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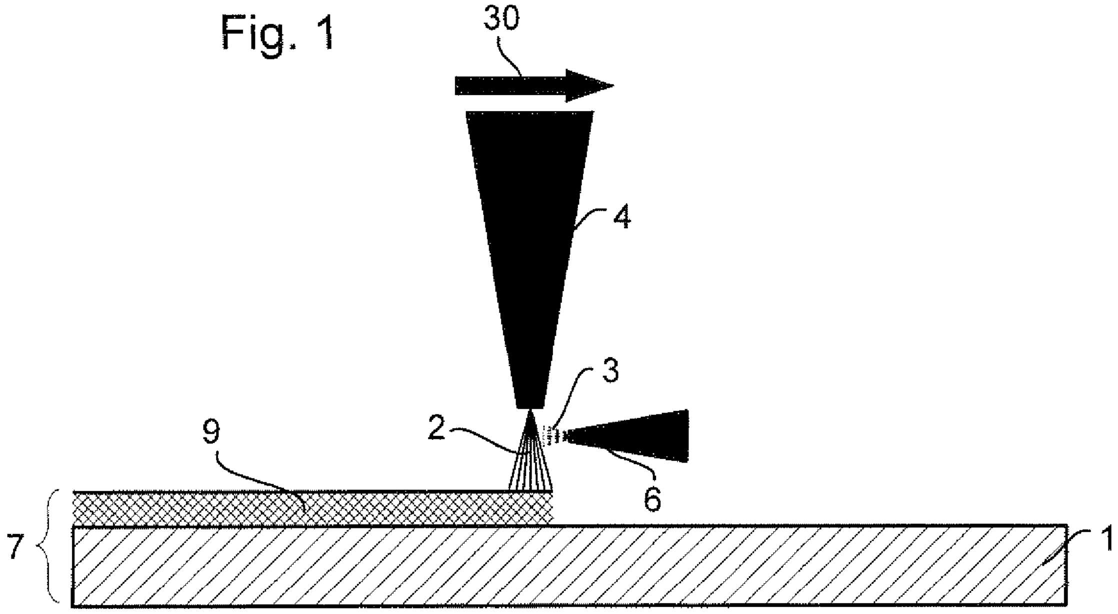
(54) Coating methods using plasma jet, substrates coated thereby and plasma coating apparatus

(57) The present invention relates to methods for coating substrates with inorganic-organic hybrid polymer material, to coated substrates obtainable by the coating methods, and to a plasma coating apparatus suitable for use in the methods. There are two variants of the coating method, a one-step and a two-step method. In the former, liquid comprising hybrid inorganic-organic pre-polymers is injected in a plasma jet, and a surface of the substrate to be coated is exposed to said plasma jet, and in the latter, liquid comprising hybrid inorganic-organic pre-polymers is applied on a surface of the substrate, and the substrate is exposed to the plasma jet to cure the prepolymers thus giving inorganic-organic hybrid polymer material. Owing to the distinct coating methods, the coated substrates were shown to exhibit excellent oxygen and water vapour barrier properties, as well as chemical and abrasion resistance.

Fig. 1



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Description

FIELD OF THE INVENTION

[0001] The present invention relates to methods for coating substrates with inorganic-organic hybrid polymer material, to coated substrates obtainable by the coating methods, as well as to a plasma coating apparatus suitable for use in the methods. Substrates, such as plastic substrates, coated with the inorganic-organic hybrid polymer material according to the coating methods of the invention have excellent surface properties, in particular barrier properties against oxygen permeation and scratch resistance.

BACKGROUND OF THE INVENTION

[0002] The coating of materials allows the tailoring of the surface properties thereof. For instance, a coating can change the colour of plastics, reduce the oxygen permeation through plastic films or enhance the abrasion resistance of leather.

[0003] Generally, optimal properties of the coatings at low cost are required. As a rule the costs of a coating will increase with the thickness of the coating. Consequently, from a viewpoint of cost, coatings as thin as possible are desirable. Also, versatile coating methods insofar as the surface properties and the shape of the article to be coated are concerned are demanded.

[0004] Coatings can be applied by lacquering, CVD or PVD processes. Lacquers, for instance on the basis of hybrid polymers, can be applied by conventional lacquering techniques, such as spraying, rolling or application with a doctor knife. Conventionally, the lacquer has been hardened (cured) in a second process step by heat treatment in a furnace or by irradiation with light. In the case of barrier layers, the typical thickness of such layers on the basis of hybrid polymers is about 8 μm. Such a barrier layer improves the oxygen barrier properties usually by a factor of about 2. In conventional coating application methods the use of masks is necessary to apply the coating only at specific locations of the substrate. As it turned out, conventional coatings based on hybrid polymers left much to be desired in connection with the surface properties of the coatings. In particular, the barrier properties of the hybrid material coatings against oxygen proved insufficient for demanding applications.

[0005] EP 1 582 270 A1 aims at overcoming the drawbacks of conventional lacquering techniques, namely the insufficient utilization of the full potential of the hybrid materials. The patent application relates to an atmospheric pressure plasma technology, in which a plasma is generated and maintained according to the Dielectric Barrier Discharge (DBD) technique. The method comprises the steps of introducing the sample to be coated in the space between two electrodes, generating a plasma discharge between the electrodes and mixing aerosols containing hybrid inorganic-organic cross-linked pre-polymers into the plasma discharge. The method of EP 1 582 270 A1 imposes severe restrictions on the size of the substrate to be coated. In the DBD techniques, the space, i.e. gap between the two electrodes is at most 5 mm, typically 2 to 3 mm. As the substrate to be coated must fit in the gap, larger articles cannot be coated by the method. In addition, it is very difficult if not impossible to coat conductive substrates, such as metals. This is because the plasma discharge generated between the electrodes is very difficult to maintain when a conductive substrate is interposed between the electrodes. In spite of these problems, PET films could be coated by the method. As is shown in Fig. 1 of REP 1 582 270 A1, the oxygen transmission rate (OTR) of a PET substrate of unspecified thickness could be reduced from 130 $cm^3/m^2 \cdot d \cdot bar$ to about 80 $cm^3/m^2 \cdot d \cdot bar$ by the coating. So, the OTR could be reduced by a factor of about 1.6 through the coating method of EP 1 582 270 A1.

[0006] Plasma nozzles such as described in DE 195 32 412 A1 and DE 299 21 694 U1 are typically used to activate surfaces, e.g. to enhance the wettability of plastics.

[0007] In WO 01/32949, plasma nozzles are exceptionally employed in the coating of surfaces. In said coating method, a plasma jet is generated by passing a process gas through an excitation zone, and precursor material is fed into the plasma jet separately from the process gas. For instance, the feeding of the precursor material can take place in the excitation zone of the plasma. According to one embodiment, the precursor material is fed with a tube arranged downstream of the plasma nozzle exit. The precursor material is reacted with the aid of the plasma, and the reaction product is deposited on the surface. Generally, the precursor materials used in WO 01/32949 are small molecules that are easy to volatilize. Hexamethyldisiloxane, tetraethoxysilane and propane are specifically mentioned in the reference.

[0008] DE 10 2006 038 780 A1 is concerned with an apparatus and method for preparing anti-corrosion coatings. Precursor materials are injected into the relaxing plasma generated in a plasma nozzle. In the plasma, the precursor is partially fragmented and impinges on the surface of the substrate, where it polymerizes to result in an anti-corrosion coating. Like in WO 01/32949, silicon-containing low-molecular species, such as hexamethyldisiloxane (HMDSO) and tetraethoxysilane (TEOS), are used as precursor materials.

[0009] In view of the above, there was a strong demand to provide a method for coating substrates, which overcomes the downsides of the prior art such as described above, in particular which does not impose any limitations on the size or material of the substrate and which allows the production of coated substrates having further improved surface properties, in particular enhanced barrier properties against oxygen. Also, it was highly desirable to provide a coating method, which is not restricted to small volatile compounds such as HMDSO or TEOS, but which allows large non-volatile molecules to be employed.

SUMMARY OF THE INVENTION

[0010] The present inventors have surprisingly found that the above object can be attained by the distinct coating methods as recited in the independent claims 1 and 6 involving the use of a liquid comprising hybrid inorganic-organic pre-polymers and a plasma jet, in particular an atmospheric pressure plasma jet, that is preferably prepared by a plasma nozzle.

[0011] The present invention provides two alternative methods for coating a substrate with an inorganic-organic hybrid polymer material. The first method, which is sometimes referred to in this description as the "one-step method of the invention", comprises injecting liquid comprising hybrid inorganic-organic pre-polymers in a plasma jet and exposing a surface of the substrate to the plasma jet. According to an alternative embodiment, the coating method of the present invention comprises a step (i) of applying liquid comprising hybrid inorganic-organic pre-polymers on a surface of the substrate, and a step (ii) of exposing said surface, i.e. the surface of the substrate with the liquid applied thereon, to a plasma jet to cure the hybrid inorganic-organic pre-polymers. This method will sometimes be denoted the "two-step method of the invention", below. Moreover, the term "coating methods of the invention" as occasionally used herein is understood as a collective term encompassing both, the one-step and the two-step method of the invention.

[0012] The coating methods of the invention allow the preparation of substrates coated with inorganic-organic hybrid polymer material, which coated substrates have physical properties, in particular oxygen barrier properties that are substantially improved over the coated materials of the prior art acknowledged above.

[0013] For instance, the OTR values could be reduced in the one-step method of the invention with respect to the starting substrate by a factor of at least 10 through the coating, whereas the corresponding reduction was only about 1.6 when using the technique of EP 1 562 270 A1. This is highly unexpected, for the following reasons. To achieve good barrier properties against oxygen, one would aim at a coating as dense and as pore-free as possible. To accomplish this, one would normally strive for a fragmentation of precursors to be polymerized into parts as small as possible. Generally speaking, the electron density (plasma intensity) is higher in DBD plasmas than in plasma jets obtained in a plasma nozzle. Higher electron density will result in higher degree of ionization and fragmentation of precursors. This being the case, higher oxygen barrier properties of the materials obtained in EP 1 582 270 A1 (using DBD plasma) in comparison to those obtained by using a plasma nozzle had to be expected. This is surprisingly not the case. As the present inventors found, in spite of the electron density in a plasma jet, i.e. prepared in a plasma nozzle, being lower than in a DBD plasma, the oxygen barrier properties of the coated materials prepared in the method of the invention are enhanced significantly. For instance, coated articles obtainable with the coating method of the invention can have an OTR of less than 5 $cm^3/m^2 \cdot d \cdot bar$ for 23 μm thick PET films as substrates. In addition, the water vapor transmission rate (WVTR) could be improved from 12 to 9 $g/d \cdot m^2$ through the coating. The OTR values mentioned in this specification were measured in accordance with DIN 53380 (July 1998), and the WVTR values in accordance with DIN 53122 (August 2001).

[0014] The difference in electron density to a DBD plasma is even more significant in the relaxing plasma, i.e. the plasma jet outside the plasma nozzle, in which the liquid comprising the hybrid inorganic-organic pre-polymers is injected according to a preferred embodiment of the invention. In this case, the significantly improved oxygen barrier properties of the coated substrates or coated articles of the invention are even more unexpected.

[0015] In the coating methods of the invention, a plasma jet that does not have an external electric field is used. Therefore, metal substrates can be coated with ease. Also, the coating of articles of arbitrary size and shape is possible. This is another advantage over the DBD technique of EP 1 582 270 A1.

[0016] As the present inventors found, in the two-step method of the invention, the full potential of the inorganic-organic hybrid polymers is utilized by curing in a plasma jet. In particular, the oxygen barrier properties could be enhanced significantly over corresponding coatings cured conventionally, e.g. by heat treatment in a furnace or by irradiation with light. The enhanced oxygen barrier properties are due to a higher degree of crosslinking/curing of the inorganic-organic hybrid polymer material obtained in the two-step method of the present invention. This could be confirmed by NMR measurements.

[0017] The present invention is also concerned with substrates coated with inorganic-organic hybrid polymer material obtainable by the coating methods of the invention. As will be appreciated, the coated substrates as meant herein refer to coated articles of arbitrary size and shape. The coated substrates/articles excel in their surface properties, in particular in their oxygen barrier properties.

[0018] Finally, the present invention is concerned with a plasma coating apparatus according to the independent Claim 12. A plasma coating apparatus comprising a plasma nozzle having a nozzle exit and a precursor feeding unit arranged downstream of the nozzle exit according to the preamble of Claim 12 is known from WO 01/32949. The plasma coating apparatus of the present invention is characterized by the feature of the precursor feeding unit being a liquid spray nozzle. The plasma coating apparatus according to the present invention is specifically adapted for use in the one-step coating method of the invention.

[0019] Preferred embodiments of the various aspects of the present invention are subject of the dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020]

Fig. 1 is a schematic drawing showing the one-step method of the invention.

Figs. 2a to 2c illustrate the steps of the two-step method of the invention.

Fig. 3 is an illustration of a plasma coating apparatus of the invention when this is used in the one-step method of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0021] In the coating methods of the invention, the plasma jet is preferably generated by a plasma nozzle having a nozzle exit. As will be appreciated, for generating an atmospheric pressure plasma jet, an atmospheric pressure plasma nozzle can be used with benefit. As used herein, the "atmospheric pressure plasma jet" is a plasma jet that is generated, maintained and operated at approximately atmospheric pressure.

[0022] The plasma nozzle for use in the present invention will be further illustrated by reference to Fig. 3. In Fig. 3, the plasma nozzle 4 is shown as a part of a plasma coating apparatus 10. A plasma nozzle that can be used with benefit in the present invention has an electrically conductive housing 12, which is preferably elongated and is more preferably a tubular housing. The housing 12 forms a nozzle channel 13 through which a working gas is flowing. An electrode 14 is provided, preferably coaxially, in the nozzle channel 13. A tube 16 of dielectric material, for instance a ceramic tube is inserted in the nozzle channel. A voltage is applied between the electrode 14 and the housing 12. It proved to be advantageous to the formation of the plasma, when the voltage is pulsed. In the plasma nozzle 4 shown in Fig. 3 this is achieved with the high frequency generator 15. The pulse frequency is not specifically limited and can be 5 to 100 kHz, with the range of 10 to 50 kHz being preferred. A working gas 20 is fed to the nozzle channel 13 through a conduit 22, preferably such that the working gas shows a twisted flow through the channel. Such flow of the working gas can be achieved by way of a twisting device 17, which can be a plate having openings. One of average skill in the art knows which working gases 20 are useful in plasma nozzles. For instance, air, nitrogen, oxygen, ammonia (NH_3), hydrogen sulfide (H_2S), noble gases, hydrogen and mixtures thereof can be used. The preferred noble gas is argon.

[0023] When the atmospheric pressure plasma nozzle is in operation, the arc-like plasma discharge runs from the tip of the central electrode 14 essentially in axial direction of the nozzle channel 13 to the counter electrode 24, which is earthed like the housing. As a result, a plasma jet 2 is generated below the nozzle exit 5.

[0024] The operating mode of a plasma nozzle is known to the skilled person and is for instance further described in DE-A-195 32 412 and DE-U-299 21 694.

[0025] The plasma nozzle for use in the method and plasma coating apparatus of the present invention is not particularly limited. According to a preferred embodiment, plasma nozzles, such as described in DE-A-195 32 412 or DE-U-299 21 694, are used. More preferably, plasma nozzles are employed, which are within the scope of DE-A-195 32 412, especially commercially available standard-single nozzles of the firm Plasmatreat (Germany).

[0026] As opposed to conventional low pressure CVD and PVD processes, no vacuum equipment is required in the coating methods of the invention when an atmospheric pressure plasma jet is used.

[0027] In the coating methods of the invention, the plasma jet is preferably a jet of a so-called "relaxing" plasma (occasionally also referred to as a "relaxed" plasma in the literature). The "relaxing" plasma in the plasma jet is oftentimes also referred to as "after-glow" plasma. In the relaxing plasma, the plasma is located outside the excitation zone which is confined by the electrodes, preferably the housing. This is different from so-called "active" plasma, which is generally understood to refer to a plasma which is located inside the space that is confined by the electrodes, wherein one electrode is usually the housing.

[0028] In the coating methods of the invention, hybrid inorganic-organic pre-polymers comprised in a liquid are converted to inorganic-organic hybrid polymer material by the action of a plasma jet. In the following, the hybrid inorganic-organic pre-polymers for use in the present invention will be described in more detail. For the sake of brevity, the hybrid inorganic-organic pre-polymers will occasionally simply be referred to as "hybrid pre-polymers" or "pre-paiymers" in the present application.

[0029] As used herein, the term "hybrid inorganic-organic pre-polymer" refers to a pre-polymer comprising both, inorganic and organic regions that can also be referred to as inorganic and organic domains. Thereby, the inorganic regions comprise elements that are generally referred to as inorganic elements, such as Si, B, Al, P, Sn, Pb, the transition metals, lanthanides and actinides. Preferably, the inorganic region of the hybrid inorganic-organic pre-polymers for use in the coating methods of the present invention comprises, or is composed of, M-O-M-units, with M representing Si, B, Al, P, Sn, Pb, a transition metal, a lanthanide or an actinide, preferably Si, Ti, Zr or Al. The organic regions in the hybrid inorganic-organic pre-polymers for use in the present invention typically consist of C, H, O, N, S and halogens.

[0030] The use of the term "pre-polymer" is intended to indicate that the molar mass of the hybrid inorganic-organic pre-polymers is increased in the coating methods of the invention, in which they are converted by curing reactions (to be further described below) to inorganic-organic hybrid polymer material in and/or through the action of, the plasma jet. The pre-polymers for use in the present invention preferably have a molar mass of at least 500 g/mol, more preferably at least 1,000 g/mol. As used in the present specification, the molar mass refers to the average molar mass, more specifically the weight average molar mass M_W. There are no particular limitations as to the upper limit of the molar mass of the pre-polymers, as long as this can be increased by the action of the plasma jet in the coating methods of the invention to form inorganic-organic hybrid polymer material. However, the upper limit of molar mass is preferably 12,000. Overall, the range of molar mass of the hybrid inorganic-organic pre-polymers for use in the present invention is according to a more preferred embodiment in the range of 1000 to 10,000. The hybrid inorganic-organic pre-polymers for use in the present invention are preferably crosslinked pre-polymers.

[0031] The hybrid inorganic-organic pre-polymers for use in the present invention are preferably obtainable by hydrolytic condensation of one or more hydrolytically condensable compounds of silicon and optionally other elements from the group consisting of B, Al, P, Sn, Pb, the transition metals, the lanthanides, and the actinides (collectively referred to as "hydrolytically condensable compounds" herein), and/or precondensates derived from the above mentioned compounds wherein 10 to 100% by mol, preferably 20 to 100% by mol, more preferably 40 to 100% by mol, in terms of monomeric compounds, of the hydrolytically condensable compounds are silanes represented by the general formula (I),

$$SiX_aR_{4-a} \qquad (I)$$

wherein the groups and indices are the same or different and have the following meanings: R represents optionally substituted alkyl, alkenyl, aryl, alkylaryl, or arylalkyl having 1 to 50 carbon atoms; X represents hydrogen, halogen, hydroxy, alkoxy, acyloxy, alkylcarbonyl, alkoxycarbonyl, or NR'_2 with R' = hydrogen, alkyl or aryl; and a represents 1, 2, or 3.

[0032] Hereinbelow, the term "hydrolytically condensable precursors" is intended to encompass the above hydrolytically condensable compounds and/or precondensates thereof, and the silanes of formula (I).

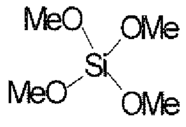
[0033] As used herein, the precondensates derived from the hydrolytically condensable compounds means molecules resulting from condensation of from 2 to 6, preferably 3 to 4 individual molecules of hydrolytically condensable compounds.

[0034] As will be appreciated, the group X in the silanes of formula (I) is hyrolyzable. Through the groups R an organic network is formed in the pre-polymers, and through the groups X and, if applicable, the hydrolytically condensable compounds, an inorganic network having M-Q-M-units with M representing Si, B, Al, P, Sn, Pb, transition metal, lanthanide or actinide, preferably Si, Ti, Zr or Al is formed in the pre-polymers for use in the present invention.

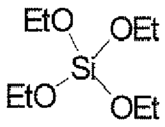
[0035] According to a preferred embodiment, the hydrolytically condensable compounds are represented by the following formula (II):

$$M(OR^1)_b \qquad (II)$$

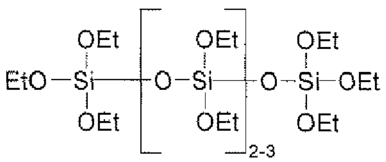
wherein M represents Si, Ti, Zr or Al, and b represents the valence of M, i.e. 4 in the case of Si, Ti and Zr, and 3 in the case of Al; and R^1 is substituted or unsubstituted alkyl, preferably C_{1-6} alkyl, more preferably C_{1-4} alkyl. Most preferably, R^1 is unsubstituted C_{1-6} alkyl, especially unsubstituted C_{1-4} alkyl, namely, methyl, ethyl, propyl or butyl. Examples of the hydrolytically condensable compounds of formula (II) and precondensates derived therefrom are, without limitation, the following:



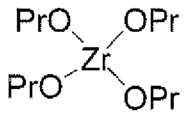
Tetramethoxysilane



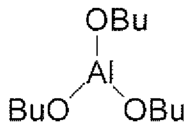
Tetraethoxysilane



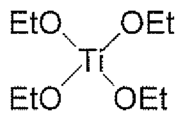
Dynasil 40



Zirconium-tetrapropoxide



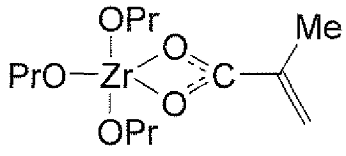
Aluminium-tributoxide



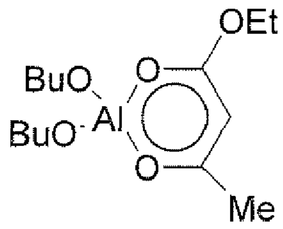
Titanium-tetraethoxide.

[0036] The hydrolytically condensable compounds for use in the present invention may bear an organic complex ligand.

[0037] Examples of such hydrolytically condensable compounds are the following:



Zirkonium-tripropoxide methylacrylate



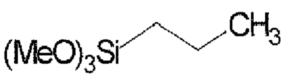
Aluminium-dibutoxide ethylacetoacetate

[0038] A preferred group within the silanes of formula (III) is represented by the following formula (III):

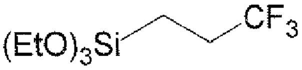
$$Si(OR^2)_cR^3_{4-c} \qquad (III)$$

[0039] In the above formula (III), R^2 represents alkyl, preferably C_{1-6} alkyl, more preferably C_{1-4} alkyl, namely, methyl, ethyl, propyl or butyl. The index c represents 2 or 3. The group(s) R^3 in formula (III) independently represent optionally substituted C_{1-10}, preferably C_{3-8} alkyl; optionally substituted C_{2-10}, preferably C_{2-6} alkenyl; or optionally substituted C_{3-10}, preferably C_{6-10} aryl. The aryl group R^3 is especially phenyl. The optional substitutents of the alkyl or aryl group R^3 are not specifically limited and can be selected from amino (including monoalkyl- and dialkylamino), mercapto, halo (in particular fluoro or chloro), ammonio (including mono-, di- and trialkylammonio), and anhydrido. The counter ion of the ammonio group is not specifically limited in kind and can for instance be chloride or acetate. Each of the above substituents can optionally be further substituted, preferably by the above substituents. Also, the substituents can comprise -O-, -C(O)-, -CO(O)-, -C(O)O- linkages.

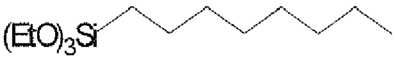
[0040] Examples of such silanes of formula (III) are given below, but may of course not be construed in a limiting sense. In the list of examples, which follows, the groups R^3 are nonreactive, in particular non-polymerizable groups, but which can impart certain chemical properties to the inorganic-organic hybrid polymer material coating, which will be formed from the hybrid inorganic-organic pre-polymers in the coating methods of the invention.



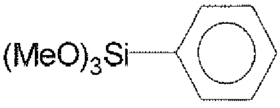
Propyltrimethoxysilane



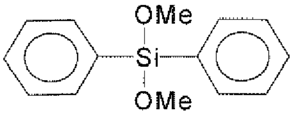
Trifluoropropyltriethoxysilane



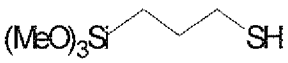
Octyltriethoxysilane



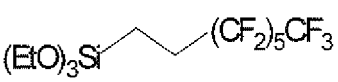
Phenyltrimethoxysilane



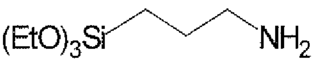
Diphenyldimethoxysilane



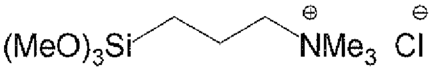
Mercaptopropyltrimethoxy-silane



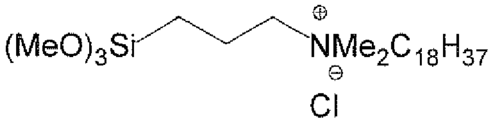
Tridecafluorotriethoxysilane



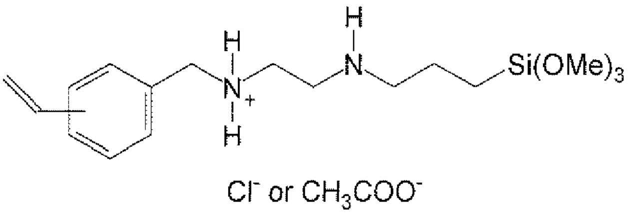
Aminoproyltriethoxysilane



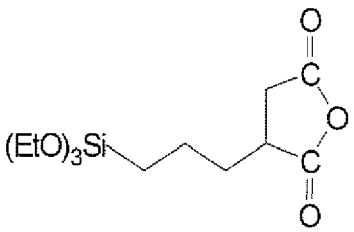
Trimethylammoniumpropyltrimethoxysilane



Octadecyldimethylammoniumpropyltrimethoxysilane



Vinylbenzyl ammoniumethyl aminopropyltrimethoxysilane

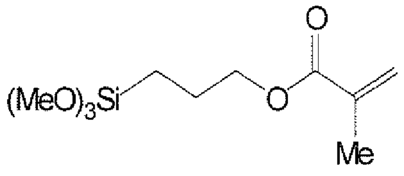


Succinic acid anhydride propyl triethoxysilane

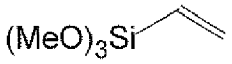
[0041] According to the usual terminology, Me represents methyl, Et represents ethyl, Pr represents propyl and Bu represents butyl in the present specification.

[0042] It is preferable for the silanes of formula (I) or (III) to have at least one group R and R^3, respectively, which has, as a substituent, a polymerizable functional group, i.e. a group which can undergo polymerization in the liquid comprising hybrid inorganic-organic pre-polymers and/or in the plasma jet during the coating methods of the invention.

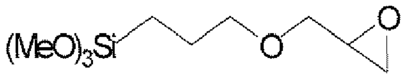
The groups R or R^3 preferably comprise 1 to 3 of such functional groups, especially in terminal positions of the groups R/R^3. When such polymerizable functional groups are present in R or R^3, an additional organic polymer network can be formed in the hybrid inorganic-organic pre-polymers and eventually in the inorganic-organic hybrid polymer material. Useful polymerizable functional groups can for instance comprise at least one C=C carbon bond and/or at least one epoxy moiety. Specifically, the polymerizable functional groups can be selected from vinyl, glycidyl, acryl, methacryl and allyl. Examples of silanes of formula (I) or (III) having such terminal polymerizable groups are given without restriction to generality, below.



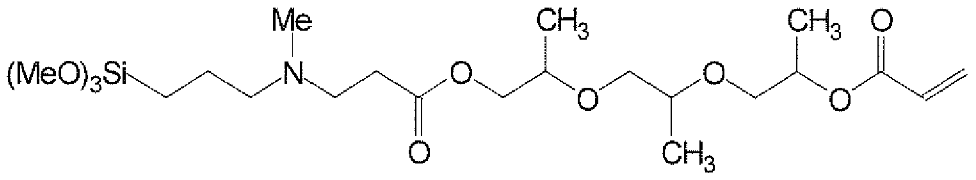
Methacryloxypropyltrimethoxysilane



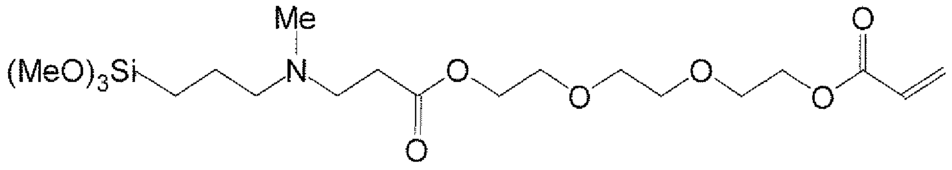
Vinyltrimethoxysilane



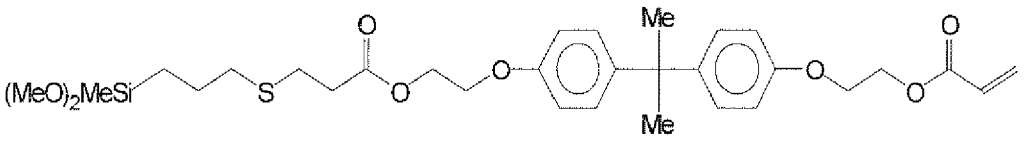
Glycidoxypropyltrimethoxysilane



TPGDA-silane



TEGDA-silane



BPADA-silane

[0043] Further examples of groups R and/or R^3 having at least one polymerizable functional group are those exemplified in EP 0 802 218 A2, page 4, line 20 through page 11, line 34. Moreover, concrete examples of silanes of formula (I) having at least one group R comprising at least one polymerizable functional epoxy group are given at page 11, lines

35 to 49 of EP 0 802 218 A2.

[0044] According to a particularly preferred embodiment, the hybrid inorganic-organic pre-polymers for use in the coating methods of the invention are obtainable from tetramethoxysilane, tetraethoxysilane, Dyansil 40®, zirconium-tetrapropoxide, aluminium-tributoxide, titaniumtetraethoxide, aluminium-dibutoxide ethylacetoacetate, zirkonium-tripropoxide methylacrylate, propyltrimethoxysilane, trifluoropropyl-triethoxysilane, octyltriethoxysilane, phenyltrimethoxysilane, diphenyldimethoxysilane mercaptopropyltrimethoxy-silane, tridecafluorotriethoxysilane, aminopropyltriethoxy-silane, trimethylammonium-propyltrimethoxysilane, octadecyldimethylammonium-propyltrimethoxysilane, vinylbenzyl ammoniumethyl aminopropyltrimethoxysilane, succinic acid anhydride propyl triethoxysilane, glycidoxypropyltrimethoxysilane, vinyltrimethoxy-silane, methacryloxypropyl-trimethoxysilane, TPGDA-silane, TEGDA-silane, BPADA-silane and/or suitable mixtures thereof.

[0045] The hydrolytically condensable precursors will undergo hydrolysis and condensation, and possibly at least partial polymerization (in the case of groups R comprising polymerizable functional groups) so as to form hybrid inorganic-organic pre-polymers in the liquid. The condensation reaction resulting in the pre-polymers is preferably carried out in accordance with the sol-gel process. In practice, the hydrolysis and condensation to give hybrid inorganic-organic pre-polymers for use in the present invention is carried out by adding to the hydrolytically condensable precursors the necessary amount of water at room temperature or under cooling, and stirring the resultant mixture.

[0046] Thereby, the hydrolytically condensable precursors can be present dissolved in a suitable solvent. Examples of the solvent are, apart from aliphatic C_{1-6} alcohols such as ethanol or i-propanol, ketones, preferably dialkyl ketones such as acetone or methylisobutyl ketone, ethers, preferably dialkyl ethers such as diethyl ether or dibutyl ether, THF, amides, esters, in particular ethyl acetate, dimethyl formamide, amines, in particular triethylamine, and suitable mixtures thereof. According to a particularly preferred embodiment, the liquid comprising hybrid inorganic-organic pre-polymers is an aliphatic C_{1-6} alcohol.

[0047] To accelerate the hydrolysis and polycondensation reactions of the hydrolytically condensable precursors, suitable catalysts may be added to the liquid.

[0048] In the present invention, further compounds may be added to the liquid comprising inorganic-organic hybrid pre-polymers, before this is exposed to the plasma jet. Examples of such compounds may be organic coating forming materials such as carboxylates, methacrylates, acrylates, styrenes, methacrylonitriles, alkenes and dienes, e.g. methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate and/or other alkyl (meth)acrylates, organofunctional (meth)acrylates, glycidyl methacrylate, allyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates, and fluoroalkyl (meth)acrylates, methacrylic acid, arylic acid, fumaric acid and esters, itaconic acid (and esters), maleic anhydride, styrene, α-methylstyrene, halogenated alkenes, for example, vinyl halides, such as vinyl chlorides and vinyl fluorides, and fluorinated alkenes, for example perfluoroalkenes, acrylonitrile, methacrylonitrile, ethylene, propylene, allyl amine, vinylidene halides, butadienes, acrylamide, such as N-isopropylacrylamide, methacrylamide, epoxy compounds, for example glycidyl, styrene oxide, butadiene monoxide, ethyleneglycol diglycidylether, glycidyl methacrylate, bisphenol A diglycidylether (and its oligomers), vinylcyclohexene oxide and phosphorous-containing compounds, for example dimethylallylphosphonate. Additional inorganic coating forming materials which can be added include colloidal metals and metal oxides and organometallic compounds.

[0049] As used herein (meth)acrylate(s) is a collective term for acrylate(s) and methacrylate(s).

[0050] According to a particularly preferred embodiment, the liquid comprising hybrid inorganic-organic pre-polymers used in the coating methods of the invention is one that is sold under the trademark ORMOCER®.

[0051] In the coating methods of the invention, the material of the substrate is not specifically limited in kind, as long as it does not disintegrate or decompose in the plasma jet. For instance, the substrate may comprise, or consist of, metal, plastics (such as PET, i.e. polyethylene terephthalate, or polycarbonate), cellulosic material, leather, or ceramics. The form and shape of the substrates to be coated in the coating methods of the invention is also not specifically limited. Examples of the substrates are films, fibres, powders or moulded articles. Further examples of useful substrates are materials already having at least one barrier layer. In this case, the provision of an additional coating layer by means of the coating methods of the invention results in a multilayer structure. Concretely, the coating methods of the invention can be used in the field of packaging and technical applications, e.g. for providing barrier films for flexible displays or photovoltaic panels, or abrasion resistant coatings for transparent polymers, e.g. displays for mobile phones, or leather, as well as functional coatings for paper and textile finishing.

[0052] According to one aspect, the present invention is also directed to the coated substrates as such that are obtainable by the coating methods of the invention, i.e. the one-step method or the two-step method. Owing to the coating methods of the invention, the coated substrates can have an Oxygen Transmission Rate (OTR) as low as < 5 $cm^3/m^2 \cdot d \cdot bar$ for 23 μm thick PET substrates. Therefore, the coating methods of the invention are excellently suited for providing oxygen barrier layers, e.g. in the field of food or beverage packaging. A typical coated substrate in accordance with the present invention would be a packaging film, or an encapsulation film for solar panels or OLEDs, which film has been subjected to the coating methods of the invention.

[0053] The one-step method of the invention will be described below by reference to Fig. 1. As shown in the schematic drawing of Fig. 1, the plasma coating apparatus comprising the plasma nozzle 4 and the liquid spray nozzle 6 is moved relative to the substrate 1 to be coated. The relative movement of the plasma nozzle 4 and the liquid spray nozzle 6 (jointly forming the plasma coating apparatus 10) with respect to the substrate 1 is shown in Fig. 1 by the horizontal arrow 30. In or owing to the action of the plasma jet 2, the hybrid inorganic-organic pre-polymers included in the liquid 3 that is injected in the plasma jet 2 will deposit as an inorganic-organic hybrid polymer material 9 on the substrate 1 thus forming a coated substrate 7. In this specification, the inorganic-organic hybrid polymer material will sometimes be denoted as "hybrid polymer material".

[0054] In the one-step method of the invention, the relative velocity of the plasma coating apparatus 10 (comprising the plasma nozzle 4 and the liquid spray nozzle 6) and the substrate is not specifically limited and can for instance be 0.1 to 300 m/min. Preferably, the relative velocity is 1 to 30, more preferably 2 to 20 m/min.

[0055] Within the plasma jet, the hybrid inorganic-organic pre-polymers comprised in the liquid injected in the plasma jet will undergo curing to give inorganic-organic polymer material. This requires the evaporation of the liquid, e.g. the solvent surrounding the hybrid inorganic-organic pre-polymers. As will be appreciated, the evaporation heat consumed thereby will reduce the local energy within the plasma jet. This is different from the methods described in the prior art, such as WO 01/32949, wherein precursor gases rather than liquids are fed to a plasma zone. As the present inventors found, owing to the use of liquids comprising hybrid inorganic-organic pre-polymers, the curing reactions occurring in the coating methods of the invention within the plasma jet, possibly after the pre-polymers have impinged on the surface of the substrate, are different from those of the prior art. In more detail, the influence of the plasma will lead, e.g. through bond cleavage, ring opening reactions and polymerisation (for instance of polymerizable functional groups) to an increase of the molar mass of the hybrid inorganic-organic pre-polymers to give hybrid polymer material. In the coating methods of the invention, curing reactions may occur on the surface of the substrate even after the plasma jet has been moved further along the surface of the substrate.

[0056] As the present inventors found, the curing of the hybrid inorganic-organic pre-polymers in the plasma jet to give inorganic-organic hybrid polymer material can be controlled, and the physical properties, such as the barrier properties, in particular oxygen barrier properties, of the inorganic-organic hybrid polymer material can be fine-tuned with ease in the coating methods of the invention.

[0057] Several parameters proved suitable for such control and fine-tuning. Such parameters are the selection of the particular hybrid inorganic-organic pre-polymer, and the concentration of the pre-polymers in the liquid to be injected in the plasma jet (in the one-step method) or to be applied on a surface of the substrate (in the two-step method). Furthermore, in the one-step method, the form in which the liquid comprising hybrid inorganic-organic pre-polymers is injected in the plasma jet was found to influence the characteristics of the resultant inorganic-organic hybrid polymer material. Preferably, the liquid is injected in the form of an aerosol that is sprayed in the plasma jet in the one-step method of the invention. A droplet size of the liquid in the range of 0.5 to 100 μm proved to be particularly beneficial to the properties of the resultant inorganic-organic hybrid polymer material.

[0058] Aerosols of liquid having a droplet size within that range can be generated with a liquid spray nozzle, which will be further illustrated below, using a suitable carrier gas, such as air or nitrogen. This is another significant advantage of the coating methods of the invention. Namely, as opposed to earlier technologies, the coating methods of the invention do not require noble gases such as helium, or some sort of protection of the coating zone, such as by means of a closed vessel or by means of protective gases. This represents significant advantages in terms of cost.

[0059] In the one-step coating method of the invention, in particular when a liquid spray nozzle is used for injecting in the plasma jet the liquid comprising hybrid inorganic-organic pre-polymers and the plasma jet is generated by a plasma nozzle having a nozzle exit, it proved beneficial to the properties of the resultant hybrid polymer material coated on the substrate if certain geometric requirements are met. Such geometric requirements will be illustrated below by reference to Fig. 3, which shows a more detailed view on a plasma coating apparatus when it is used in the one-step method of the invention. Specifically, the distance g along a parallel to the central axis 11 of the plasma nozzle, between the exit of the liquid spray nozzle 5 and the surface of the substrate 1 is preferably in the range of 4 to 50 mm, more preferably 10 to 30 mm. Most preferably, the distance g is about 20 mm. Moreover, it proved beneficial to the properties of the hybrid polymer material obtained in the method to adjust the distance d between the nozzle exit 5 of the plasma nozzle 4, and the exit of the liquid spray nozzle 6, along a parallel to the central axis 11 of the plasma nozzle to 2 to 30 mm, more preferably 5 to 15 mm, most preferably to about 10 mm. As can be seen from Fig. 3, the distance between the exit of the liquid spray nozzle 6 along a parallel to the central axis 11 of the plasma nozzle 4 and the substrate 1 is $e = g - d$. Furthermore, the horizontal distance f between the central axis 11 of the plasma nozzle 4 and the exit of the liquid spray nozzle 6 is preferably 2 to 50 mm, more preferably 10 to 30 mm, and most preferably it is about 20 mm. Finally, the angle between the central axis 11 of the plasma nozzle 4 and the central axis of the liquid spray nozzle is preferably 80 to 100°, more preferably 85 to 95°, and most preferably it is approximately 90° as is shown in Figs. 1 and 3.

[0060] As the present inventors found, the parameters d and f in particular will have some influence on the properties of the hybrid polymer material obtained in the one-step method. Without being bound by theory, it is assumed that the activity of the plasma in the plasma jet will decrease with increasing d resulting in less fragmentation of the pre-polymers injected in the plasma jet. As regards the distance f, this will influence the homogeneity of the injection of the liquid comprising the pre-polymers. The larger the distance f, the more inhomogeneous will be the feeding in the plasma jet due to an increasing divergence angle.

[0061] As the present inventors found, an inorganic-organic hybrid polymer material having outstanding oxygen barrier properties can be obtained when f is between 10 and 30 mm, d is between 5 and 15 mm, the angle between the central axis 11 of the plasma nozzle 4 and the central axis of the liquid spray nozzle 6 is approximately 90°, and the liquid comprising hybrid inorganic-organic pre-polymers is injected in the plasma jet in the form of an aerosol, such as having a droplet size of 0.5 to 100 μm. In addition, in the above embodiment of the one-step coating method of the invention, the distance g may be 4 to 50 mm, and preferably it is 10 to 30 mm.

[0062] The plasma-coating apparatus according to the present invention is suitable to, and specifically adapted to, carrying out the one-step coating method of the invention. As such, it is equipped with a liquid spray nozzle for feeding the precursors, in particular the liquid comprising hybrid inorganic-organic pre-polymers. The liquid spray nozzle of the plasma coating apparatus is preferably designed such that liquid, such as liquid comprising pre-polymers can be injected into a plasma jet exiting the plasma nozzle through the nozzle exit. This is illustrated in Fig. 3. The liquid spray nozzle 6 is different from the tube shown e.g. in Fig. 1 of WO 01/32949, which serves to feed gases. The liquid spray nozzle is, as suggested by the name, a nozzle for spraying liquids. According to a preferred embodiment, the opening diameter of the exit of said nozzle is less than 1 mm. Specific examples of the liquid spray nozzles for use in the plasma coating apparatus according to the present invention are "Meinhard Zerstauber TR-30-A1 (A3)", available from Spectec GmbH (Erding, Germany) and "Burgener Zerstauber PMM-4000", obtainable from Maassen GmbH (Reutlingen, Germany). These liquid spray nozzles, which are commercially available, can be used with particular benefit in the plasma coating apparatus and the one-step coating method according to the present invention. Also, the liquid spray nozzle 6 is preferably arranged in the plasma coating apparatus of the invention such that the distances d and f, and the angle between the central axis 11 of the plasma nozzle and the central axis of the liquid spray nozzle 6 are in the ranges that have been defined for the one-step method of the invention, above.

[0063] In the following, the two-step coating method of the invention as defined in the appending Claim 6 will be further described by reference to Figs. 2a to 2c. In step (i), liquid comprising hybrid inorganic-organic pre-polymers 3 is applied on a surface of the substrate 1. This is shown in Fig. 2b, wherein the application of the liquid 3 is symbolized by pouring the liquid contained in a vessel onto the substrate resulting in a liquid 8 applied on the substrate. The method of applying the liquid 3 can be conventional methods of applying lacquer, for instance spraying, rolling, or applying by using e.g. a plate, knife or doctor knife. As indicated by the arrow 31, the vessel containing liquid 3 for pouring the liquid on the substrate 1 is moved relative to the substrate 1. As illustrated in Fig. 2c, the liquid 8 applied on the substrate is subsequently exposed in step (ii) to a plasma jet 2, which is generated in Fig. 2c by a plasma nozzle 4. Through the exposure of the applied liquid 8 to the plasma jet 2, the hybrid inorganic-organic pre-polymers in the applied liquid 8 are cured to give (cured) inorganic-organic hybrid polymer material 9. As symbolized in Fig. 2c by the arrow 32, the plasma nozzle 4 and the substrate 1 are moved relative to each other at a speed that is not particularly limited but is preferably 0.5 to 200 m/min, more preferably 5 to 100 m/min and especially 10 to 20 m/min. Said relative velocity of the substrate 1 and the plasma nozzle 4 in the two-step coating method of the invention can also be referred to as a scanning speed.

[0064] As the present inventors found, the distance g as illustrated in Fig. 3, i.e. the distance between the nozzle exit 5 of the plasma nozzle 4 along a parallel line to the central axis 11 thereof and the substrate 1 is preferably in the range of 3 to 50 mm in the two-step method. More preferably, the distance g is 4 to 20 mm and especially 5 to 10 mm. In the two-step method of the invention, the time between application step (i) and exposure step (ii) may be in the range of seconds but can also be in the range of days.

[0065] In the plasma of the plasma jet for use in the two-step coating method of the invention, radicals, ions, electrons, species in excited states and photones act collectively. The combined effect of these species will lead to a high degree of crosslinking within the inorganic-organic hybrid polymer material upon curing. The high degree of crosslinking is reflected in the good barrier values of the hybrid polymer material coating. The above combined effect of different species does not take place in the conventional curing treatments such as e.g. by thermal oven treatment.

[0066] When the plasma generated by the plasma jet used in the two-step coating method of the invention is a relaxing plasma, which is a preferred embodiment of the coating methods of the invention, the distribution of plasma species therein is rich on radicals and species in excited states, while it has a comparably low content of ions and electrons. Radicals are expected to be particularly efficient in crosslinking upon curing to give the inorganic-organic hybrid polymer material. Consequently, the embodiments of the two-step coating method of the invention wherein the substrate having liquid 8 applied thereon is exposed to a relaxing plasma of a plasma jet will yield hybrid polymer materials having particularly outstanding barrier properties.

EXAMPLES

1-step method

[0067] A plasma coating apparatus according to the invention was used, in which the liquid spray nozzle was arranged in a horizontal distance f of 20 mm with respect to the central axis of the plasma nozzle, and at a distance d to the nozzle exit of the plasma nozzle along a parallel to the central axis of the plasma nozzle of 10 mm. The liquid spray nozzle was made of glass, and the exit of the liquid spray nozzle had an opening diameter of 400 μm. An aerosol of an ORMOCER® liquid was generated by mixing the liquid with nitrogen as a carrier gas. The thus-created aerosol was sprayed in the plasma jet through the liquid spray nozzle. A polycarbonate plate was used as a substrate. The substrate was moved at a velocity of 10 m/min through the plasma jet. The distance g between the substrate surface and the nozzle exit was 20 mm.

[0068] There was observed a 2-fold improvement of the chemical and abrasion resistance in comparison to conventional lacquers. Thereby, the haze determined in accordance with a taber-abraser-test was used as an index of the abrasion resistance, and the chemical resistance was measured in accordance with DIN68861 part 1.

2-step method

[0069] The ORMOCER® liquid is applied with a doctor knife on a PET film having a thickness of 23 μm until a coating thickness of 10 μm was obtained. Then, the substrate with the liquid applied thereon was scanned with a plasma nozzle with the distance between the nozzle exit and the film g being 5 mm at a velocity of 20 m/min, to cure the ORMOCER® and obtaining an inorganic-organic hybrid polymer material coating. The measurement of the Oxygen Transmission Rate (OTR) (in accordance with DIN 53380) was reduced 10-fold in comparison to a corresponding coating, which was cured in a furnace at 120 °C for 2 hours.

Claims

1. A method for coating a substrate (1) with an inorganic-organic hybrid polymer material, the method comprising injecting liquid comprising hybrid inorganic-organic pre-polymers (3) in a plasma jet (2), preferably an atmospheric pressure plasma jet, and exposing a surface of the substrate (1) to said plasma jet (2).

2. The method of Claim 1, wherein the plasma jet (2) is generated by a plasma nozzle (4) having a nozzle exit (5), and the liquid comprising the hybrid inorganic-organic pre-polymers (3) is injected in the plasma jet (2) after leaving the nozzle exit and prior to impinging on the surface of the substrate (1).

3. The method according to Claim 1 or 2, wherein the liquid comprising the hybrid inorganic-organic pre-polymers (3) is injected in the plasma jet through a liquid spray nozzle (6).

4. The method according to Claim 2 or 3, wherein the distance (d) along a parallel to the central axis (11) of the plasma nozzle (4), between the exit of the liquid spray nozzle (6) and the nozzle exit (5) of the plasma nozzle is in the range of 2 to 30 mm, preferably 5 to 15 mm.

5. The method according to any one of Claims 1 to 4, wherein the liquid comprising the hybrid inorganic-organic pre-polymers (3) is injected in the plasma jet in the form of an aerosol.

6. A method for coating a substrate (1) with an inorganic-organic hybrid polymer material, the method comprising the following steps:

   (i) applying liquid comprising hybrid inorganic-organic pre-polymers (3) on a surface of the substrate, and
   (ii) exposing said substrate to a plasma jet (2), which is preferably an atmospheric pressure plasma jet, to cure said hybrid inorganic-organic pre-polymers to give inorganic-organic hybrid polymer material.

7. The method according to Claim 6, wherein the plasma jet used in step (ii) is generated by a plasma nozzle (4), and the substrate (1) with the applied liquid is scanned with said plasma nozzle.

8. The method according to Claim 6 or 7, wherein the distance (g) along a parallel to the central axis (11) of the plasma nozzle (4) between the nozzle exit (5) of the plasma nozzle and the substrate (1) is in the range of 3 to 40 mm,

preferably 3 to 20 mm.

9. The method according to any one of Claims 1 to 8, wherein the hybrid inorganic-organic pre-polymers are obtainable by hydrolytic condensation of one or more hydrolytically condensable compounds of silicon and optionally other elements from the group consisting of B, A1, P, Sn, Pb, the transition metals, the lanthanides, and the actinides, and/or precondensates derived from the above mentioned compounds wherein 10 to 100% by mol, in terms of monomeric compounds, of the hydrolytically condensable compounds are silanes represented by the general formula (I),

$$SiXaR_{4-a} \qquad (I)$$

wherein the groups and indices are the same or different and have the following meanings:

R = optionally substituted alkyl, alkenyl, aryl, alkylaryl, or arylalkyl having 1 to 50 carbon atoms, X = hydrogen, halogen, hydroxy, alkoxy, acyloxy, alkylcarbonyl, alkoxycarbonyl, or NR'_2 with R' = hydrogen, alkyl or aryl; a = 1, 2, or 3.

10. A substrate coated with an inorganic-organic hybrid polymer material (7) that is obtainable by the method according to any one of Claims 1 to 9.

11. The coated substrate (7) of Claim 10, wherein the substrate is a PET substrate and wherein the coated substrate (7) has, for a substrate thickness of 23 μm, an Oxygen Transmission Rate of less than 5 $cm^3/m^2 \cdot d \cdot bar$.

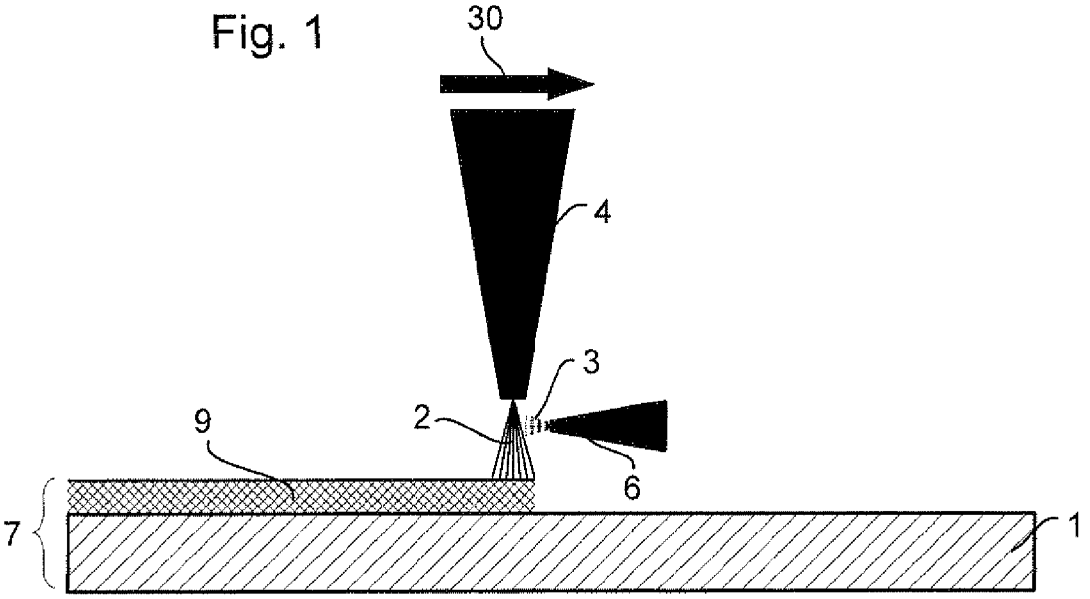
12. A plasma coating apparatus (10) comprising a plasma nozzle (4) having a nozzle exit (5), and a precursor feeding unit arranged downstream of the nozzle exit, **characterized in that** the precursor feeding unit is a liquid spray nozzle (6).

13. The plasma coating apparatus (10) according to Claim 12, **characterized in that** the opening diameter of the exit of the liquid spray nozzle (6) is less than 1 mm.

14. The plasma coating apparatus (10) according to Claim 12 or 13, wherein the liquid spray nozzle (6) is designed so as to be capable of generating an aerosol having a mean droplet size in the range of 0.5 to 100 μm.

15. A use of the plasma coating apparatus (10) according to any one of Claims 12 to 14 in a coating method as defined in any one of Claims 1 to 5.

Fig. 1



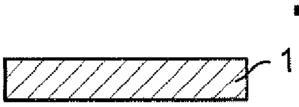


Fig. 2a

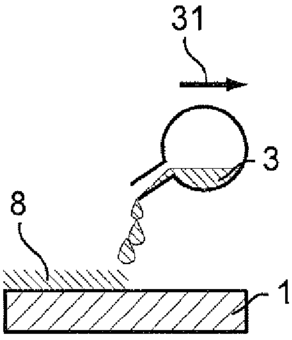


Fig. 2b

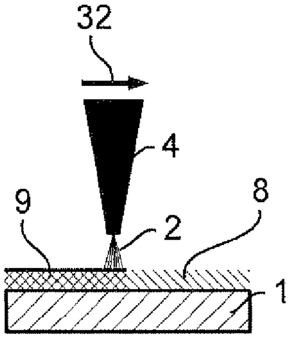
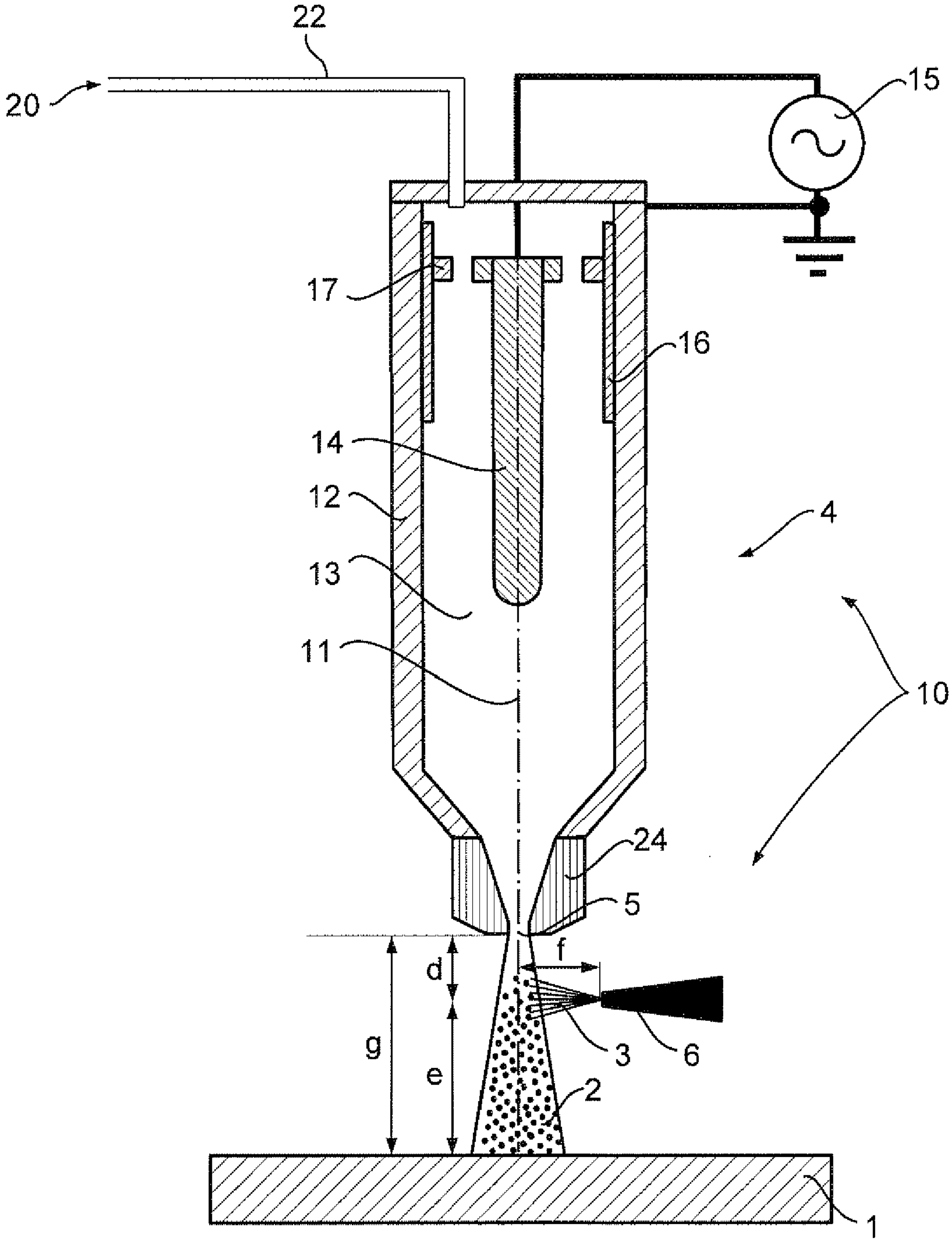


Fig. 2c

Fig. 3



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EUROPEAN SEARCH REPORT

Application Number
EP 09 16 6450

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 10 2006 038780 A1 (FRAUNHOFER GES FORSCHUNG [DE]) 21 February 2008 (2008-02-21) * abstract * * paragraphs [0009], [0014], [0018], [0019], [0026], [0029], [36.42], [0043] * * figure 1 * * claims 1,2,4,6,7 * -----	1-2,4-5, 10-15	INV. B05D7/24 C23C16/513
X	WO 01/40542 A (BOSCH GMBH ROBERT [DE]; GROSSE STEFAN [DE]; VOIGT JOHANNES [DE]) 7 June 2001 (2001-06-07) * abstract * * page 11, paragraph 1 * * page 13, paragraph 2 * * claims 1,3,5-7,14,22 * * figures 1,2 * -----	1-2, 10-11	
X	DE 198 07 086 A1 (FRAUNHOFER GES FORSCHUNG [DE]) 26 August 1999 (1999-08-26) * abstract * * column 1, lines 9-15,37-45,66 - column 2, line 10 * * column 5, lines 13-15 * * column 6, line 8 * * figure 1 * * claims 1,11,12 * -----	1-3, 10-12,15	TECHNICAL FIELDS SEARCHED (IPC) B05D C23C
X	WO 99/20809 A (UNIV CALIFORNIA [US]; BABAYAN STEVE E [US]; SELWYN GARY S [US]; HICKS) 29 April 1999 (1999-04-29) * page 1, lines 1-8 * * page 2, lines 10-15 * * page 3, lines 1-15 * * page 5, lines 6-22 * * figure 1a * * claims 1,3 * ----- -/--	1-2	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	7 December 2009	Riederer, Florian

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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D : document cited in the application
L : document cited for other reasons

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Application Number
EP 09 16 6450

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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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
The Hague	7 December 2009	Riederer, Florian

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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Application Number

EP 09 16 6450

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

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☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION SHEET B

Application Number
EP 09 16 6450

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 6-8,9(part),10(part),11

   A method of coating a substrate, comprising to apply a precursor to a surface of a substrate and subsequently expose the surface to a plasma jet.

   ---

2. claims: 1-5,9(part),10(part),12-15

   A method of coating a substrate, comrising injecting a liquid prepolymer in a plasma jet and expose the surface of the substrate to the plasma jet.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 09 16 6450

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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07-12-2009

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