 1 and 15 eV, preferably between eV and 10 eV, the processing time being less than 10 minutes, preferably between 30 seconds and 5 minutes, with power ranging between 1 W/cm^2 and 10 W/cm^2.

[0176] Embodiment 30. Process for increasing and/or controlling the affinity of the surface of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara to colorants or resins using the method according to any one of the Embodiments from 1 to 26.

[0177] Embodiment 31. Process according to Embodiment 30 wherein the surface of said woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara is processed with plasma under vacuum at a pressure level between 0.01 and 20 mbar, preferably between 0.1 and 10 mbar for a period of time less than 15 minutes, preferably less than 10 minutes.

[0178] Embodiment 32. Process for cleaning the surface of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara using the method according to any one of the Embodiments from 1 to 26.

[0179] Embodiment 33. Process according to Embodiment 32 wherein said surface layers are treated at a plasma pressure ranging between 10^{-4} and 20 mbar for a period of time less than 20 minutes, preferably less than 10 minutes.

[0180] Embodiment 34. Process according to any one of the Embodiments from 32 to 33 wherein said process produces a de-inking action on the surface of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara.

[0181] Embodiment 35. Process to make the surface of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara water repellent using the method according to any one of the Embodiments from 1 to 26.

[0182] Embodiment 36. Process according to Embodiment 35 wherein said surface is processed with plasma comprising fluorocarbons and/or organosilanes at a pressure level ranging between 0.1 and 10 mbar for a period of time less than 15 minutes.

[0183] Embodiment 37. Process according to Embodiment 35 wherein the plasma processing pressure ranges between 0.2 and 5 mbar, preferably between 0.2 and 3 mbar, the processing time lapse being less than 10 minutes.

[0184] Embodiment 38. Process according to Embodiment 35 wherein when hexamethyledisiloxane is employed, the pressure ranges between 0.1 mbar and 10 mbar, the plasma processing times being less than 10 minutes, and power ranging between 0.1 W/cm^2 and 20 W/cm^2.

[0185] Embodiment 39. Process according to Embodiment 38 wherein the pressure ranges between 0.4 mbar and 5 mbar, preferably between 0.6 mbar and 3 mbar, the plasma processing times being less than 5 minutes, preferably less than 3 minutes, and power ranging between 1 W/cm^2 and 10 W/cm^2, preferably between 1W/cm^2 and 5 W/cm^2.

[0186] Embodiment 40. Process to make the surfaces of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara oil repellent using the method according to any one of the Embodiments from 1 to 26.

[0187] Embodiment 41. Process of grafting and deposit of polymers, organic or inorganic materials, or metals on the surface of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara using the method according to any one of the Embodiments from 1 to 26.

[0188] Embodiment 42. Process according to Embodiment 41 comprising the following methods either individually or in combination:

- production of plasma from the substance that is to be deposited according to the process according to Embodiment 35;
- activation of the surface using a plasma according to the process described in Embodiment 30 and followed by the creation of an interaction between the substrate with the substance during the gaseous stage with or without plasma in the same processing chamber;
- operating successive cycles of the methods a) or b) using a pulsed source;

- activation of the surface with plasma according to the process described in Embodiment 30, with the application of a deposit according to conventional methods.

[0189] Embodiment 43. Woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara obtainable through the process according to any one of the Embodiments from 1 to 42.

[0190] Embodiment 44. Hydrophile woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara **characterised in that** the degradation time of a drop of water of 20 μl on their surfaces is less than one second, while the absorption time of said drop of water on said surface is less than 1 second.

[0191] Embodiment 45. Hydrophobic woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara **characterised in that** the absorption time for a drop of water of 20 μl is longer than 100 minutes.

[0192] Embodiment 46. Hydrophobic woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara characterised by the fact that the roll-off angle for a drop of water of 20 μl deposited on the surface of the material in question is less than 30°.

[0193] Embodiment 47. Woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara **characterised in that** the angle of contact of a drop of water of 20 μl is greater than 90°.

[0194] Embodiment 48. Woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara comprising layers of organic or inorganic material, polymeric film deposited on the surfaces in question, **characterised in that** said layers vary in thickness between 1 nm and 10 μm.

[0195] Embodiment 49. Articles in woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara according to the Embodiments from 43 to 48.

[0196] Naturally in order to satisfy associated or specific necessities, a technician skilled in the art is able to apply numerous modifications and variations to the above-described method, while remaining within the context of the invention as it has been defined and described in the following claims.

Claims

1. Method for the working of woven and non-woven fabrics, yarns, natural, polymeric, and inorganic fibres and films, alcantara and glass, comprising at least one treatment stage with cold plasma, realised using a source of plasma that originates particles that are substantially neutral, wherein
   said plasma is produced at a pressure approximately the same as the atmospheric pressure, and
   said plasma source originating substantially neutral particles is obtained through pulsed plasma.

2. Method according to claim 1 wherein the source power is modulated in a manner to produce plasma for a period ranging between 10 μs and 10 ms interrupted at intervals by the switching off of said source for periods of time ranging between 10 μs and 1 s.

3. Method according to claim 2, wherein a flow of process gas is sent during the treatment stage at a tangent to the surface to be processed.

4. Method according to any one of the claims from 1 to 3 wherein said cold plasma is obtained from gases chosen from the group consisting of noble gases, air, oxygen, inert gases, fluorated gases chosen from the group of fluorocarbons, on condition that said gas is not SF_6, hydrocarbons, CO_2, hydrogen, silicon, silane siloxane and organosilane compounds, chlorine, acrylate, vinylic monomers, styrenes and metals as well as blends of said gases.

5. Method according to claim 4 wherein said noble gases are chosen from helium, argon, neon, and their blends with air, oxygen or hydrogen, said inert gas being nitrogen, said fluorated gases being chosen among CF_4. WF_6, XeF_2 and CFC or their blends, and said silanes being organomethylsilanes, and more specifically hexamethyldisilane.

6. Method according to any one of the previous claims, wherein the plasma treatment stage includes the use of polymers in gaseous and liquid stage.

7. Method according to claim 1, wherein the atmospheric pressure is between 100 mbar and 2 atm.

8. Method according to any one of the previous claims, wherein the electrical power of the plasma ranges between 0.1 W/cm^2 and 50 W/cm^2.

9. Method according to any one of the previous claims, comprising a pre-exsiccation stage of the materials to be treated before the gas removal stage, wherein the gas removal stage takes place during the actual processing of the materials and relative fibres with plasma.

10. Method according to any one of the previous claims, wherein the woven, and non-woven fabrics, yarns, natural and polymeric fibres and inorganic fibres and films are maintained at a temperature lower than 70°C, preferably lower than or equal to environmental temperature, during said plasma treatment.

11. Method according to claim 7, wherein the plasma is a crown plasma produced at atmospheric pressure, with power ranging 50 W and 2 kW, frequency ranging between 1 kHz and 200 kHz, having crown doses ranging between 1 and 30 W minute/m^2 and individual treatment times between 1/100 seconds and 5/10 seconds.

12. Method according to any one of the previous claims, wherein said plasma application comprises the following stages, either individually or in any combination whatsoever:

a) removal of the layers of material closest to the surface (ETCHING);
b) surface insertion and grafting of atoms or chemical groups (GRAFTING) wherein the continuous flow of reactive components produced in the plasma facilitates their adsorption inside the surface of the material to be treated, facilitating the grafting of functional groups on the surface in question, in other words, realising chemical bonds between the reactive components in the plasma and those belonging to the surface in question;
c) deposit of a fine film, for example of a metal, polymer, biopolymer, organic or inorganic material on the surface of the material;
d) activation of the surface through the breaking of the chemical bonds, and the generation of free radicals on the surface to be used successively to form chemical bonds, among which, covalent bonds having molecules of various types, including organic molecules;
e) formation of new bonds on the surface of said materials without the application of reactive components of the plasma (cross-linking);
f) radical activation of the non-activated carbonhydrogen bond on the fibres and the consequential reaction with biodegradable organic molecules or polymers.

13. Process to increase the wettability and hydrophilic capacity of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara using the method according to any one of the claims from 1 to 12.

14. Process for increasing and/or controlling the affinity of the surface of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara to colorants or resins using the method according to any one of the claims from 1 to 12.

15. Process for cleaning the surface of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara using the method according to any one of the claims from 1 to 12, wherein the plasma is a crown plasma with air or noble gases, or a blend or air and noble gases.

16. Process of grafting or depositing polymers, organic or inorganic materials, or metals on the surface of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara using the method according to claim 1, the process comprising the following methods either individually or in combination:

- production of plasma from the substance that is to be deposited according to the process to make the surface of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara water repellent using the method according to claim 1;
- activation of the surface using a plasma according to a process for increasing and/or controlling the affinity of the surface of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films, glass and alcantara to colorants or resins using the method according to claim 1 and followed by the creation of an interaction between the substrate with the substance during the gaseous stage with or without plasma in the same processing chamber;
- operating successive cycles of the following methods a) or b) using a pulsed source: method a) activating the surface by the charge from the substance and method b) with inert gases;
- activation of the surface with plasma according to a process or increasing and/or controlling the affinity of the surface of woven and non-woven fabrics, yarns, natural and polymeric fibres, and inorganic fibres and films,

glass and alcantara to colorants or resins using the method according to claim 1, with the application of a deposit according to conventional methods.

17. Method according to claim 1, wherein the cold plasma is of crown type produced at a frequency ranging between 1 and 200 kHz.

18. Method according to claim 17, wherein the plasma is produced between two conductor electrodes or between one conductor electrode and one dielectric coated conductors or between two dielectric coated conductor electrodes.

19. Method according to claim 18, wherein the plasma is produced with gases such as air, inert gases and noble gases, including blends with the aforementioned gases.

20. Method according to claim 19, wherein the materials and the relative fibres are placed at a distance from the electrodes from 0.2 cm to 3 cm.

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EUROPEAN SEARCH REPORT

Application Number
EP 10 18 4545

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	1 December 2010	Koegler-Hoffmann, S

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X : particularly relevant if taken alone
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