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(54) SURFACE COATINGS

(57) The present invention concerns a method for depositing a halogen-free water repellent nanocoating on textile products by means of a low-pressure plasma polymerization coating process with an organosilane monomer, wherein the halogen-free water repellent nanocoating is resistant against washing, laundering and dry cleaning.

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Description

Technical field

[0001] The present invention relates to a low pressure plasma polymerization process applied to textile products, in particular to methods, systems and uses to apply a durable water repellent polymer nanocoating to a textile product as well as the products obtainable by such methods and systems. The textile products can be sheets or can be semi-finished or finished textile products.

Background of the invention

[0002] Durable water repellent (DWR) coatings on textile products are nowadays widespread. The DWR market for Outdoor textiles is a volume market with a turnover of 10 billion EURO in 2011 in Europe only, and garments and accessories for outdoor comprise 52% of this market. The DWR section is about 22%, or 2.2 billion EURO.

[0003] Textile products have a certain degree of breathability. DWR coatings which are applied on textile for garments generally need to maintain the breathability properties of the textile product. Hereto, the DWR coating thickness is usually kept in the micrometer range. The applicants have discovered that when maintaining the thickness in nanometer range, optimal breathability is ensured. Typically, coatings of less than 1000 nm are applied, and preferably even less than 500 nm.

[0004] Textile products can also be subject to repeated washing. Thereby, a coating applied to a textile product is also subjected to washing. Herein, the coating is subjected to a combination of abrasion and extensive rinsing with water and detergent. Consequently, a coating of a textile product with good washability properties is a coating which is resistant against abrasion and rinsing with water and detergent, thereby maintaining its DWR properties after (repeated) washing.

[0005] Coatings to textile products with good washability properties generally need to have a minimal thickness and need to be well-adhered to the textile product. Typically, a thickness of at least 20 nm is desirable, and preferably of at least 50 nm. Furthermore, in particular to have a good adherence, it is desirable that the coating impregnates the yarns and the fibres of the textile product as deep as possible.

[0006] Polymer coatings applied to a textile product by a low pressure plasma polymerization process typically have a thickness in the range between 20 nm and 1000 nm, more preferably between 50 nm and 500 nm. In a low pressure plasma polymerization process, a monomer is introduced into a vacuum chamber at low pressure and a plasma is ignited, thereby bringing the monomers in a plasma phase and allowing the excited monomers to polymerize directly onto the surfaces of the textile, in particular on the surfaces of the individual fibres and yarns of the textile. Furthermore, the inventors have found that a degree of impregnation of the textile product by the coating can be achieved which is much more difficult or even impossible to achieve with other types of coating processes such as wet (chemical) coating processes or vapour deposition process, including graft processes. Such process are clearly even less suited for application of a DWR coating on 3D-products, finished textile products after final confection, such as jackets, trousers and gloves.

[0007] DWR coatings make all kinds of textiles water repellent, and often impart oil repellent properties as well for stain repellency. Nowadays, the best performance in repellency is obtained by using fluorine-based or halogen-based chemistries applied to textile products. The coating can hereby be applied by a low pressure plasma polymerization process.

[0008] Historically, DWR technology using long-chain perfluoroalkyl chains has been the primary chemistry of choice because of their highest levels of water, oil and stain repellency. Typical monomers used in the polymerization processes are monomers which lead to a high fluor content per surface area, such as perfluoro-alkyl acids (PFAAs) or other alkyl acids with a high amount of fluor, which may comprise long perfluoro-chains of up to 8 and more carbon atoms.

[0009] Document EP0988412A1 for instance discloses a method for coating a surface by exposing the surface, optionally the surface of a textile product, to a plasma comprising 1H, 1H, 2H-perfluoro-1-dodecene or 1H, 1H, 2H, 2H-heptadecafluorodecyl acrylate.

[0010] Document WO2014056968A1 discloses a method and apparatus for applying a surface coating on, for example, a sheet of fabric and further provides a plasma chamber for coating a sheet of fabric, e.g. a textile material, with a polymer layer, the plasma chamber comprising a plurality of specifically arranged electrode layers. Preferred monomers include acrylates and methacrylates having perfluorocarbon backbones comprising two to six carbon atoms, such as 1H, 1H, 2H, 2H-Perfluorooctyl methacrylate or 1H, 1H, 2H, 2H-Perfluorooctyl acrylate.

[0011] However, during production of the preferential monomers, harmful side-products, such as perfluoro-octanoic acids (PFOAs) and perfluoro-octane sulfonates (PFOS's) are produced, which are found to be persistent in the environment, in animals and in humans. When subsequently using the thusly obtained monomers in a plasma polymerization process, these side-products are also deposited onto the textile, thereby leading to a health and environmental hazard.

[0012] Since 2015 it is even forbidden in many countries to produce products that contain PFOS and large quantities of PFOA. This has started a shift from long-chain perfluoroalkyl based DWRs to short-chain perfluoroalkyl based DWRs, which have 6 or less carbon atoms in the perfluoroalkyl chain.

[0013] However, these short-chain monomers and polymers still contain a fair amount of fluorine, a halogen, in order to obtain a DWR coating with the highest performance next to long-chain perfluoroalkyl based DWRs. As the effects of long-term exposure of humans and wildlife to halogen-containing chemicals is not yet fully known, a health hazard exists even for short-chain perhalo-alkyl based DWR coatings.

[0014] The present invention provides a solution to the problem of providing DWR coatings for textile products, with good washability properties which ensure that no halogen-containing, such as fluorine-containing, (by-)products, and in particular no PFOS's or PFOAs, are produced in the full process of providing a textile product with a DWR coating.

[0015] Thereto, the present invention relates to a method for coating a textile product with a DWR polymer nanocoating by a low pressure plasma polymerization process, wherein the coating is completely halogen-free. The method thereby advantageously combines a halogen-free "health" aspect with a low environmental footprint of the used technology.

[0016] The halogen-free water repellent nanocoatings of the present invention are deposited by means of low pressure plasma polymerization, a technology that is known for its "dry and clean" aspect, since no water is consumed, a reduced amount of chemicals is used, and no drying and curing is needed, hence a highly reduced energy consumption and CO_2-emission.

[0017] The halogen-free low pressure plasma polymerization coatings of the present invention offer a solution to coating of both textiles and fabrics on rolls (2D), and finished textile products (3D), since the technology doesn't require a continuous line to dip, dry and cure.

[0018] The method of the present invention provides a number of advantages over prior art methods with regards to the obtainable coating:

- Halogen-free water repellent coatings, hence no health risks due to use of halogens like fluorine;
- Nanometre thick coatings - nanocoatings - which maintain the breathability of the fabric and make them suited for application onto textiles;
- Method with lowest environmental footprint;
- Excellent resistance against washing, laundering and dry cleaning;
- Applicable onto textiles on roll (2D) and onto finished textile products (3D);
- No toxic by-products are formed upon coating;
- No change in handfeel or colour of the fabrics.

Summary of the invention

[0019] The present application solves the abovementioned technical problems by providing a method for depositing a halogen-free durable water repellent nanocoating onto a textile product by means of a low pressure plasma polymerization process with an organosilane monomer. The thusly obtained coating thereby provides the textile product with a water repellency which is maintained upon washing, laundering and dry cleaning. Furthermore, the breathability of the fabric is maintained after application of the coating.

[0020] The present inventors have found that the properties of the coatings on textile products obtained by the use of halogen-free organosilane monomers in the method of the present invention comprise DWR and washability properties comparable to prior art halogen-containing coatings. Furthermore, the resulting coatings do not contain halogens and no halogen-containing products, by-products or rest products are produced.

[0021] In a second aspect, the present invention relates to a method for improving the quality of halogen-free coatings, by applying a post-treatment to a substrate coated with a nanocoating obtained by means of a low pressure plasma polymerization process with an organosilane monomer. Hereby, the substrate preferably comprises or is a textile product. The post-treatment comprises the step of exposing the coated substrate, which is obtained by coating a substrate by means of a low pressure plasma polymerization process with an organosilane monomer, to a low pressure post-treatment gas. Hereby, in an embodiment, no plasma is ignited, i.e. the post-treatment gas essentially consists of neutral gas molecules. However, in a preferred embodiment, the post-treatment gas is provided at a post-treatment power which is comparable to a plasma polymerization power, i.e. the power which is applied during the plasma polymerization process to ignite the monomers, and a plasma is thus ignited during the post-treatment. More preferably, the post-treatment power is at least 10% of the plasma polymerization power and/or at most 190% of the plasma polymerization power. The inventors have found that the post-treatment may improve the strength and durability of the coating. Without wishing to be bound by theory, it is believed that the post-treatment by a substantially neutral gas and preferably at appliance of a low power, promotes cross-linking in the deposited polymer coating.

[0022] Alternatively or additionally, the inventors have found that the above-mentioned post-treatment step for a substrate coated with a nanocoating obtained by means of low pressure plasma polymerization process with an organosilane monomer, also improves the coating properties for other types of substrates, in particular for substrates comprising smooth surfaces, e.g. metallic and/or organic substrates with smooth surfaces, such as electronic components.

Brief description of the figures

[0023]

Figure 1 shows the spray test results and **Figure 2** shows the water contact angle measurements, for the different pre-treatments, before and after washing.

Figure 3 shows the spray test quotations for varying additional gas mixtures, as function of number of washing cycles.

Figure 4 shows the water contact angles for varying additional gas mixtures, as function of number of washing cycles.

Detailed description of the invention

[0024] As used herein, the following terms have the following meanings:

"A", "an", and "the" as used herein refers to both singular and plural referents unless the context clearly dictates otherwise. By way of example, "a compartment" refers to one or more than one compartment.

"About" as used herein referring to a measurable value such as a parameter, an amount, a temporal duration, and the like, is meant to encompass variations of +/-20% or less, preferably +/-10% or less, more preferably +/-5% or less, even more preferably +/-1% or less, and still more preferably +/-0.1% or less of and from the specified value, in so far such variations are appropriate to perform in the disclosed invention. However, it is to be understood that the value to which the modifier "about" refers is itself also specifically disclosed.

"Comprise," "comprising," and "comprises" and "comprised of" as used herein are synonymous with "include", "including", "includes" or "contain", "containing", "contains" and are inclusive or open-ended terms that specifies the presence of what follows e.g. component and do not exclude or preclude the presence of additional, non-recited components, features, elements, members or steps, known in the art or disclosed therein.

[0025] The recitation of numerical ranges by endpoints includes all numbers and fractions subsumed within that range, as well as the recited endpoints.

[0026] The expression "% by weight" (weight percent), here and throughout the description unless otherwise defined, refers to the relative weight of the respective component based on the overall weight of the formulation.

[0027] The terms "outgassing" and "degassing", as used herein, are used interchangeably and refer to a process of removing gasses and liquids, more in particular within the context of this document, removing contaminants, gasses and liquids from items of footwear or parts thereof, in order to ensure a good adhesion between coating and at least part and preferably all, of the internal surface of the item. The terms "fabric" and "textile" or "textile product", as used herein, are used interchangeably to any material made of interlacing fibres, woven or nonwoven, which can be made by weaving, knitting, crocheting, knotting, felting or other type of bonding.

[0028] The present application solves the abovementioned technical problems by providing a method for depositing a halogen-free DWR nanocoating onto textiles, by means of low pressure plasma polymerization, wherein the water repellency is maintained upon washing and laundering, and wherein the breathability of the fabric is not changed by application of the coating.

[0029] It is a first aspect of the present invention to provide a method to obtain a halogen-free water repellent nanocoating on textiles, whereby the coating is deposited by means of low pressure plasma polymerization, whereby the coating is resistant against repeated washing, laundering and dry cleaning, whereby the coating doesn't significantly change the breathability of the fabric, measured in terms of air permeability and water vapour permeability.

[0030] Preferably, the textile is a sheet of textile, e.g. wound to a roll (2D).

[0031] Alternatively, the textile is a finished textile product, confectioned into its final design, including zippers, buttons, pockets, etc (3D). In another alternative, the textile is a semi-finished textile product, confectioned into an semi-finished design, such as a shirt containing seams, but not yet any buttons.

[0032] Preferably, the fabric or textile is one of a woven, nonwoven, knitted, film, foil or membrane fabric, or a laminate of several layers of the foregoing.

[0033] Woven, nonwoven and knitted fabrics may have smooth surfaces or textured surfaces, in the cases of a pile weave or a pile knit for example.

[0034] Preferably the fabric comprises a synthetic material, a natural material or a blend.

[0035] Examples of materials include but are not limited to:

Synthetic: polypropylene (PP), polyethylene (PE), polyvinylchloride (PVC), polystyrene (PS), polyphenylene sulfide (PPS), polyacrylonitrile (PAN), polyurethane (PUR), polyurea, polytetrafluoroethylene (PTFE) and expanded polytetrafluoroethylene (ePTFE), polyester (PES) - such as polyethylene terephthalate (PET), recycled PET and polybutylene terephthalate (PBT), polyamide (PA) - such as PA6, PA66, and PA12, polyaramide, elastane (polyurethane-polyurea copolymer).

[0036] Natural and man-made: cotton, cellulose, cellulose acetate, silk, wool, etc.

Blends: cotton/PES 50:50, PES/carbon 99:1, recycled PES/elastane 92:8, etc.

[0037] Woven and knitted fabrics may have a thickness of from 50 μm to 10 mm. Nonwoven fabrics may have a thickness of from 5 μm to 10 mm. Film or foil fabrics may have a thickness of from 20 μm to 1 mm. Membrane fabrics and laminates may have a thickness of from 20 μm to 20 mm.

[0038] In an embodiment, the low pressure plasma polymerization is a low pressure plasma polymerization of an organosilane precursor monomer which is introduced into a plasma chamber, said organosilane being of the formula (I), (II), (III), (IV) or (V).

$$Y_1\text{-X-}Y_2 \qquad \text{(I)}$$

or

$$\text{-[Si(CH}_3)_q\text{(H)}_{2\text{-}q}\text{-X-]}_n\text{-} \qquad \text{(II)}$$

or

$$CH_2 = C(R_1)\text{-Si}(R_2)(R_3)\text{-}R_4 \qquad \text{(III)}$$

or

$$R_5\text{-Si}(R_6)(R_7)\text{-}R_8 \qquad \text{(IV)}$$

or

$$CH_2{=}C(R_9)C(O)\text{-O-}(CH_2)_p\text{-Si}(R_{10})(R_{11})\text{-}R_{12} \qquad \text{(V)}$$

- wherein for Formula (I) X is O or NH, Y_1 is -Si(Y_3)(Y_4)Y_5 and Y_2 is Si($Y_{3'}$)($Y_{4'}$)$Y_{5'}$ wherein Y_3, Y_4, Y_5, $Y_{3'}$, $Y_{4'}$, and $Y_{5'}$ are each independently H or an alkyl group of up to 10 carbon atoms; wherein at most one of Y_3, Y_4 and Y_5 is hydrogen, at most one of $Y_{3'}$, Y_4, and $Y_{5'}$ is hydrogen; and the total number of carbon atoms is not more than 20.
- wherein Formula (II) is cyclic where n is 2 to 10, wherein q is 0 to 2 and wherein the total number of carbon atoms is not more than 20.
- wherein for Formula (III) R_1 is H or an alkyl group, e.g. -CH_3, and wherein R_1, R_2 and R_3 are each independently H, an alkyl group of up to 10 carbon atoms or an alkoxy group -O-Z, wherein Z is preferably -C_tH_{2t+1}, wherein t is 1 to 10.
- wherein for Formula (IV) R_5 is H or an alkyl group, e.g. -CH_3, and wherein R_6, R_7 and R_8 are each independently H, an alkyl group of up to 10 carbon atoms or an alkoxy group -O-Z, wherein Z is preferably -C_tH_{2t+1}, wherein t is 1 to 10.
- wherein for Formula (V) R_9 is H or an alkyl group, e.g. -CH_3, wherein p is from 0 to 10, and wherein P_{10}, R_{11} and R_{12} are each independently H, an alkyl group of up to 10 carbon atoms or an alkoxy group -O-Z, wherein Z is preferably -C_tH_{2t+1}, wherein t is 1 to 10.

[0039] The alkyl groups may be straight or branched-chain but straight groups are preferred. Such alkyl groups are aptly methyl or ethyl groups of which methyl is preferred. Aptly all of Y_3, Y_4, Y_5, $Y_{3'}$, $Y_{4'}$ or $Y_{5'}$ are alkyl groups.

[0040] The alkoxy groups may be straight, branched-chain or cyclic but straight groups are preferred. Such alkoxy groups are aptly methoxy or ethoxy groups.

[0041] The monomer of Formula I may be one containing six methyl groups. Aptly the monomer of Formula I is hexamethyldisiloxane. Aptly the monomer of Formula I is hexamethyldisilazane.

[0042] The monomer of Formula II may be one wherein n is 3, or n is 4, or n is 5, or n is 6. Aptly the monomer of

Formula II is octamethylcyclotetrasiloxane. Aptly the monomer of Formula II is hexamethylcyclotrisilazane.

[0043] The monomer of Formula V may be one wherein p is 2 and wherein each of R10, R11 and R12 are an alkoxy group, e.g. methoxy. Aptly the monomer of Formula V is 3-(trimethoxysilyl)propyl methacrylate. Aptly the monomer of Formula V is 3-(trimethoxysilyl)propyl acrylate.

[0044] Preferably, the liquid monomer is transported to the plasma chamber without the use of a carrier gas. However, in some embodiments, an additional gas may be used as carrier gas to introduce the organosilane precursor monomer into the plasma chamber.

[0045] Preferably the organosilane monomer precursor is supplied as a liquid monomer which is subsequently vaporized and transported to the plasma chamber in its vaporized form. Preferably the vaporized monomer is transported to the plasma chamber without the use of a carrier gas. Alternatively, if necessary, the liquid monomer supply system uses a carrier gas to transport the vaporized organosilane monomer precursor into the plasma chamber.

[0046] Preferably, when a carrier gas is used, the carrier gas is selected from H_2, N_2, O_2, N_2O, CH_4, He or Ar, and/or any mixture of these gases. In one preferred process, a single carrier gas is used. This is most preferably O_2, He, or Ar.

[0047] Preferably, when a carrier gas is used, the amount of carrier gas is about 5 % to about 1500 % carrier gas based on the flow of monomer, preferably about 10 % to about 1000 % additional gas, more preferably 20 % to 750 %, for example 25 % to 500 %, such as 500, 450, 400, 350, 300, 250, 200, 175, 150, 125, 100, 90, 80, 75, 70, 60, 50, 40, 35, 30, or 25 % carrier gas.

[0048] In other embodiments, an additional gas may be used as a functional gas. A functional gas is defined as a gas that contributes to the low pressure plasma polymerization reaction in terms of striking the plasma to ignite the plasma, or in terms of influencing the low pressure plasma polymerization reaction to realize coatings with a better performance.

[0049] The additional functional gas is preferably introduced into the chamber through a separate supply line, coming from e.g. the gas bottle, and hereby is not used as a carrier gas to introduce monomer vapour into the plasma chamber.

[0050] In an embodiment, the additional functional gas may be introduced into the plasma chamber together with the monomer precursor vapour via the same plasma chamber inlet or inlets, whereby the additional functional gas supply line and the liquid monomer supply lines come together right before the chamber inlet or inlets, and are thus introduced together in the plasma chamber. Such embodiments allow to control the relative amounts of monomer and additional functional gas to a very accurate degree.

[0051] In another embodiment, the monomer and the additional functional gas supply lines stay separated and one or more separate additional gas inlets and one or more separate monomer precursor inlets are foreseen in the chamber.

[0052] In another embodiment, the additional gas is both a carrier gas and a functional gas.

[0053] In an embodiment, the organosilane precursor monomer may be used to strike the plasma without any additional gas being present in the chamber.

[0054] In some embodiments, the organosilane precursor monomer comprises a carbon-carbon double bond. Monomers having a carbon-carbon double bond may not require an additional gas to ignite the plasma and to start the polymerisation. In such embodiments, the organosilane precursor monomer may be used to strike the plasma without any additional gas being present in the chamber.

[0055] In other embodiments, one or more additional gases may be introduced into the plasma chamber containing the organosilane precursor monomer to strike and ignite a stable plasma, and are therefore seen as functional gasses.

[0056] In prior art methods wherein the monomer typically comprises long-chain perfluoro-alkyl chains, fragmentation of the perfluoro-alkyl chain is an unwanted phenomenon as it leads to a decrease of water-repellency. Surprisingly, specifically for the organosilane monomers of the present invention, controlled fragmentation can improve the water repellency, and especially the washability properties of the resulting coating.

[0057] In a preferred embodiment, the applicants have surprisingly found that an additional gas, or a mixture of additional gases, may be used to generate more fragmentation of the monomer in a controlled fashion, which leads to a more cross-linked, more dense polymer, which provides better water repellency properties, and better resistance against washing, laundering and dry cleaning. The additional gas or gas mixture may comprise a carrier gas, a functional gas and/or a functional carrier gas.

[0058] Preferably, the additional gas is selected from H_2, N_2, O_2, N_2O, CH_4, He or Ar, and/or any mixture of these gases. In one preferred process, a single carrier gas is used. This is most preferably O_2 or Ar. In another preferred process, a mixture of a reactive and an inert gas is used. This is most preferably O_2 and Ar.

[0059] Preferably the amount of additional gas used as functional gas together with the organosilane monomer precursor is about 5 % to about 50 % additional gas based on the flow of monomer, preferably about 5 % to about 40 % additional gas, such as 40, 35, 30, 25, 20, 15, 10, or 5 % additional gas.

[0060] Preferably, when two or more additional gases are used, the total amount of additional gases, used together with the organosilane monomer precursor is about 5 % to about 50 % additional gases based on the flow of monomer, preferably about 5 % to about 40 % additional gases, such as 40, 35, 30, 25, 20, 15, 10, or 5 % additional gases.

[0061] Preferable, when two additional gases are used, the amount of additional gas 1 is about 5 % to 95 % of the total amount of additional gases, more preferably 10 % to 90 %, for example 15 % to 85 %, such as 20 % to 80 %, e.g.

80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, or 20 %.

[0062] Preferable, when two additional gases are used, the amount of additional gas 2 is about 5 % to 95 % of the total amount of additional gases, more preferably 10 % to 90 %, for example 15 % to 85 %, such as 20 % to 80 %, e.g. 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, or 20 %.

[0063] In order to perform the low pressure plasma polymerization step, the plasma chamber is evacuated, preferably to a set low base pressure, after the substrates to be coated have been placed in the plasma chamber and the door has been closed. Next, one or more monomer inlets are opened to allow a constant flow of monomer, optionally together with a constant flow of additional gas, to enter the plasma chamber.

[0064] Upon stabilization of the monomer, optionally combined with an additional gas, inside the plasma chamber to a set work pressure in the plasma chamber, a power is applied to the radiofrequency electrode or electrodes to generate an electromagnetic field. A plasma is struck, and the monomer molecules become activated. The substrates or products in the plasma chamber act as an initiation promoter or facilitator for the initiation of the plasma polymerization reaction, which will start upon contact of the activated monomer molecules, and will continue as long as there are activated monomer molecules present in the plasma chamber. During the plasma polymerization process, there is a constant flow of fresh monomer, optionally combined with an additional gas, into the plasma chamber to keep the polymerization going.

[0065] Once a set plasma polymerization duration has been reached, the power applied to the radiofrequency electrode or electrodes is turned off, and the chamber is brought back to atmospheric pressure to allow removal of the treated products from the chamber. Optionally a post-treatment process as disclosed in this document is performed after the set plasma polymerization duration is reached, and before the chamber is brought back to atmospheric pressure.

[0066] A halogen-free water repellent nanocoating is deposited using a method according the present invention. This coating is also resistant against washing, laundering and dry cleaning, and doesn't have a negative impact on the breathability of the textile.

[0067] The plasma polymerization time (3D) or speed (2D roll-to-roll) needed to deposit this coating of the present invention, using the method and monomers of the present invention, is determined in function of the design of the substrate and the chamber, on the type of substrate that is coated (thickness, openness, polymer type), and on the performance that is required in terms of resistance against washing - a ski jacket is washed less frequently than a jogging shirt.

[0068] Preferably, for coating 3D items (e.g. finished garments), the plasma polymerization time, expressed in the time that a power is applied to the electrodes, is from about 1 minute to about 30 minutes, more preferably from about 2 minutes to about 25 minutes, such as from about 5 minutes to about 20 minutes, such as 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, or 5 minutes.

[0069] The plasma polymerization may be continuous plasma polymerization. The plasma polymerization may be pulsed wave polymerization. Whether a continuous plasma or a pulsed plasma is used for the polymerization, depends on the chemistry used and on the volume and design of the plasma chamber.

[0070] Preferably, in a 1836 litre plasma chamber, designed with 4 vertical slots to contain for example 8 to 12 jackets, the applied power for the coating process, when applied in continuous wave mode, is approximately 5 to 5000 W, more preferably approximately 10 to 2500 W, even more preferably approximately, say 15 to 2000W, for example 20 to 1500 W, say 25 to 1000 W, say 30 to 750 W, say 35 to 500 W, say 500, 475, 450, 425, 400, 375, 350, 325, 300, 275, 250, 225, 200, 190, 180, 175, 170, 160, 150, 140, 130, 125, 120, 110, 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, or 35 W. In a preferred embodiment, the applied power density (i.e. power per unit chamber volume) for the coating process, when applied in continuous wave mode, is equivalent to the above mentioned ranges, i.e. the applied power density is approximately 5 to 5000 W, more preferably approximately 10 to 2500 W, even more preferably approximately, say 15 to 2000W, for example 20 to 1500 W, say 25 to 1000 W, say 30 to 750 W, say 35 to 500 W, say 500, 475, 450, 425, 400, 375, 350, 325, 300, 275, 250, 225, 200, 190, 180, 175, 170, 160, 150, 140, 130, 125, 120, 110, 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, or 35 W, divided by 1836 litre.

[0071] Preferably, in a 1836 litre plasma chamber, designed with 4 vertical slots to contain for example 8 to 12 jackets, the applied power for the coating process, when applied in pulsed wave mode, is approximately 5 to 5000 W, more preferably approximately 10 to 2500 W, even more preferably approximately, say 20 to 1500W, for example 30 to 1000 W, say 50 to 900 W, say 75 to 800 W, say 100 to 750 W, say 750, 725, 700, 675, 650, 625, 600, 575, 550, 525, 500, 475, 450, 425, 400, 375, 350, 325, 300, 275, 250, 225, 200, 190, 180, 175, 170, 160, 150, 140, 130, 125, 120, 110, or 100 W. In a preferred embodiment, the applied power density (i.e. power per unit chamber volume) for the coating process, when applied in pulsed wave mode, is equivalent to the above mentioned ranges, i.e. the applied power density is approximately 5 to 5000 W, more preferably approximately 10 to 2500 W, even more preferably approximately, say 20 to 1500W, for example 30 to 1000 W, say 50 to 900 W, say 75 to 800 W, say 100 to 750 W, say 750, 725, 700, 675, 650, 625, 600, 575, 550, 525, 500, 475, 450, 425, 400, 375, 350, 325, 300, 275, 250, 225, 200, 190, 180, 175, 170, 160, 150, 140, 130, 125, 120, 110, or 100 W, divided by 1836 litre.

[0072] Preferably, when in pulsed power mode, the pulse repetition frequency may be from 100 Hz to 10 kHz having a duty cycle from approximately 0.05 to 50 %, with the optimum parameters being dependent on the monomer used.

[0073] Preferably, the plasma chamber comprises one or more electrode layers, which may be radiofrequency electrode layers or ground electrode layers, to generate an electromagnetic field.

[0074] Preferably, the or each radiofrequency electrode generates a high frequency electric field at frequencies of from 20 kHz to 2.45 GHz, more preferably of from 40 kHz to 13.56 MHz, with 13.56 MHz being preferred.

[0075] Preferably, the operating pressure for the coating step is approximately 10 to 500 mTorr, preferably approximately 15 to 200 mTorr, more preferably approximately 20 to 150 mTorr, say 30 to 100 mTorr, say less than 100, 90, 80, 70, 60, 50, 40, 30 mTorr. For example, in a 1836 litre plasma chamber, used to apply a coating on 8 to 12 jackets in one single batch, such pressure ranges are particularly preferred.

[0076] Preferably, when coating textiles and fabrics on rolls (2D), during the coating process, the system runs at a speed of 0.1 m/min up to 20 m/min, for example 0.5 m/min to 15 m/min, such as 1 m/min to 10 m/min, say less than 9, 8, 7, 6 m/min, most preferably 1 to 5 m/min.

[0077] Preferably, when applied in continuous wave mode in a 12000 l chamber, used to coat rolls of textile up to 1.8 m wide, the applied power is approximately 10 to 5000 W, more preferably approximately 20 to 4000 W, even more preferably approximately, say 25 to 3000 W, even further preferably, for example 30 to 2000 W, preferably still, for example 40 to 1500 W, and even further preferably from 50 to 1000, 950, 900, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 250, 200, 175, 150, 125, 100, 90, 80, 75, 70, 60, or 50 W. In a preferred embodiment, the applied power density (i.e. power per unit chamber volume) for the coating process, when applied in continuous wave mode, is equivalent to the above mentioned ranges, i.e. the applied power density is approximately 10 to 5000 W, more preferably approximately 20 to 4000 W, even more preferably approximately, say 25 to 3000 W, even further preferably, for example 30 to 2000 W, preferably still, for example 40 to 1500 W, and even further preferably from 50 to 1000, 950, 900, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 250, 200, 175, 150, 125, 100, 90, 80, 75, 70, 60, or 50 W, divided by 12000 litre.

[0078] Preferably, when applied in pulsed wave mode in a 12000 l chamber, used to coat rolls of textile up to 1.8 m wide, the applied power is approximately 10 to 5000 W, more preferably approximately 25 to 4000 W, even more preferably approximately 50 to 3500 W, preferably, for example 75 to 3000 W, preferably still, for example 100 to 2500 W, and even further preferably from 150 to 2000, 1900, 1800, 1750, 1700, 1600, 1500, 1400, 1300, 1250, 1200, 1100, 1000, 950, 900, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 250, 200, or 175 W. In a preferred embodiment, the applied power density (i.e. power per unit chamber volume) for the coating process, when applied in pulsed wave mode, is equivalent to the above mentioned ranges, i.e. the applied power density is approximately 10 to 5000 W, more preferably approximately 25 to 4000 W, even more preferably approximately 50 to 3500 W, preferably, for example 75 to 3000 W, preferably still, for example 100 to 2500 W, and even further preferably from 150 to 2000, 1900, 1800, 1750, 1700, 1600, 1500, 1400, 1300, 1250, 1200, 1100, 1000, 950, 900, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 250, 200, or 175 W, divided by 12000 litre.

[0079] Preferably, when in pulsed power mode, the pulse repetition frequency may be from 100 Hz to 10 kHz having a duty cycle from approximately 0.05 to 50 %, with the optimum parameters being dependent on the monomer used.

[0080] Preferably, the plasma chamber comprises one or more electrode layers, which may be radiofrequency electrode layers or ground electrode layers, to generate an electromagnetic field.

[0081] Preferably, the or each radiofrequency electrode generates a high frequency electric field at frequencies of from 20 kHz to 2.45 GHz, more preferably of from 40 kHz to 13.56 MHz, with 13.56 MHz being preferred.

[0082] In a 12000 litre plasma chamber, used to apply a coating on rolls of textile up to 1.8 m wide, the operating pressure for the coating step is approximately 10 to 500 mTorr, preferably approximately 15 to 200 mTorr, more preferably approximately 20 to 150 mTorr, say 25 to 100 mTorr, say less than 100, 90, 80, 75, 70, 60, 50, 40, 30, or 25 mTorr.

[0083] In a further embodiment, an outgassing and/or a pre-treatment step may be performed before the low pressure plasma polymerization process. Preferably, the outgassing is performed in the low pressure plasma chamber. Preferably, the pre-treatment is a low pressure plasma process.

[0084] An outgassing may be performed prior to starting the first process step. The applicants have surprisingly discovered that an outgassing allows the deposition of a more uniform coating, that has a better performance in terms of water repellency and resistance against washing. This is because the outgassing removes not only contaminants and moisture from the surface and the plasma chamber, but also from the internal surfaces and deeper lying areas of the textile, which is not the case without outgassing.

[0085] In an embodiment to coat garments (3D), said textile product or products are degassed to a degassing level of at most 50 mTorr, more preferably at most 20 mTorr, even more preferably at most 10 mTorr. Additionally or alternatively, said garment(s) are degassed in a vacuum chamber until said vacuum chamber comprises a degassing level of at most 100 mTorr, more preferably at most 50 mTorr, such as 40 mTorr or less. Note that the degassing level of the vacuum chamber may depend on the load, i.e. on the number and design of the textile products placed inside the chamber.

[0086] In an embodiment to coat textiles and fabrics on rolls (2D), the roll of fabric is degassed to a degassing level of at most 50 mTorr, more preferably at most 40 mTorr, even more preferably at most 25 mTorr. Additionally or alternatively, said roll of fabric is degassed in a vacuum chamber until said vacuum chamber comprises a degassing level of at most

100 mTorr, more preferably at most 50 mTorr, such as 40 mTorr or less. Note that the degassing level of the vacuum chamber may depend on the load, i.c. on the fabric structure, polymer, thickness, and openness, and on the roll dimensions of the roll of fabric placed inside the chamber.

[0087] In order to determine the degassing level of a finished fabric (3D) or a roll of fabric (2D), the pressure increase in a vacuum chamber due to gases released from the textile needs to be determined. Thereto, the item is positioned in a vacuum chamber, e.g. a plasma chamber, which is pumped down to a degassing pressure $P_{degassing}$, which is less than 200 mTorr, preferably less than 100 mTorr, such as less than 50 mTorr, and next the inlets and outlets of the vacuum chamber are closed off. After a preset time of 60 seconds, the pressure increase, ΔP, inside the chamber is measured. The degassing level of the textile is then given by the pressure increase, ΔP, minus the whistling leak pressure of the vacuum chamber at the degassing pressure $P_{degassing}$. Optionally, if more than one finished textile product (3D) is positioned inside the vacuum chamber, the degassing level of one textile product is given by the pressure increase, ΔP, minus the whistling leak pressure of the vacuum chamber at the degassing pressure $P_{degassing}$, divided by the number of substrates in the vacuum chamber. Hereby, the whistling leak pressure of the vacuum chamber at the degassing pressure $P_{degassing}$ is determined by repeating the same procedure for an empty chamber with all electronic substrates removed from the vacuum chamber - pumping down to the same degassing pressure $P_{degassing}$, closing off all inlets and outlets of the vacuum chamber and measuring the pressure increase after the same preset time as for the loaded chamber, i.e. 60 seconds.

[0088] In order to determine the degassing level of a vacuum chamber which is loaded with a number of textile products, the pressure increase in the vacuum chamber due to gases released from the textile products needs to be determined. Thereto, the textile products are positioned in a vacuum chamber, e.g. a plasma chamber, which is pumped down to a degassing pressure $P_{degassing}$, which is less than 200 mTorr, preferably less than 100 mTorr, such as less than 50 mTorr, and next the inlets and outlets of the vacuum chamber are closed off. After a preset time of 60 seconds, the pressure increase, ΔP, inside the chamber is measured. The degassing level of the chamber is then given by the pressure increase, ΔP, minus the whistling leak pressure of the vacuum chamber at the degassing pressure $P_{degassing}$. Hereby, the whistling leak pressure of the vacuum chamber at the degassing pressure $P_{degassing}$ is determined by repeating the same procedure for an empty chamber with all textile products removed from the vacuum chamber - pumping down to the same degassing pressure $P_{degassing}$, closing off all inlets and outlets of the vacuum chamber and measuring the pressure increase after the same preset time as for the loaded chamber, i.e. 60 seconds.

[0089] In some embodiments, the low pressure plasma polymerization is preceded by a low pressure plasma pre-treatment step, preferably the degassing and the pre-treatment being combined in a single processing step.

[0090] A pre-treatment may be carried out before the coating polymerization step and after the outgassing step, when an outgassing step is performed. Preferably, the pre-treatment is a low pressure plasma process. Whether a low pressure plasma pre-treatment is carried out or not, depends on the cleanliness of the substrates to be coated, and on the monomer used in the low pressure plasma polymerization process as well.

[0091] The applicants have surprisingly discovered that for some monomers the performance and quality of the coating is better when no pre-treatment is carried out. For other monomers, a pre-treatment in the form of a low pressure plasma cleaning and/or activation and/or etching may be advantageous.

[0092] The best performance of the coatings is measured by water contact angle measurement according to ASTM D5946-04, spray testing according to AATCC 22-2010, or ISO 9073 - part 17 and ISO 4920, and resistance against washing. Resistance against washing, laundering and dry cleaning is typically tested by washing, laundering or dry cleaning the product or sheet, followed by a spray test or a water contact angle measurement, to follow up the spray test quotation or the water contact angle measurement as function of the number of washing/laundering/dry cleaning cycles.

[0093] In order to obtain said best performance, it is necessary that the adhesion between the coating and the substrate is sufficient, that there is an uniform coverage of the surfaces of the substrate - such as the surfaces of the yarns - and that the coating is pinhole free and water repellent.

[0094] In an embodiment, a pre-treatment step in the form of an activation and/or cleaning and/or etching step is performed before the plasma polymerization process. A pre-treatment step in the form of an activation and/or cleaning and/or etching step might be advantageous for improving the adhesion and cross-linking of the polymer coating.

[0095] When a low pressure plasma pre-treatment is performed, this pre-treatment is preferably done using reactive gases, e.g. H_2, O_2, and etching reagents such as CF_4, but also inert gases, such as Ar, N_2 or He may be used. Mixtures of the foregoing gases may be used as well.

[0096] In particularly preferred embodiments of the invention, the polymer deposition step may be performed in the presence of an additional gas, which may be the same gas (or mixture of gases) employed in the pre-treatment step, if such pre-treatment step is performed.

[0097] Preferably the pre-treatment is done with O_2, Ar, or a mixture of O_2 and Ar, of which O_2 is favoured.

[0098] Preferably, when applied in a batch process to coat finished textile products such as garments (3D), the pre-treatment is performed from 15 seconds to 15 minutes, for example from 30 seconds to 10 minutes, preferably 45 seconds to 5 minutes, e.g. 5, 4, 3, 2, or 1 minutes. The duration of the pre-treatment depends on the precursor monomer used, on the design and the materials of the substrate to be coated, on the degree of contamination on the substrate to be coated, and on the low pressure plasma equipment.

[0099] The power of the pre-treatment can be applied in continuous wave mode or in pulsed wave mode.

[0100] Preferably, when applied in continuous wave mode in a 1836 litre plasma chamber, the pre-treatment takes place at powers of 10 to 5000 W, more preferably 25 to 4000 W, even more preferably at 50 to 3000 W, say 75 to 2500 W, such as 100 to 2000 W, e.g. 2000, 1900, 1800, 1750, 1700, 1600, 1500, 1400, 1300, 1250, 1200, 1100, 1000, 950, 900, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 250, 200, 175, 150, 125, or 100 W. In plasma chambers of other volumes, a power density equivalent to the above ranges for a 1836 litre plasma chamber is preferably used.

[0101] Preferably, when applied in pulsed wave mode in a 1836 litre plasma chamber, the pre-treatment takes place at a power of 10 to 5000 W, more preferably 25 to 4000 W, even more preferably at 50 to 3000 W, say 75 to 2500 W, such as 100 to 2000 W, e.g. 2000, 1900, 1800, 1750, 1700, 1600, 1500, 1400, 1300, 1250, 1200, 1100, 1000, 950, 900, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 250, 200, 175, 150, 125, or 100 W. In plasma chambers of other volumes, a power density equivalent to the above ranges for a 1836 litre plasma chamber is preferably used.

[0102] When applied in pulsed power mode, the pulse frequency may be from 100 Hz to 10 kHz having a duty cycle from approximately 0.05 to 50 %, with the optimum parameters being dependent on the gas or gas mixture used.

[0103] The operating pressure, e.g. in a 1836 litre or a 12000 litre plasma chamber, for the pre-treatment is 10 to 500 mTorr, more preferably 15 to 250 mTorr, even more preferably 20 to 200 mTorr, say 25 to 175 mTorr, such as 30 to 150 mTorr, e.g. 150, 140, 130, 125, 120, 110, 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, or 30 mTorr.

[0104] Preferably, when applied in a roll-to-roll process to coat textiles and fabrics on rolls (2D), the activation and/or cleaning and/or etching runs at a speed from 1 to 30 m/min, for example 2 to 20 m/min, such as 3 m/min to 15 m/min, most preferably at approximately 5 to 10 m/min.

[0105] Preferably, when applied in continuous wave mode in a 12000 l chamber, the pre-treatment takes place at 25 to 10000 W, more preferably 50 to 7500 W, even more preferably at 100 to 5000 W, and further preferably 200 to 4000 W, and preferably still from 300 to 3000, such as 3000, 2900, 2800, 2750, 2700, 2600, 2500, 2400, 2300, 2250, 2200, 2100, 2000, 1900, 1800, 1750, 1700, 1600, 1500, 1400, 1300, 1250, 1200, 1100, 1000, 950, 900, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, or 300 W. In plasma chambers of other volumes, a power density equivalent to the above ranges for a 12000 litre plasma chamber is preferably used.

[0106] Preferably, when applied in pulsed wave mode in a 12000 l chamber, the pre-treatment takes place at a peak power value of 25 to 10000 W, more preferably 50 to 9000 W, even more preferably at 100 to 8000 W, and further preferably at 200 to 7500 W, and preferably still at 300 to 7000, such as 7000, 6750, 6500, 6250, 6000, 5750, 5550, 5250, 5000, 4750, 4500, 4250, 4000, 3750, 3500, 3250, 3000, 2900, 2800, 2750, 2700, 2600, 2500, 2400, 2300, 2250, 2200, 2100, 2000, 1900, 1800, 1750, 1700, 1600, 1500, 1400, 1300, 1250, 1200, 1100, 1000, 950, 900, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, or 300 W. In plasma chambers of other volumes, a power density equivalent to the above ranges for a 12000 litre plasma chamber is preferably used.

[0107] When applied in pulsed power mode, the pulse frequency may be from 100 Hz to 10 kHz having a duty cycle from approximately 0.05 to 50 %, with the optimum parameters being dependent on the gas or gas mixture used.

[0108] For systems of other dimensions, with another volume and/or electrode set-up as in the exemplary or preferred embodiments mentioned in this document, the power value, the operating pressure and the pre-treatment time can be varied in a way that the best process parameters for the pre-treatment are used, taking into account the present teaching.

[0109] When a pre-treatment is used, the polymer coating is applied in a next step, which may be carried out in the same equipment.

[0110] Preferably, the pre-treatment and the coating step are carried out in the same chamber without opening the chamber in between the steps, to avoid deposition of additional contamination from the atmosphere in between pre-treatment step and coating step.

[0111] In yet a further embodiment, a post-treatment step may be performed after the low pressure plasma polymerization process. Whether this post-treatment is performed or not depends on the polymers deposited and on the substrate design.

[0112] A post-treatment may allow to obtain a denser polymer structure, or a polymer structure with improved orientation of the functional groups. A denser polymer structure as well as an improved orientation of the functional groups contribute largely to a better performance of the coating in terms of water repellency, and more specifically in a better resistance against washing, laundering and dry cleaning.

[0113] In one embodiment, the post-treatment is a low pressure plasma process.
In another embodiment, the post-treatment is a low pressure process without ignition of a plasma.

[0114] Preferably, the post-treatment, when carried out, is performed in the same chamber as the low pressure plasma polymerization without opening the chamber in between the steps, to avoid influence from the atmosphere in between both steps.

[0115] When a post-treatment is performed as a low pressure plasma process, this post-treatment is preferably done using inert gases, such as Ar, N_2 or He, but reactive gases, such as H_2, O_2, and etching reagents such as CF_4 may be used as well. Mixtures of the foregoing gases may be used as well.

[0116] Preferably the post-treatment is done with He or Ar.

[0117] Preferably, when applied in a batch process to coat finished textile products such as garments (3D), the low pressure plasma post-treatment is performed from 10 seconds to 15 minutes, for example from 15 seconds to 10 minutes, preferably 30 seconds to 7.5 minutes, e.g. 7.5, 7, 6, 5, 4, 3, 2, or 1 minutes, or 45 or 30 seconds. The duration of the post-treatment depends on the polymer deposited and on the design of the substrate.

[0118] The power of the post-treatment can be applied in continuous wave mode or in pulsed wave mode. Preferably, the average power applied during the post-treatment step is lower than the average power used during a low pressure plasma pre-treatment step, thereby preferably avoiding partial destruction of the deposited polymer coating. This is particularly preferred if the same gas or gas mixture is used during the pre-treatment step as during the post-treatment step.

[0119] Preferably, when applied in continuous wave mode in a 1836 l big plasma chamber, designed with 4 vertical slots to contain for example 8 to 12 jackets, the post-treatment takes place at 5 to 1000 W, more preferably 10 to 750 W, even more preferably at 15 to 500 W, say 20 to 250 W, such as 25 to 200 W, e.g. 200, 175, 150, 125, 100, 90, 80, 75, 70, 60, 50, 45, 40, 35, 30, or 25 W. In plasma chambers of other volumes, a power density equivalent to the above ranges for a 1836 litre plasma chamber is preferably used.

[0120] Preferably, when applied in pulsed wave mode in a 1836 l big plasma chamber, designed with 4 vertical slots to contain for example 8 to 12 jackets, the post-treatment takes place at a peak power value of 5 to 2000 W, more preferably 10 to 1500 W, even more preferably at 15 to 1000 W, say 20 to 750 W, such as 25 to 500 W, e.g. 500, 450, 400, 350, 300, 250, 200, 175, 150, 125, 100, 90, 80, 75, 70, 60, 50, 45, 40, 35, 30, or 25 W. In plasma chambers of other volumes, a power density equivalent to the above ranges for a 1836 litre plasma chamber is preferably used.

[0121] When applied in pulsed power mode, the pulse repetition frequency may be from 100 Hz to 10 kHz having a duty cycle from approximately 0.05 to 50 %, with the optimum parameters being dependent on the gas or gas mixture used.

[0122] Preferably, when applied in a roll-to-roll process to coat textile and fabric on rolls (2D), the low pressure plasma post-treatment is performed at a speed from 1 to 30 m/min, for example 2 to 20 m/min, such as 3 m/min to 15 m/min, most preferably at approximately 5 to 10 m/min. The speed of the post-treatment depends on the polymer deposited and on the design of the substrate.

[0123] The power of the post-treatment can be applied in continuous wave mode or in pulsed wave mode. Preferably, the average power is lower than the typical powers used for a low pressure plasma pre-treatment, since the deposited polymer coating must not be destroyed.

[0124] Preferably, when applied in continuous wave mode in a 12000 l chamber, the post-treatment takes place at 10 to 5000 W, more preferably 20 to 4000 W, even more preferably at 25 to 3000 W, and further preferably 50 to 2500 W, and preferably still from 75 to 2000, such as 2000, 1900, 1800, 1750, 1700, 1600, 1500, 1400, 1300, 1250, 1200, 1100, 1000, 950, 900, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 275, 250, 225, 200, 175, 150, 125, 100, 90, 80, or 75 W. In plasma chambers of other volumes, a power density equivalent to the above ranges for a 12000 litre plasma chamber is preferably used.

[0125] Preferably, when applied in pulsed wave mode in a 12000 l chamber, the post-treatment takes place at 20 to 10000 W, more preferably 25 to 7500 W, even more preferably at 50 to 5000 W, and further preferably 75 to 4000 W, and preferably still from 100 to 3000, such as 3000, 2900, 2800, 2750, 2700, 2600, 2500, 2400, 2300, 2250, 2200, 2100, 2000, 1900, 1800, 1750, 1700, 1600, 1500, 1400, 1300, 1250, 1200, 1100, 1000, 950, 900, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 275, 250, 225, 200, 175, 150, 125, or 100 W. In plasma chambers of other volumes, a power density equivalent to the above ranges for a 12000 litre plasma chamber is preferably used.

[0126] When applied in pulsed power mode, the pulse repetition frequency may be from 100 Hz to 10 kHz having a duty cycle from approximately 0.05 to 50 %, with the optimum parameters being dependent on the gas or gas mixture used.

[0127] When a post-treatment is performed as a low pressure process without ignition of a plasma, this post-treatment is preferably done using inert gases, such as Ar, N_2 or He, but reactive gases, such as H_2, O_2, and etching reagents such as CF_4 may be used as well. Mixtures of the foregoing gases may be used as well.

[0128] Preferably the post-treatment without ignition of a plasma is done with He, Ar, or O_2.

[0129] Preferably, when applied in a batch process to coat finished textile products such as garments (3D), the low pressure post-treatment without ignition of a plasma is performed from 10 seconds to 15 minutes, for example from 15 seconds to 10 minutes, preferably 30 seconds to 7.5 minutes, e.g. 7.5, 7, 6, 5, 4, 3, 2.5, 2, or 1 minutes, or 45 or 30 seconds. The duration of the post-treatment without ignition of a plasma depends on the polymer deposited and on the design of the substrate.

[0130] Preferably, when applied in a roll-to-roll process to coat textile and fabric on rolls (2D), the low pressure plasma post-treatment without ignition of a plasma is performed at a speed from 1 to 30 m/min, for example 2 to 20 m/min, such as 3 m/min to 15 m/min, most preferably at approximately 5 to 10 m/min. The speed of the post-treatment without ignition of a plasma depends on the polymer deposited and on the design of the substrate.

[0131] Preferably, the method according to the present invention includes the step of applying a low pressure plasma polymer coating having a thickness of from 50 to 1000 nm, more preferably of from 75 to 500 nm, such as 500, 475, 450, 425, 400, 375, 350, 325, 300, 275, 250, 225, 200, 175, 150, 125, 100, or 75 nm.

[0132] In the current invention, when using organosilane monomers according to any of formula (I) to formula (V), hydrophobic surfaces can be created with contact angles for water of more than 90°, even more than 100°, such as more than 110°, or more than 120°, according to ASTM D5946-04.

[0133] Preferably, the method includes applying a polymer coating having a uniformity variation of the contact angles for water of less than 10° according to ASTM D5946-04.

[0134] In the current invention, when using organosilane monomer according to any of formula (I) to formula (V), hydrophobic surfaces can be created with a spray test quotation of at least 3 or higher, such as a quotation of 4 or 5, according to AATCC 22-2010, or ISO 9073 - part 17 and ISO 4920.

[0135] The water contact angle and the spray test quotation obtained depends on the monomer used, any additional gases that may be used optionally, on the process parameters used, but also on the substrate onto which the nanocoating is deposited, e.g. roughness, complexity of design, etc.

[0136] The best performance of the coatings is measured by means of water contact angle measurement, spray test, and this before and after washing, laundering or dry cleaning.

EXAMPLES

[0137] In order that the invention may be more readily understood, it will now be described by way of the following non-limiting examples.

Example 1: Influence of pre-treatment

[0138] In order to examine the influence of a pre-treatment prior to low pressure plasma polymerization, 4 different low pressure plasma pre-treatments are carried out on a hydrophilic 100% recycled PES fabric (details in Table 2), followed by the same low pressure plasma polymerization process (Table 1). Performance has been evaluated by water contact angle measurement and spray test quotation, before and after washing. Details on the washing process are listed in Table 3.

Table 1: Process parameters in a 600 litre chamber according to Example 1

Parameter	Value
Plasma Chamber	
Dimensions	600 x 600 x 600 mm
Temperature wall	30 - 60 °C
Electrodes	RF/ground
Pre-treatment	
Details	Table 2
Coating	
Monomer	Hexamethyldisiloxane
Flow	75 - 125 sccm
Additional gas	Oxygen (O_2)
Flow (% of monomer flow)	5 - 20%
Base pressure	10 - 30 mTorr
Work pressure	20 - 75 mTorr
Power	150 - 250 W
Frequency	13.56 MHz
Frequency mode	cw

Table 2: Process parameters for pre-treatments according to Example 1

Gas	None	Ar	O2	He	N_2
Flow	-	100-300 sccm	100-300 sccm	100-300 sccm	100-300 sccm

(continued)

Gas	**None**	**Ar**	**O2**	**He**	**N_2**
Power	-	200-400 W	200-400 W	200-400 W	200-400 W
Frequency	-	13.56 MHz	13.56 MHz	13.56 MHz	13.56 MHz
Frequency mode	-	CW	CW	CW	CW
Time	-	2 - 10 min	2 - 10 min	2 - 10 min	2 - 10 min

Table 3: Details on washing procedure

Temperature	40 °C
Duration washing cycle	1h30
Detergent	66 g regular washing powder
Ballast load	2 kg PES ballast according to ISO 6330
Drying method	Line dry
Drying duration	At least 12h

[0139] Figure 1 shows the spray test results and Figure 2 shows the water contact angle measurements, for the different pre-treatments, before and after washing. It is clear from Figure 1 that only the samples coated without pre-treatment give a spray test quotation higher than 0 after 1 and 2 washing cycles. It is also clear from Figure 2 that the samples without any pre-treatment and a coating according to Table 1 give water contact angles higher than 0° after 3 washing cycles. It is concluded that for the tested monomer, no plasma pre-treatment gives the best performance in terms of resistance against washing. Prior to washing, no clear differences are noted between the pre-treatments

Example 2: Influence of additional gas

[0140] In order to investigate the influence of the additional gas used in the process, the low pressure plasma process according to Table 4 has been carried out (no pre-treatment). The additional gas or gas mixture has been varied according to the three variations in Table 5. Spray test and water contact angle have been measured before and after washing according to the washing details in Table 3.

Table 4: Process parameters in a 600 litre chamber according to Example 2

Parameter	**Value**
Plasma Chamber	
Dimensions	600 x 600 x 600 mm
Temperature wall	30 - 60 °C
Electrodes	RF/ground
Pre-treatment	
None	
Coating	
Monomer	Hexamethyldisiloxane
Flow	75 - 125 sccm
Additional gas	See Table 5
Base pressure	10 - 30 mTorr
Work pressure	20 - 75 mTorr
Power	150 - 250 W
Frequency	13.56 MHz
Frequency mode	cw

Table 5: Process parameters for additional gases according to Example 2

Gas	**O_2**	**O_2 + Ar**	**O_2 + He**
Flow (% of monomer flow)	10 %	10%+10%	10%+10%

[0141] Figure 3 shows the spray test quotations for varying additional gas mixtures, as function of number of washing cycles. Figure 4 shows the water contact angles for varying additional gas mixtures, as function of number of washing cycles. It is clear that no significant difference was noticed in terms of resistance against washing.

[0142] The conclusion is that for the monomer used in this example, a wide range of additional gas mixtures can be used.

Example 3: Influence of monomer

[0143] Different monomers allows to deposit halogen-free water repellent nanocoatings onto textiles. To this end, processes have been carried out on 2 different monomers, and afterwards the water contact angles has been measured. The coating according to Table 6 lead to a water contact angle of 128 °, and the coating according to Table 7 to a water contact angle of 92 °.

Table 6: Process parameters in a 50 litre chamber according to Example 3

Parameter	**Value**
Plasma Chamber	
Dimensions	500 x 400 x 250 mm
Temperature wall	30 - 60 °C
Electrodes	RF/ground
Pre-treatment	
None	
Coating	
Monomer	Hexamethyldisiloxane
Flow	5 - 15 sccm
Additional gas	O_2
Flow	5 - 20 % of monomer flow
Base pressure	10 - 30 mTorr
Work pressure	15 - 75 mTorr
Power	100 - 275 W
Frequency	13.56 MHz
Frequency mode	cw

Table 7: Process parameters in a 50 litre chamber according to Example 3

Parameter	**Value**
Plasma Chamber	
Dimensions	500 x 400 x 250 mm
Temperature wall	50 - 80 °C
Electrodes	RF/ground
Pre-treatment	
None	
Coating	
Monomer	3-(trimethoxysilyl)propyl methacrylate
Flow	5 - 30 sccm
Base pressure	10 - 30 mTorr
Work pressure	15 - 75 mTorr

(continued)

Coating	
Power	10 - 100 W
Frequency	13.56 MHz
Frequency mode	cw

Claims

1. Method for depositing a halogen-free durable water repellent (DWR) nanocoating onto a textile product by means of low pressure plasma polymerization process with an organosilane monomer, thereby obtaining a a DWR nanocoating resistant against repeated washing.

2. Method according to any preceding Claim wherein the organosilane monomer is an organosilane according to

   - Y_1-X-Y_2, wherein X is O or NH, Y_1 is -Si(Y_3)(Y_4)Y_5 and Y_2 is Si($Y_{3'}$)($Y_{4'}$)$Y_{5'}$ wherein Y_3, Y_4, Y_5, $Y_{3'}$, $Y_{4'}$, and $Y_{5'}$ are each independently H or an alkyl group of up to 10 carbon atoms; wherein at most one of Y_3, Y_4 and Y_5 is hydrogen, at most one of $Y_{3'}$, $Y_{4'}$ and $Y_{5'}$ is hydrogen; and the total number of carbon atoms is not more than 20;
   - -[Si(CH_3)$_q$(H)$_{2-q}$-X-]$_n$-, which is a cyclic monomer, where n is 2 to 10, wherein q is 0 to 2 and wherein the total number of carbon atoms is not more than 20;
   - CH_2 = C(R_1)-Si(R_2)(R_3)-R_4, wherein R_1 is H or an alkyl group, e.g. -CH_3, and wherein R_1, R_2 and R_3 are each independently H, an alkyl group of up to 10 carbon atoms or an alkoxy group -O-Z, wherein Z is preferably -C_tH_{2t+1}, wherein t is 1 to 10;
   - R_5-Si(R_6)(R_7)-R_8, wherein R_5 is H or an alkyl group, e.g. -CH_3, and wherein R_6, R_7 and R_8 are each independently H, an alkyl group of up to 10 carbon atoms or an alkoxy group -O-Z, wherein Z is preferably -CtH2t+1, wherein t is 1 to 10;
   - CH_2=C(R_9)C(O)-O-(CH_2)$_p$-Si(R_{10})(R_{11})-R_{12}, wherein R_9 is H or an alkyl group, e.g. -CH_3, wherein p is from 0 to 10, and wherein P_{10}, R_{11} and R_{12} are each independently H, an alkyl group of up to 10 carbon atoms or an alkoxy group -O-Z, wherein Z is preferably -C_tH_{2t+1}, wherein t is 1 to 10.

3. Method according to any preceding Claim, wherein the textile product is a 3D finished textile product after confectioning, such as a garment or accessories, treated in a batch process.

4. Method according to any preceding Claim, wherein the textile product is a fabric on a roll (2D), treated in a roll-to-roll process.

5. Method according to any preceding Claim, wherein the low pressure plasma polymerization process is preceded by an outgassing of the textile products.

6. Method according to any preceding Claim, wherein the low pressure plasma polymerization process is preceded by a low pressure plasma pre-treatment process.

7. Method according to Claim 6, wherein the low pressure plasma pre-treatment process is performed using an inert gas and/or a reactive gas.

8. Method according to any preceding Claim, wherein the low pressure plasma polymerization process is followed by a post-treatment process comprising the step of exposing the coated textile to a low pressure post-treatment gas.

9. Method according to Claim 8, wherein the post-treatment process is performed using an inert gas and/or a reactive gas.

10. Method according to claims 8 or 9, wherein the post-treatment gas is provided at a post-treatment power which is at least 10% and at most 190% of a plasma polymerization power which is applied during said low pressure plasma polymerization process to ignite the organosilane monomer.

11. Method according to any of the preceding claims, wherein an additional gas or additional gas mixture is used during the low pressure plasma polymerization process, said additional gas or gas mixture comprising a carrier gas, a functional gas and/or a functional carrier gas.

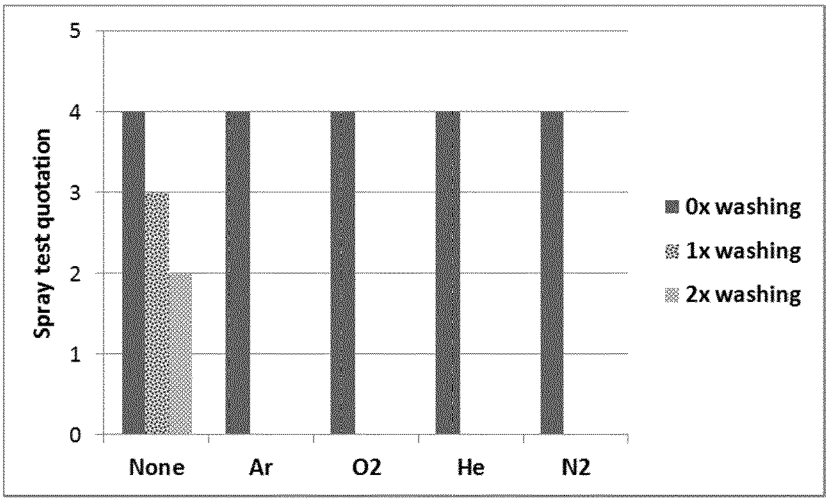

Figure 1

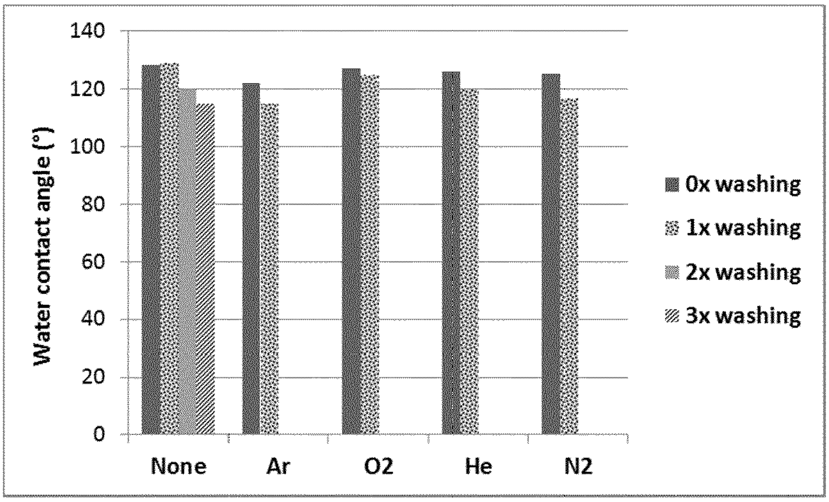

Figure 2

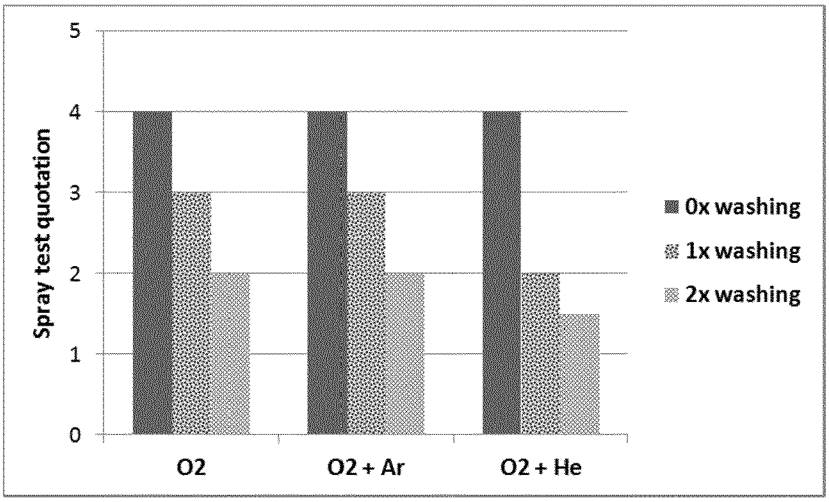

Figure 3

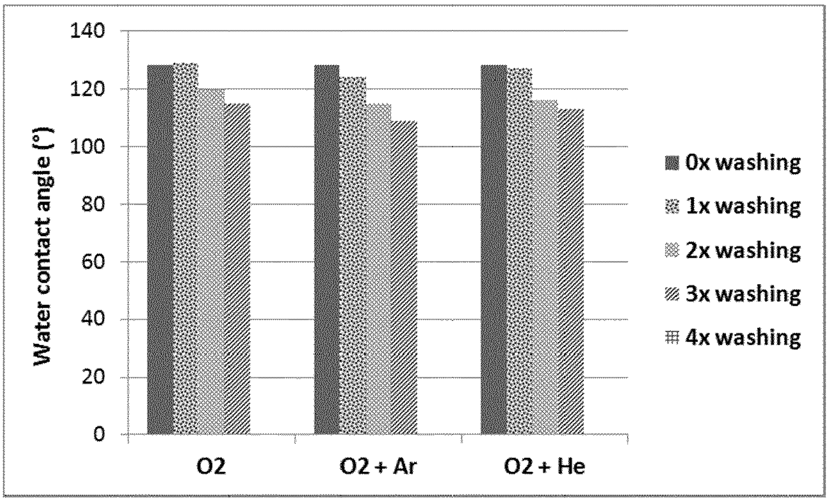

Figure 4

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EUROPEAN SEARCH REPORT

Application Number
EP 15 17 0410

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TECHNICAL FIELDS SEARCHED (IPC)

D06M

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Place of search	Date of completion of the search	Examiner
The Hague	18 November 2015	Fiocco, Marco

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Place of search	Date of completion of the search	Examiner
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