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(54) Title: PLASMA POLYMER COATINGS

(57) Abstract: The invention relates to the use of a plasma polymer coating as a fire and/or flame retardant coating on the surface of natural and/or synthetic organic materials. The coating results from exposing the surface to plasma of a monomer vapour, in particular of monomers containing halogen and/or phosphor and/or nitrogen and/or silicon, such as fluor containing compounds, phosphor containing compounds, silicon containing compounds, nitrogen containing compounds. The coating can be applied on equipment like windows, textiles, carpets, etc. used in public areas like aircrafts, cinemas, cars, trains, restaurants, etc., by exposing the surface to plasma at a pressure ranging from 10 to 1200 mtorr, for an exposing time length ranging from 30 seconds to 5 hours. The invention also relates to the method of applying the plasma coating and to objects having a fire and/or flame retardant plasma polymer coating.

PLASMA POLYMER COATINGS

The invention relates to polymer coatings resulting from exposing a substrate to plasma polymerization, and in particular to such coatings which provide a protective layer at the surface of the substrate.

Plasma polymerization is a process by which a thin layer of polymeric film is deposited on any surface which is in contact with the plasma of the organic monomer. Depending on the deposition conditions, referred to as the plasma parameters e.g. power, pressure, flow rate, etc., the properties of the film can be adapted to the requirements.

The film is formed at the face surface of a substrate from polymerizable species introduced into a plasma-forming gas. The starting material monomers interact with energetic species, such as electrons, ions or photons, in the gas phase, consequently effecting the breaking of chemical bonds and thus creating free radicals, that then are absorbed at the surface of the substrate, and bond together and polymerize.

Plasma polymerization is a technique that is frequently used for applying a protective layer or film on surfaces, for instance to avoid abrasion or crazing of the surface.

U.S. patent n° 5,569,497 discloses a process for the deposition of a layer or of a protective film onto the

surface of a plastic substrate via plasma polymerization. The process comprises a stage of pretreatment of the plastic substrate wherein the substrate is subjected to a plasma established in a reactor under primary vacuum by electrical discharge in a gaseous medium.

U.S. patent n° 4,096,315 gives a description of a method for providing an anti-abrasion coating for a plastic lens. The substrate is firstly exposed in an evacuated plasma polymerization reactor chamber to a first plasma that forms hydroxyl groups on the lens surface, which is believed to allow good adherence qualities of coatings. The reactor chamber is then evacuated. Subsequently, the substrate in the reactor chamber is exposed to a second or monomer plasma for a predetermined time and at a predermined pressure. The substrate is finally removed from the reactor chamber.

WO 97/31034 describes a method for reducing crazing in plastics material, preferably transparant plastics material where visual clarity is important, which comprises the steps of firstly cleaning the surface by any method which leaves the surface substantially free of any contamination capable of interfering with the adhesion of the plasma polymer coating, and subsequently exposing the cleaned surface to plasma of a monomer vapour as to produce a substantially non-oxidising plasma polymer coating on the surface.

Whereas plasma polymerization is thus known, per se, for providing coatings on various substrates, and in

particular for providing certain protective properties to the surface of plastic materials, it has now been found that certain plasma polymer coatings can be used, in particular, to provide fire retardant and/or flame retardant properties to the surface of organic materials in general.

The subject matter of this invention is therefore the specific use, as a fire and/or flame retardant coating on the surface of natural and/or synthetic organic materials, of a plasma polymer coating resulting from exposing said surface to plasma of a monomer vapour.
For this specific use according to the invention the plasma polymer coating results more in particular from a monomer or mixture of monomers containing halogen and/or, phosphor and/or nitrogen and/or silicon, preferably from precursor gas(es) or liquid(s) selected from fluor containing compounds, phosphor containing compounds, silicon containing compounds, and nitrogen containing compounds .

Particularly suitable halogen containing precursors are for instance CF_4, C_2F_6, C_3F_8, C_3F_6, C_4F_8, C_5F_{12} and C_6F_{14}, and other saturated or unsaturated fluorcarbons and hydrofluorcarbons.

Particularly suitable phospor containing precursors are for instance trimethylphosphate, triethylphosphate and tripropylphosphate and other phosphoric acid derivates.

Particularly suitable silicon containing precursors are for instance hexamethyldisiloxane (HMDSO), polymethylsiloxane, tetraethoxysilan (**TEOS**), tetramethylsilan... (**TMS**) and the like.

Particularly suitable nitrogen containing precursors are for instance ethylamin, triethylamin, allylamin, acrylonitrile and the like

For the specific use according to the invention, the plasma polymer coating will preferably result from exposing the surface of the substrate to be treated to the preferred plasma species at a pressure ranging from 10 to 1200 mtorr, for an exposing time length ranging from 30 seconds to 5 hours.

According to a further aspect of the invention, the plasma polymer coating is more particularly used for equipment, like plastic windows, textiles, carpets, wall coverings, furniture, etc., used in public areas, in particular for equipment for aircrafts, cinemas, cars, trains, restaurants, etc.
The purpose of the coating is to provide sufficient fire and/or flame retardency to increase the available time for evacuation of people from these areas, in case of a starting fire, and even to prevent said equipment from catching fire.

The coatings may very suitably be used on objects made of polyethylene, polypropylene, polystyrene, polymethylmethacrylate, polycarbonate, polyoxymethylene,

polyethylene-terephthalate, polybutylene-terephthalate, elastomers, rubbers, natural or synthetic fibers, etc..

A particularly preferred embodiment of the invention involves the use of a plasma polymer coating resulting from the precursor HMDSO, applied on the surface of a polycarbonate or a polymethylmethacrylate object.

The invention also relates to the method for providing fire and/or flame retardant properties to objects of natural and/or synthetic organic materials, by applying a protective coating on the surface of such objects, by exposing the surface to plasma of a monomer vapour.
The method according to the invention is characterized by the specific precursor monomers used, by the specific substrates treated, and by the specific purpose of the coating prepared.
The specific process steps and operating conditions of the method according to the invention, as well as the typical equipment applied, are well known to those skilled in the art of high frequency (cold) plasma treatment. Reference is made to the general handbooks, publications and patents in this area, in particular to
US patent n° 4,096,315 to
Chan, C.M. : Polymer surface modification and characterization
Hanser 1994, ISBN 3-56990-158-9, and to
Terlingen, Johannes Gijsbertus Antonius
"Introduction of functional groups at polymer surfaces by glow discharge techniques", ISBN 90-9005620-3,

the disclosure of which is incorporated here in by reference.

Typically the power supply for the plasma can work for example with 10-400KHz, 13,56 MHz, 27,16 MHz, 2.45 GHz or other available industrial frequencies. It can also be a pulse-generator. Typical plasma power depends on the size of the system and can be from 50 -10000 Watt.

A suitable process pressure range lies between 10 and 1200 mtorr.

Typically a pressure of 50-500 mtorr is used.

For the process, the substrate is placed somewhere in the plasma chamber. Typically it can be placed somewhere between the electrodes or on one of the electrodes or even in the downstream region of the plasma.

Small pieces are preferably treated in a tumbler system. Woven and nonwoven fabrics and also fibers can be treated in pieces or on a roll-to-roll system.

In the process the substrate is placed in the chamber and the chamber is being pumped down to a base pressure of typically 1 - 200 mtorr. The precursor flow is started to establish a pressure in the range between 10 and 1200 mtorr. The precursor can also be mixed with other gases like noble gases, oxygen, nitrogen, carbon dioxide, hydrocarbons, hydrogene or even with other precursors. Then the plasma is started and the treatment is performed for a time which can be from 30 seconds up to 5 hours.

The process can involve several steps, during which the gas mixture, the pressure, the plasma power, etc. are changed. Prior to the coating step(s) an activation plasma can be applied to the substrate to clean the

surface and obtain a better adhesion of the flame retardant coating.

The invention furthermore relates to objects of natural or synthetic material which have a fire and/or flame retardant surface coating consisting of a plasma polymer coating, in particular resulting from a precursor monomer or a mixture of precursor monomers containing halogen and/or phosphor and/or nitrogen and/or silicon.

Preferred plasma polymer coatings result from a precursor monomer or a mixture of precursor monomers selected from fluor containing compounds and/or, phosphor containing compounds and/or silicon containing compounds and/or nitrogen containing compounds.

Preferred objects according to the invention are those mainly made of polyethylene, polypropylene, polystyrene, polymethylmethacrylate, polycarbonate, polyoxymethylene..., polyethyleneterephthalate, polybutyleneterephthalate, elastomers, rubbers and natural or synthetic fibers.

Most preferred objects according to the invention are objects mainly made of polycarbonate or polymethylmetracrylate, having a plasma polymer coating mainly resulting from HMDSO as monomer precursor.

Further features and specific aspects of the invention, as well as the use thereof, will become apparent from the following examples, describing preferred embodiments of the invention in mor detail. It should be observed that the specific aspects of these examples are only set forth as an explanation of what is ment in the context of the above general disclosure of the invention, and should not

be interpretted as a limitation of the scope of the invention as such and as expressed in the claims and the end of this specification.

EXAMPLE 1

Method of providing a plasma coating on the surface of aircraft windows to increase their flame retardant properties.

For applying said coating on an aircraft window, made from polymethylmethacrylate or Polycarbonate, the window is placed in the process chamber of a plasma system equipment type CD600 or CD1000, which are manufactured and distributed by EUROPLASMA, Oudenaerde. After pumping down the chamber to base pressure, a gas, for example argon or oxygen is introduced and a plasma is ignited for 2 minutes to preclean and activate the window surface. Afterwards, the chamber is pumped down again and the precursor HMDSO is introduced, mixed with Argon. The plasma is started again. After 5 minutes, the Argon flow is replaced by oxygen flow in 3 steps, thus changing the properties of the coating stepwise.

The complete coating treatment needs 20 minutes.

In case of an accident with a fire starting on the outside, the coating increases the available evacuation time for the passengers to leave the plane, before the fire reaches the the inside of the plane (« burn-through-time »).

EXAMPLE 2

Characterisation of the coating properties.

X-Ray Photoelectron Spectroscopy (XPS) was used to characterise the structure and chemical composition of the coating surfaces. Scanning Electron Microscopy (SEM) was used for the coating topography characterisation.

Atomic Force Microscopy (AFM) was used for the measurement of the thickness of the coating.

EXAMPLE 3

Measurement of the fire retardant properties.

The fire resistance properties of the objects of example 1 are measured by exposing the treated surface to an open flame and measuring the time, until the object catches fire and/or the flame reaches the backside of the object (« burn-through-time »).

Fire resistance is measured by means of a small Bunzen brander test and a big bunzen brander to evaluate the resistance against heat of a direct flame and heat generated by a flame on a distance of 30 cm. The tests used are existing tests and a prenorm test for burn through evaluation.

EXAMPLE 4

The coatings can be used for carpets, textiles, wallpapers to increase their inflamability. Said coatings increase the evacuation time for public areas like restaurants, discos etc. in case of a fire.

C L A I M S

1. Use, as a fire and/or flame retardant coating on the surface of natural and/or synthetic organic materials, of a plasma polymer coating resulting from exposing said surface to plasma of a monomer vapour.

2. Use of a plasma polymer coating according to claim 1, **characterised in that** the plasma polymer coating results from a monomer or mixture of monomers containing halogen and/or phosphor and/or nitrogen and/or silicon.

3. Use of a plasma polymer coating according to claim 2, **characterised in that** the monomer(s) result from precursor gas(es) or liquid(s) selected from fluor containing compounds and/or phosphor containing compounds and/or silicon containing compounds and/or nitrogen containing compounds

4. Use of a plasma polymer coating according to claim 3, **characterised in that** the monomer(s) result from precursor(s) selected from CF_4, C_2F_6, C_3F_6, C_3F_8, C_4F_8, C_5F_{12} and C_6F_{14} or other saturated or unsaturated fluorcarbons or hydrofluorcarbons.

5. Use of a plasma polymer coating according to claim 3, **characterised in that** the monomer(s) result from precursor(s) selected from trimethylphosphate,

triethylphosphate and tripropylphosphate or other derivates of phosphoric acid.

6. Use of a plasma polymer coating according to claim 3, **characterised in that** the monomer(s) result from precursor(s) selected from hexamethyldisiloxane (HMDSO), polymethylsiloxane, tetraethoxysilan (TEOS), tetramethylsilan (TMS) and other siloxanes or silanes.

7. Use of a plasma polymer coating according to claim 3, **characterised in that** the monomer(s) result from precursor(s)selected from ethylamin, triethylamin, allylamin, acrylonitrile and the like

8. Use of a plasma polymer coating according to any one of the preceding claims, **characterised in that** the plasma polymer coating results from exposing said surface to plasma at a pressure ranging from 10 to 1200 mtorr, for an exposing time length ranging from 30 seconds to 5 hours.

9. Use of a plasma polymer coating according to any one of the preceding claims, for equipment used in public areas like aircrafts, cinemas, cars, trains, restaurants, etc.

10. Use of a plasma polymer coating according to claim 9 for aircraft windows.

11. Use of a plasma polymer coating according to any one of the preceding claims for objects made of polyethylene, polypropylene, polystyrene, polymethylmethacrylate, polycarbonate, polyoxymethylene, polyethyleneterephthalate, polybutyleneterephthalate, elastomers, rubbers and natural or synthetic fibers.

12. Use of a plasma polymer coating according to any one of the preceding claims, **characterised in that** the plasma polymer coating results from the precursor HMDSO, applied on the surface of a polycarbonate object or a polymethylmethacrylate object.

13. Use of a plasma polymer coating according to any one of the preceding claims, **characterised in that** the plasma polymer coating results from the precursor C_3F_6, applied on the surface of a polycarbonate object or a polymethylmethacrylate object.

14. Use of a plasma polymer coating according to any one of the preceding claims, **characterised in that** the plasma polymer coating results from the precursor triethylphosphate, applied on the surface of a polycarbonate object or a polymethylmethacrylate object.

15. A method for providing fire and/or flame retardant properties to objects of natural and/or synthetic organic materials by applying a protective coating on the surface of said objects, **characterised in**

that said coating is applied on said surface by exposing it to plasma of a monomer vapour so as to produce a plasma polymer coating.

16. Object of natural or synthetic material with a fire and/or flame retardant surface coating, **characterised in that** the coating consists of a plasma polymer coating resulting from a precursor monomer or a mixture of precursor monomers containing halogen and/or , phosphor and/or nitrogen and/or silicon.

17. Object according to claim 16, **characterised in that** the coating consists of a polymer resulting from a precursor monomer or a mixture of precursor monomers selected from fluor containing compounds and/or phosphor containing compounds, and/or silicon containing compounds, and/or nitrogen containing compounds.

18. Object according to any one of claims 16 and 17, **characterised in that** the object is mainly made of polyethylene, polyplropylene, polystyrene, polymethylmethacrylate, polycarbonate, polyoxymethylene, Polyethyleneterephthalate, polybutyleneterephthalate, elastomers, rubbers and natural or synthetic fibers.

19. Object according to any one of claims 16 to 18, **characterised in that** the object is mainly made of polycarbonate or polymethylmetracrylate, and the

plasma polymer coating mainly results from HMDSO or C_3F_6 or triethylphosphate as monomer precursor.

INTERNATIONAL SEARCH REPORT

rnational Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B05D7/24 C09K21/14

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B05D C09K

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	column 4, line 17 -column 5, line 17 column 1, line 53-67 column 6, line 9-13 column 8, line 1 column 9, line 65-67	4,6,7, 12,13
Y	EP 0 985 740 A (PROCTER & GAMBLE) 15 March 2000 (2000-03-15) page 2, line 38-58 page 4, line 26-30 page 3, line 32-35	4,13

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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