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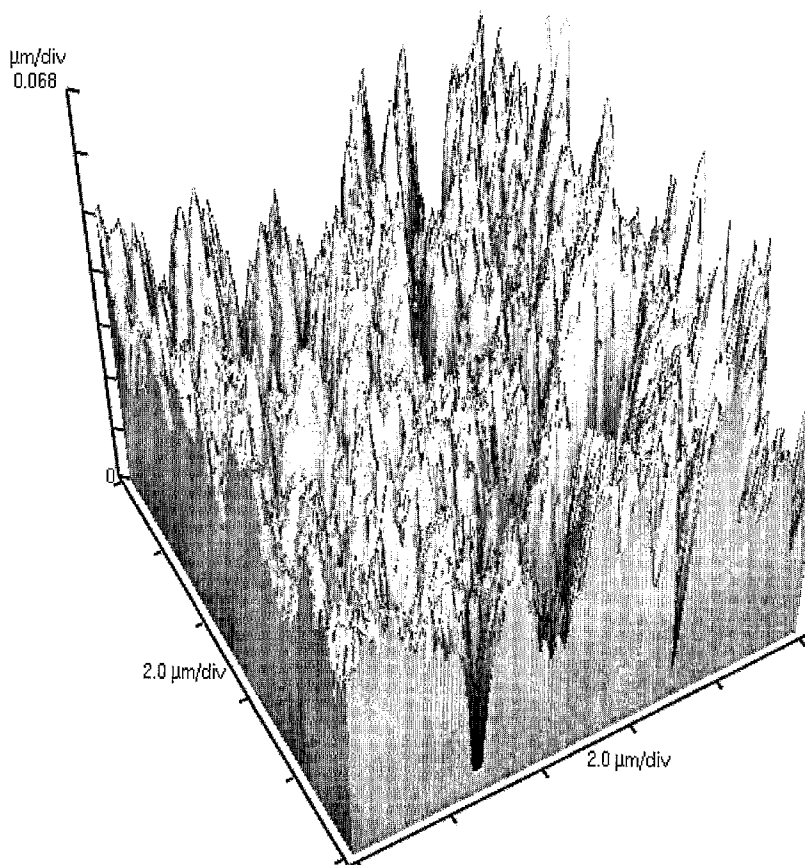
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(54) Title: USE OF POSS NANOSTRUCTURED MOLECULES FOR HYDROPHOBIC AND SELF CLEANING COATINGS



(57) Abstract: Hydrophobic coatings and processes for applying same will provide solid surfaces with high contact angles, low adhesion to water drops, and dirt repellent characteristics. The hydrophobic/self cleaning coatings are made by using of POSS, polyhedral oligomeric silsesquioxane compounds or polymers with or without the addition of a chemically hydrophobic or hydrophilic carrier and/or microstructuring agents.

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USE OF POSS NANOSTRUCTURED MOLECULES FOR HYDROPHOBIC AND SELF CLEANING COATINGS

FIELD OF THE INVENTION

5 This invention relates to hydrophobic and self cleaning coatings comprising POSS, (polyhedral oligomeric silsesquioxane compounds or polymers), with or without the addition of a carrier and/or microstructuring agents and to process for the preparation of a product coated by the same.

10 BACKGROUND OF THE INVENTION

Solid surfaces can be classified depending in their contact angle as any of the following: a. hydrophilic surfaces, which are pertained to attraction for water, are readily wetted by liquids and have a contact angle smaller than 90° . If the contact angle approaches zero, the surface is considered as ultra-hydrophilic; and b. hydrophobic surfaces, i.e. water repelling surfaces
15 that do not wet easily by liquids and have a contact angle larger than 90° . If the contact angle exceeds 150° the surface is considered as ultra-hydrophobic.

Hydrophilic and hydrophobic coatings have been used to coat surfaces, reduce adhesion, repel dirt and to make the surfaces easier to clean.

20

Hydrophilic coatings are based mainly on a hydrophilic TiO_2 thin film deposited by different methods usually on a glass surface. The coating is photoactive and photo-degrades a wide range of "dirt" as bacteria, viruses, etc. The main drawback of hydrophilic coatings is the short lifetime. The TiO_2 photo-catalytic effect diminishes with time giving a lifetime of 1 to 5
25 years.

Hydrophobic coatings are mainly silicon or fluorinated coatings. Silicone coatings are mostly based on organosiloxane polymers (polysiloxanes). These are hybrid material composed of pendant organic groups attached to an inorganic siloxane backbone like polydimethylsiloxane
30 (PDMS). Polysiloxanes typically achieve low free surface energy around 22-23 dyne/cm and contact angles ranging from 90° to 100° .

Fluorinated coatings have a very low surface energy (18 dyne/cm) are resistant to chemicals and present good thermal stability. Polytetrafluoroethylene (Teflon) coatings show contact angles close to 110° .

- 5 However, these types of coatings, while achieve some characteristics of water repelling and easy clean effect, present limited hydrophobicity and are far from being classified as self-cleaning surfaces.

10 Self cleaning surfaces exist in nature. In the beginning of the 1980s the botanist Wilhelm Barthlott discovered the "Lotus Effect". The Lotus flower is revered as a symbol of purity in Asian religions. Even when rising from muddy waters it stays clean and untouched by pollution. The mechanism of self-cleaning as seen in nature works by two main actions: first a self-cleaning surface must be hydrophobic so water drops will roll off and cannot evaporate in the surface, leaving no stains; and second, dirt particles do not adhere to the self-cleaning
15 surface and will be removed away by the sliding droplet.

To achieve this natural self-cleaning effect, the Lotus flower presents two basic features: a. an ultra-hydrophobic surface chemistry, i.e the Lotus has a contact angle greater than 150° and b. a special nanometric morphology that acts like a "Fakir bed" reducing the contact area of
20 the water drop to the surface, thus reducing the adhesion forces between them and allowing the water drop to slide down the Lotus leaf surface and clean the dirt upon it.

This invention aims to mimic nature's self cleaning mechanism, mainly the fact that while a high contact angle between the liquid and the solid is desirable, the most important feature for
25 a good self-cleaning surface is having a low sliding or rolling angle i.e. the angle at which a solid surface must be tilted so that a liquid drop will slide or roll down the tilted surface. A surface with a high contact angle does not always necessary show a low sliding angle. Murase et al. (Murase, H. and Fujibayashi, T. 1997, Characterization of Molecular Interfaces in hydrophobic Systems. Prog. Org. Coat.; 31: 97-104) have conducted extensive research
30 regarding the relationship of contact and sliding angles for polymer surfaces. They showed that a fluoropolymer with a contact angle of 117° has a higher sliding angle than PDMS with a contact angle of 95.8° . Even if a surface has a high contact angle the self-cleaning effect

will not be effective if the water drops do not slide or roll upon its surface to take dirt with them.

Up to date, methods for producing hydrophobic self cleaning coatings were found complicated. Furthermore the resulted coatings are unstable and their lifetime is very limited. Up to this date, no practical long-lasting commercial successful application has been achieved.

SUMMARY OF THE INVENTION

- 10 In an embodiment of the invention. there is provided a coating comprising a Polyhedral Oligomeric Silsesquioxane (POSS) nanostructuring agent, which comprises at least one functional hydrophobic group, wherein the POSS is dispersed in a suitable solvent, a hydrophobic or in a hydrophilic curable carrier composition.
- 15 In another embodiment of the invention, the coating of the invention may further comprise a microstructuring agent (MS agent) dispersed in same hydrophobic or hydrophilic curable carrier composition.

In some embodiments of the invention, there is provided a process for producing a coated product comprising the following steps: contacting a coating according to the embodiments of the invention onto a product substrate; and drying or curing the coating. The coating may contain one layer, two layers or three layers, wherein the layers may be identical or different. If the coating contain more than one layer, upon solidification of the first layer a second layer is added and cured or dried. In case of a coating, which includes three layers, upon the solidification of the second layer, a third layer is then added and is cured or dried.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 demonstrates one layer coating containing POSS in a solvent.

- 30 Figure 2 demonstrates one layer coating containing POSS in a Hydrophobic or Hydrophilic Curable Carrier Composition (H-Carrier).

Figure 3 demonstrates one- layer coating containing POSS and Microstructuring Agents (MS-Agent) in a Hydrophobic or Hydrophilic Curable Carrier Composition (H-Carrier).

5 Figure 4 demonstrates two- layers coating containing POSS in a solvent in the inner layer and a Hydrophobic Curable Carrier Composition (H-Carrier) as a cap layer (outer layer).

10 Figure 5 demonstrates two- layers coating containing Microstructuring Agents (MS-Agent) in a Hydrophobic or Hydrophilic Curable Carrier Composition (H-Carrier) in the inner layer and POSS in a Hydrophobic or Hydrophilic Curable Carrier Composition (H-Carrier) as a cap layer (outer layer).

15 Figure 6 demonstrates three layers coating containing Microstructuring Agents (MS-Agent) in a Hydrophobic or Hydrophilic Curable Carrier Composition (H-Carrier) in the inner layer, POSS in a solvent in an intermediate second layer, and Hydrophobic Curable Carrier Composition (H-Carrier) as a cap third layer (outer layer).

Figure 7 depicts an Atomic Force Microscope (AFM) topographic image obtained for an uncoated polycarbonate substrate.

20 Figure 8 depicts an AFM topographic image obtained for the polycarbonate substrate coated with a fluoroalkylsilane coating

Figure 9 depicts an AFM topographic image obtained for the polycarbonate substrate coated as in Example 3.

25

Figure 10 depicts a magnified photography of a 5 microliter water drop on an ultrahydrophobic surface such as described in Example 5.

30 Figure 11 depicts an AFM topographic image obtained for the polycarbonate substrate coated as in Example 5.

Figure 12 is a simplified illustrative flow chart of a method for forming one- layer coating for better an illustration for a better understanding of some embodiments of the invention

Figure 13 is a simplified illustrative flow chart of a method for forming two- layers coating, wherein the second layer is H-carrier coating for better an illustration for a better understanding of some embodiments of the invention

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Figure 14 is a simplified illustrative flow chart of a method for forming two-layers coating for better an illustration for a better understanding of some embodiments of the invention

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Figure 15 is a simplified illustrative flow chart of a method for forming three- layers coating for better an illustration for a better understanding of some embodiments of the invention

DETAILED EMBODIMENTS OF THE INVENTION

This invention relates to the use of POSS, polyhedral oligomeric silsesquioxane compounds
15 or polymers, taking advantage of their intrinsic molecular cage-like nanostructure and their hybrid organic-inorganic nature, for the production of a coating, with or without the addition of a chemically hydrophobic or hydrophilic carrier. The coating of the invention may further comprise a microstructuring agent. In an embodiment of the invention a one-layer nanostructured coating is formed on the substance. In another embodiment a multilayered
20 (micro and nanostructured) surface is formed, resembling the Lotus plant surface, that imparts hydrophobicity and reduces the adhesion to water drops and/or dirt, so the surfaces become water and dirt repellent as well as self cleaning.

The term "silsesquioxane" refers hereinabove to silicon structures having the empirical
25 formula $\text{RSiO}_{3/2}$. R can be hydrogen or carbon moieties, such as aryl or alkyl fragments with or without unsaturation and can contain functionalities such as amino or epoxy groups. The multifunctional nature of the silsesquioxane allows for a variety of structures such as oligomeric full or partial cages, ordered ladder structures or three dimensional networks. A special group of the silsesquioxane family is the Polyhedral Oligomeric Silsesquioxanes
30 (POSS). POSS present two unique features: a. a hybrid chemical composition ($\text{RSiO}_{1.5}$) intermediate between silica (SiO_2) and silicone (R_2SiO) and b. a physically large, cage-like, intrinsic nano-structured molecular structure. Therefore, POSS can be defined as intrinsically nano-structured organic-inorganic compounds. POSS are single molecules of nanoscopic

size, larger than small molecules but smaller than macromolecules, ranging from 0.7 to 50 nm, having a well defined three-dimensional polyhedral structure. Unlike silica and modified clays, each POSS molecule may contain covalently bonded functional groups . POSS molecules are tailorable, meaning that these functional groups can be varied and changed to give different properties to the molecule. In one embodiment, nonreactive organic functional groups can be used for solubility and compatibility. In another embodiment, reactive functional groups suitable for polymerization and grafting can be added to attach POSS monomers to polymer chains. The basic form is the POSS molecular silica containing a robust SiO core surrounded by non-reactive organic groups, which permits the inorganic core to be compatible with an organic matrix. These kind of molecules can be used as nanocomposites with molecular level dispersion. Molecular level dispersion, if possible, allows for a higher filler concentration without negatively affecting the processing conditions and the physical properties of the matrix (e.g. viscosity, transparency and mechanical properties). Different functional groups may be added to this basic form to give POSS functionalized monomers such as without limitation: alcohols, phenols, alkoxysilanes, amines, chlorosilanes, halides, acrylates and methacrylates, epoxides, esters, nitriles, olefins, phosphines, silanes, silanols, thiols and fluoroalkyls. POSS functional monomers may contain between one to various reactive organic groups.

Functional groups can render POSS molecules, which are hydrophobic or hydrophilic making them suitable for mixing with hydrophobic or hydrophilic carriers, respectively. If the POSS molecule is mainly hydrophobic, a hydrophobic carrier may be more appropriate to improve dispersion of the particles. Conversely, if the POSS molecule is mainly hydrophilic, a hydrophilic carrier is required for an efficient dispersion.

In an embodiment in which a POSS nanotexturing agent comprises various functional groups some hydrophobic and some hydrophilic, the POSS may be mixed with an hydrophilic carrier, wherein the hydrophilic groups in the POSS are used to obtain good mixing and dispersion of the POSS in the hydrophilic carrier, while its hydrophobic groups render the surface hydrophobicity by surface segregation .

By the term "surface segregation" it is meant that the natural thermodynamic tendency of hydrophobic groups is to segregate to the surface so as to lower the surface energy as much as possible.

5 In an embodiment of the invention, "the POSS functional hydrophobic group" may be without being limited: alkyl, fluoroalkyl, fluoroalkylsilane, alkylsilane, siloxane, di-methyl siloxane, disilazane, alkyldizilazane or any modification or combination thereof.

10 In another embodiment of the invention "the POSS functional hydrophilic group" may be without being limited, an alcohol, epoxy, urethane, acrylate, thiol or any modification or combination thereof.

In another embodiment of the invention, the POSS component may comprise one or more covalently bonded reactive groups.

15

In an embodiment of the invention, the covalently bonded reactive group is without being limited, hydroxyl, epoxy, urethane, acrylate, metha-acrylate, vinyl, amino or any modification or combination thereof, wherein the reactive group reacts with the substrate surface or enhance the coating-substrate adhesion.

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In another embodiment of the invention, the POSS used may be POSS polymers and resins in which the cage structures have been incorporated into an organic polymer structure. These are polymers in which a POSS functionalized cage has been copolymerized or grafted as a pendant group onto a polymer chain such PDMS or methylacrylate or of a silsesquioxane resin possessing some cage structure. POSS cages act as hard blocks in the polymer structure. The polymers can be either thermoplastic or thermosets. They can be used as stand-alone polymers, compounded or solution blended into traditional polymeric materials.

25

The term "copolymer" or any variation thereof refers to a material formed by polymerizing a mixture of two (or more) different starting monomers.

30

In another embodiment of the invention, the polymer in which the POSS is copolymerized or grafted, is a curable polymer.

The term "cure" or any variations thereof (curable) refers in this application to a process of hardening of the coating (by cross-linking of the molecular structure), by employing heat, air, moisture or radiation.

5

In another embodiment of the invention, the curable polymer is without being limited a polydimethylsiloxane, a polyacrylate, a polyurethane, an epoxy, an amino resin, a phenolic resin, a polyester, or a polyimide or any combination, modification and/or mixture thereof.

10 In another embodiment of the invention the POSS is a POSS polymer or POSS grafted copolymer.

In an embodiment of the invention, there is provided a hydrophobic coating comprising a Polyhedral Oligomeric Silsesquioxanes (POSS) nanostructuring agent containing at least one
15 functional hydrophobic group, the POSS dispersed in a suitable hydrophobic or hydrophilic solvent.

By at least one functional hydrophobic group, it is meant that at least one of the possible functional groups is hydrophobic while the rest may be hydrophobic or hydrophilic. At least
20 one hydrophobic functional group is needed to render a hydrophobic surface by surface segregation of the group. Hydrophilic groups may be required when the POSS nanotexturing agent is added to a hydrophilic solvent or carrier.

By a suitable solvent it is meant that causes a good dispersion of the POSS component and
25 produces an efficient free flowing, low viscosity, liquid coating.

In an example without limitation, Trifluoro(3)cyclo-pentyl-POSS, $C_{50}H_{93}F_{39}O_{12}Si_{10}$ (FL0590 Hybridplastics, USA) is dissolved in α,α,α , trifluorotoluene solvent.

30 In an embodiment of the invention, there is provided a hydrophobic coating comprising a POSS nanostructuring agent comprising at least one functional hydrophobic group, wherein the POSS is dispersed in a hydrophobic or hydrophilic curable carrier composition.

In another embodiment Trifluoro(3)cyclo-pentyl-POSS, $C_{50}H_{93}F_{39}O_{12}Si_{10}$ (FL0590 Hybridplastics, USA) is mixed with commercial curable fluoroalkylsilane formulation: tridecafluorooctyltry-ethoxysilane in i-propanol.

- 5 In another embodiment of the invention, Fluoro(13)disilanolisobutyl -POSS, $C_{38}H_{75}F_{13}O_{12}Si_8$ (FL0569 Hybridplastics, USA) is mixed in with commercial curable fluoroalkylsilane formulation: tridecafluorooctyltry-ethoxysilane in i-propanol.

- 10 In another embodiment of the invention, the POSS added to the solvent or to the H-carrier may be a physical mixture of different POSS compounds or polymers carrying different functional groups.

- In another embodiment of the invention there is provided a hydrophobic coating comprising:
15 (a) a POSS nanostructuring agent containing at least one hydrophobic functional group, wherein the POSS is dispersed in a hydrophobic or hydrophilic curable carrier composition; and (b) a hydrophobic or hydrophilic microstructuring agent dispersed in a hydrophobic or hydrophilic curable carrier composition. The curable carrier composition can be identical or different.

- 20 The term "nanostructuring agent" refers to a material that causes a structure or texture with roughness in the nanometric range (one nanometer: on billionth of a meter). The term "microstructuring agent" or MS agent refers to a material that causes a structure or texture with roughness in the micrometric range.

- 25 In another embodiment of the invention, the hydrophobic curable carrier composition comprises at least one hydrophobic chemical moiety, which may be without being limited, an alkyl, fluoroalkyl, fluoroalkylsilane, alkylsilane, siloxane, di-methyl siloxane, disilazane, alkyldizilazane or any modification or combination thereof.

- 30 By the term "modification" it is meant a molecular substitution on the chemical moieties contained in the curable carrier or in the functional groups in the POSS. By "combination" is meant a curable carrier or POSS, which contain different moieties.

In another embodiment of the invention, the hydrophilic curable carrier composition comprises at least one hydrophilic chemical moiety, which, may be without being limited, an alcohol, epoxy, urethane, acrylate, thiol or any modification or combination thereof.

- 5 In another embodiment of the invention, the H-carrier may be a physical mixture of different H-carriers carrying different hydrophobic or hydrophilic chemical moieties.

In another embodiment of the invention, the amount of POSS is in a concentration of 0.1% to 20% by weight in an organic solvent.

10

In another embodiment of the invention, the amount of POSS is in a concentration of 0.1% to 20% by weight in a curable carrier composition.

15 In another embodiment of the invention, the microstructuring agent may be without being limited, a precipitated silica, unprecipitated silica, hydrophilic fumed silica, hydrophobic fumed silica, colloidal silica, treated colloidal silica, silicate, treated silicate, PTFE micropowder, metal nanopowder, metal oxide, inorganic nanopowder, oxide, sulfide, nanoclay, hyperbranched polymer or bohemite or any modification thereof.

- 20 In another embodiment of the invention, the microstructuring agent has a particle or agglomerate size ranging from 0.1 to 50 micrometers.

In another embodiment of the invention, the microstructuring agent is in a concentration 0.1% to 20% by weight in the curable carrier.

25

In another embodiment of the invention the microstructuring agent may be a physical mixture of different microstructuring agents.

30 When the POSS particles and microstructuring agents are properly dispersed in a transparent curable carrier, the resulting coating is transparent.

By "properly dispersed" or "dispersed" it is meant that the POSS and the microstructuring agent particles are dispersed in a way where no agglomerations or particle clusters are formed

that may disturb the transmission or diffuse the light (Example 4 and 5). Proper dispersion may be achieved by mechanical stirring or any other methods known in the art.

5 In another embodiment of the invention, there is provided a process for producing a hydrophobic and nanostructured one-layer coated product as represented in Figure 1, comprising the following steps: preparing a coating comprising POSS nanostructuring agent containing at least one functional hydrophobic group, wherein the POSS is dispersed in a suitable hydrophobic or hydrophilic solvent; contacting the coating onto a product and drying the coating.

10

In an embodiment of the invention, the term "drying" refers to a physical process which involves the evaporation of solvents without breaking or creating chemical bonds.

15 In another embodiment of the invention, there is provided a process for producing a hydrophobic and nanostructured one-layer coated product as represented in Figure 2, comprising the following steps: preparing a coating comprising a POSS nanostructuring agent comprising at least one functional hydrophobic group, wherein the POSS is dispersed in a hydrophobic or hydrophilic curable carrier composition; contacting the coating onto a product substrate; and curing the coating.

20

In another embodiment of the invention, there is provided a process for producing a hydrophobic and nanostructured one-layer coated product as represented in Figure 3, comprising the following steps: preparing a coating which comprises : (a) a POSS nanostructuring agent containing at least one hydrophobic functional group, wherein the POSS is dispersed in a hydrophobic or hydrophilic curable carrier composition; and (b) a microstructuring agent dispersed in a hydrophobic or hydrophilic curable carrier composition, wherein the curable carrier composition can be identical or different; contacting the coating onto a product substrate and curing the coating.

30 In another embodiment of the invention, there is provided a process for producing a hydrophobic and nanostructured two-layer coated product as represented in Figure 4, comprising the following steps: preparing a coating comprising POSS nanostructuring agent, wherein the POSS is dispersed in a suitable solvent; contacting the coating onto a product

substrate; drying the coating; contacting a second layer of a hydrophobic curable coating to cap the first layer; and curing the product.

In another embodiment of the invention, there is provided a process for producing a hydrophobic and nanostructured two-layer coated product as represented in Figure 5, comprising the following steps: preparing a coating comprising a microstructuring agent dispersed in a hydrophobic or hydrophilic curable carrier composition; contacting the coating onto a product substrate; curing the product; preparing a coating comprising a POSS nanostructuring agent containing at least one functional hydrophobic group, the POSS dispersed in a hydrophobic or hydrophilic curable carrier composition so as to produce a second layer; contacting the second layer to the first layer; and curing the product .

In another embodiment of the invention, there is provided a process for producing a hydrophobic and nanostructured three-layer coated product as represented in Figure 6, comprising the following steps: preparing a coating comprising a microstructuring agent dispersed in a hydrophobic or hydrophilic curable carrier composition; contacting the coating onto a product substrate; curing the coating; preparing a coating comprising POSS nanostructuring agent , the POSS dispersed in a suitable solvent as a second layer; contacting the second layer onto the first layer; and drying the product; applying a third layer of a hydrophobic curable coating to cap the second layer; and curing the product.

In an embodiment of the invention the step of curing, is by air-curing, moisture-curing, thermal curing or radiation curing.

Reference is now made to Figures 1-6, which represent different one, two and three layers coatings in accordance to some embodiments of the present invention.

Numerical 10 describes the substrate which may be without being limited a: glass, a polymer, a ceramic, a metal, wood, concrete, textiles or leather.

In an embodiment of the invention the substrate may be without being limited, a transparent polymer, a polycarbonate, a polymethylmethacrylate, a polyethyleneterephthalate, a polyethylenetherftalateglycol, a polysulphone or any modification, combination, copolymer and/or blend thereof.

Numeral 20 describes a coating comprising POSS and a solvent in accordance to some embodiments of the invention.

5 Numeral 40 describes a coating layer comprising POSS and H- carrier in accordance to some embodiments of the invention

Numeral 60 describes a coating layer comprising POSS, MS agent and H- carrier in accordance to some embodiments of the invention.

Figure 1 -3 describe a substrate coated with one-layer coating which may be for example coated with numerals 20, 40 or 60.

10 Figures 4 and 5 describe substrate coated with two- layers coating according to some embodiments of the invention. Please note that the first layer of figure 4 is as numeral 20, while the second coating (numeral 80) includes H-carrier. In Figure 5, the first layer (numeral 90) includes MS agent and H- carrier whereas the second coating includes POSS and H-carrier.

15 Figure 6 describes substrate coated with three-layers coating, according to some embodiments of the invention. Please note that Figure 6 includes numeral 90 as the first layer, numeral 20 as the second and numeral 80 as the third. Practically, each or all of the layers may be substituted by another coating as describe in the invention.

20 Reference is now made to Figures 12-15, which are simplified illustrative flow chart of a method coating with the coatings of the invention in accordance to some embodiments of the present invention.

25 Numeral 100 describes the step of coating a substance with any of the coating of the invention.

Numeral 300 describes the step of drying the coating.

Numeral 200 describes the step of curing the coating by any of the methods described above.

30 Figure 12 describes the process for producing a one-layer coated substrate comprising a Polyhedral Oligomeric Silsesquioxanes (POSS) nanostructuring agent, which comprises at least one functional hydrophobic group, wherein said POSS is dispersed in a suitable solvent, a hydrophobic or in a hydrophilic curable carrier composition, optionally, the coating comprises a microstructuring agent, by coating (numeral 100) and curing (numeral 200).

Figure 13 describes the process for producing two-layer coated substrate comprising a Polyhedral Oligomeric Silsesquioxanes (POSS) nanostructuring agent, which comprises at least one functional hydrophobic group, wherein said POSS is dispersed in a suitable solvent, a hydrophobic or in a hydrophilic curable carrier composition by coating (numeral 100) and curing (numeral 200) or drying (numeral 300) the coating. Next, after the solidification of the first layer of coating, a second layer of coating (Numeral 100), which may be H-carrier is added followed by a step of curing (numeral 200).

Figure 14 describes the process for producing two-layer coated substrate comprising the steps of coating (numeral 100) by a coating which comprises a microstructuring agent and curing (numeral 200). Next, after solidification of the first layer of coating a second step of coating (numeral 100) which includes POSS is performed followed by a step of curing (numeral 200) or drying (numeral 300)..

Figure 15 describes the process for producing three-layer coated substrate comprising the steps of coating (numeral 100) by a coating which comprises a microstructuring agent (numeral 90) and curing (numeral 200). Next, after solidification of the first layer of coating a second step of coating (numeral 100) by a Polyhedral Oligomeric Silsesquioxanes (POSS) nanostructuring agent, which comprises at least one functional hydrophobic group, wherein said POSS is dispersed in a suitable solvent, a hydrophobic or in a hydrophilic curable carrier composition is performed followed by a step of curing (numeral 200) or drying (numeral 300). After solidification of the second layer, a third layer is produced by coating (numeral 100) with H-carrier coating (numeral 80) and curing (numeral 200) the coating.

In an embodiment of the invention, the POSS particles and microstructuring agents are dispersed in a transparent curable carrier resulting in transparent coatings; these coatings are further applied in one or more layers on said transparent substrates resulting in a transparent coated product (Examples 4 and 5).

In order to understand the invention, embodiments of the invention will be now described, in which the effect of a coating made of POSS mixed in an solvent or curable carrier

composition will be demonstrated and compared to a similar coating which does not include POSS.

While the invention has been described with respect to a limited number of embodiments, it will be appreciated that many variations, modifications and other applications of the invention may be made which are within the scope and spirit of the invention.

EXAMPLES

Experimental Procedures:

Measurement of the static contact angle:

The static contact angle was measured according to the sessile drop method using a commercial video based, software controlled, contact angle analyzer (OCA 20, Dataphysics Instruments GmbH, Germany). Deionized and ultra-filtered water (0.2 μm filter) was used for the measurements. For contact angle characterization a 5 μl water drop was used. The sliding angle was measured using a tilting unit (TBU90E, Dataphysics Instruments GmbH, Germany) incorporated into the contact angle analyzer. A drop was first deposited on the horizontal substrate and after equilibrium the substrate plane was tilted at a rate of $100^\circ/\text{min}$ until the onset of drop motion. The sliding angle was found to vary with drop volume and was measured as a function of water drop volume. For the sliding angle characterization a 30 μl drop was used. The contact and sliding angles were measured using video-based software (SCA 20, Dataphysics Instruments GmbH, Germany).

Evaluation of the coating transparency:

To evaluate the coatings transparency, light transmission (LT) and light diffusion (Haze) were measured using a Hazemeter (BYK Gardner, Germany). The surface morphology was investigated by atomic force microscope (AFM, Veeco, USA) in the non-contact mode. Surface region analysis was performed and surface roughness was characterized quantitatively by the root mean square (RMS) roughness and qualitatively by AFM topography images.

Example 1:

Three percents by weight (3 wt%) of Fluoro(13)disilanolisobutyl -POSS, $C_{38}H_{75}F_{13}O_{12}Si_8$ (FL0569 Hybridplastics, USA) was mixed in with commercial fluoroalkylsilane formulation: tridecafluorooctyltry-ethoxysilane in i-propanol (Dynasytan F8263, Degussa, Germany). Mixing was performed for five minutes using a high speed homogenizer. Transparent Polycarbonate samples were completely submerged in the formulation for a period of three minutes. After dipping, samples were removed from the container, dried and cured in an air-drying oven for 120 minutes at a temperature of $110^{\circ}C$. The coated substrate with POSS containing coating was compared to the same substrate coated with the fluoroalkylsilane formulation only (without POSS) and measurements were made: the addition of POSS resulted in an increase of the contact angle from 89.3° to 107.9° and a reduction on the sliding angle from 38° to 27° for a $30 \mu l$ water drop. As the volume of the water drop was reduced it came to a point that it will not roll from the surface of the solid surface even when this is tilted into a completely vertical angle (90°). For the fluoroalkylsilane coated sample (without POSS) this minimum drop volume was $10 \mu l$, while for the POSS containing coated sample the minimum drop volume was $5 \mu l$. This coating renders high light transmission but also diffuses the light. The light transmission was measured to be 93.9%, which is similar to the one measured for the plain polycarbonate before coating (92.6%). The light diffusion (haze) was measured as 22.4% which is higher than the haze measured for the plain polycarbonate before coating (0.5%).

Example 2:

Three percents by weight (3 wt%) of Trifluoro(3)cyclo-pentyl-POSS, $C_{50}H_{93}F_{39}O_{12}Si_{10}$ (FL0590 Hybridplastics, USA) was mixed with commercial fluoroalkylsilane formulation: tridecafluorooctyltry-ethoxysilane in i-propanol (Dynasytan F8263, Degussa, Germany). Mixing was performed for two hours using a magnetic stirrer. Transparent Polycarbonate samples were completely submerged in the formulation for a period of three minutes. After dipping, the samples were removed from the container, dried and cured in an air-drying oven for 120 minutes at a temperature of $110^{\circ}C$. The coated substrate with POSS containing coating was compared to the same substrate coated with the fluoroalkylsilane formulation

only (without POSS) and measurements were made. The addition of POSS to the coating resulted in an increase of the contact angle from 89.3° to 107.8° and a reduction on the sliding angle from 38° to 15° for a $30\ \mu\text{l}$ water drop. As the water drop volume was reduced it came to a point that it will not roll from the surface of the solid even when this is tilted completely vertical (90°). For the fluoroalkylsilane only coated sample (without POSS) the minimum drop volume was $10\ \mu\text{l}$, while for the POSS containing coated sample the minimum drop volume was $3\ \mu\text{l}$. This coating renders highly light transmission but also diffuses the light. The light transmission was measured to be 94.1% which is similar to the one measured for the plain polycarbonate before coating (92.6%). The haze measured was 19.9% which is higher than the haze measured for the plain polycarbonate before coating (0.5%).

Example 3:

Three percents by weight (3 wt%) of Trifluoro(3)cyclo-pentyl-POSS, $\text{C}_{50}\text{H}_{93}\text{F}_{39}\text{O}_{12}\text{Si}_{10}$ (FL0590 Hybridplastics, USA) was dissolved in α,α,α , trifluorotoluene organic solvent. Mixing was performed for two hours using a magnetic stirrer. Transparent Polycarbonate samples were completely submerged in the formulation for a period of ten seconds and dried at room temperature.. The coated substrate with POSS containing coating was compared to the same substrate coated with the fluoroalkylsilane formulation only (without POSS) and measurements were made, The POSS coated sample resulted in an increase of the contact angle from 89.3° to 110.0° and a reduction on the sliding angle from 38° to 8° for a $30\ \mu\text{l}$ water drop. As the water drop volume was reduced it came to a point that it will not roll from the surface of the solid even when this is tilted completely vertical (90°). For the fluoroalkylsilane coated sample (without POSS), the minimum drop volume was $10\ \mu\text{l}$, while for the POSS containing coated sample the minimum drop volume was $1\ \mu\text{l}$. Figure 7 depicts an Atomic Force Microscope (AFM) topographic image obtained for an uncoated polycarbonate substrate. The root mean square (RMS) roughness as measured by the AFM for the polycarbonate substrate is very low: 1.51 nm, which indicates a smooth surface. Figure 8 depicts an AFM topographic image obtained for the polycarbonate substrate coated with the fluoroalkylsilane coating only (no POSS). The RMS roughness measurement for this sample was also very low: 3.1 nm. Figure 9 depicts the AFM topographic image obtained for the polycarbonate substrate coated as in Example 3. The RMS roughness for this sample was 14.5 nm showing good nanometric dispersion of the POSS additive. This coating rendered

highly clear and transparent products. The light transmission was 93.9%, which is similar to the one measured for non coated polycarbonate (92.6%). The Haze was 5.9%.

Example 4:

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Half percent by weight (0.5 wt%) Hydrophilic Fumed Silica (Aerosil 200, Degussa, Frankfurt, Germany) and (1.5 wt%) Fluoro(13)disilanol-isobutyl-POSS, $C_{38}H_{75}F_{13}O_{12}Si_8$ (FL0569 Hybridplastics, USA) were dissolved in isopropyl alcohol organic solvent. Mixing was performed for two hours using a magnetic stirrer. Transparent Polycarbonate samples were completely submerged in the formulation for a period of one minute and dried in a drying oven for one hour at 120⁰C. The coating rendered a very hydrophobic surface on the polycarbonate sample. The water contact angle was 130⁰. The sliding angle was 64⁰ for a 5 μ l water drop. This coating rendered highly clear and transparent products. The light transmission was measured to be 90.0%, which is similar to the one measured for the plain polycarbonate before coating (92.6%). The haze was 7.5%.

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Example 5:

Half percent by weight (0.5 wt%) Hydrophilic Fumed Silica (Aerosil 200, Degussa, Frankfurt, Germany) was dissolved in isopropyl alcohol organic solvent. Mixing was performed for two hours using a magnetic stirrer. Transparent Polycarbonate samples were completely submerged in the formulation for a period of one minute and dried in a drying oven for one hour at 120⁰C. The coated sample was coated by a second layer, which was formed as follows: half percent by weight (1.5 wt%) Fluoro(13)disilanol-isobutyl-POSS, $C_{38}H_{75}F_{13}O_{12}Si_8$ (FL0569 Hybridplastics, USA) was dissolved in isopropyl alcohol organic solvent. Mixing was performed for two hours using a magnetic stirrer. The coated Polycarbonate samples were completely submerged in the second formulation for a period of one minute and dried in a drying oven for one hour at 120⁰C.

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The double coating resulted in an ultrahydrophobic surface on the polycarbonate sample. The measured water contact angle was close to 180⁰ i.e. the water drop stayed almost completely spherical (neglecting some gravitational deformation) as can be seen in Figure 10. In this ultrahydrophobic sample, the water drop virtually jumped on the sample surface and rolled off although the surface was in horizontal position (sliding angle approximately 0⁰). Figure

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11 depicts AFM topographic image obtained for the polycarbonate substrate coated as in Example 5. The RMS roughness for this sample was 60 nm showing nanostructured morphology. This coating rendered highly clear and transparent products. The light transmission was measured to be 90.0% which is similar to the one measured for the non-
5 coated polycarbonate (92.6%). The haze was 5.0%.

What is claimed is:

1. A coating comprising a Polyhedral Oligomeric Silsesquioxanes (POSS) nanostructuring agent, which comprises at least one functional hydrophobic group, wherein said POSS is dispersed in a suitable solvent, a hydrophobic or in a hydrophilic curable carrier composition.
2. The coating of claim 1 further comprises a microstructuring agent dispersed in same solvent, hydrophobic or hydrophilic curable carrier composition.
3. The coating of claim 1, wherein the POSS particles are dispersed into the solvent, hydrophobic or hydrophilic carrier which is transparent so as to form a transparent coating.
4. The coating of claim 2, wherein POSS particles and the microstructuring agent particles are dispersed into the solvent, hydrophobic or hydrophilic carrier which is transparent so as to form a transparent coating.
5. A process for producing a coated product comprising the following steps: contacting a coating according to any of the claims 1 or 2 onto a product substrate; and drying or curing said coating.
6. A process for producing a two-layers coated product comprising the following steps:
 - contacting a coating according to any of the claims 1 or 2 onto a product substrate;
 - drying or curing said coating;
 - contacting a second layer of a hydrophobic curable coating onto the first layer; and
 - curing the product.
7. A process for producing a two-layers coated product comprising the following steps:
 - Preparing a coating comprising a microstructuring agent dispersed in a suitable solvent or in a hydrophobic or hydrophilic curable carrier composition;
 - contacting said coating onto a product substrate;
 - drying or curing the coating;
 - contacting a coating according to any of the claims 1 or 2 onto the first layer; and
 - drying or curing the product.

8. A process for producing a three-layers coated product comprising the following steps:
Preparing a coating comprising a microstructuring agent dispersed in a suitable solvent or in a hydrophobic or hydrophilic curable carrier composition;
contacting said coating onto a product substrate;
drying or curing the coating;
contacting a coating according to any of the claims 1 or 2 so as to produce a second coating layer;
drying or curing the coating;
contacting a third layer of a hydrophobic curable coating to cover the second layer; and
curing the product.
9. A coating according to any of the claims 1 or 2, wherein the POSS functional hydrophobic group is an alkyl, fluoroalkyl, fluoroalkylsilane, alkylsilanes, siloxane, di-methyl siloxane, disilazane, alkyldizilazane or any modification or combination thereof.
10. A coating according to any of the claims 1 or 2, wherein the POSS functional hydrophilic group is an alcohol, epoxy, urethane, acrylate, thiol or any modification or combination thereof.
11. A coating according to any of the claims 1 or 2, wherein the POSS comprises one or more covalently bonded reactive groups such as hydroxyl, epoxy, urethane, acrylate, methacrylate, vinyl, amino or any modification or combination thereof.
12. A coating according to any of the claims 1 or 2, wherein the POSS is a POSS polymer or a POSS grafted copolymer.
13. The coating of claim 12, wherein said POSS grafted polymer is a thermoplastic, or a curable polymer such as polydimethylsiloxane, polyacrylate, polyurethane, epoxy, amino resin, phenolic resin, polyester, or polyimide.
14. A coating according to any of the claims 1 or 2, wherein the POSS is a physical mixture of different POSS compounds or polymers carrying different functional or reactive groups.

15. A coating according to any of the claims 1 or 2, wherein the amount of POSS is between 0.1% to 20% by weight in the organic solvent, hydrophobic or hydrophilic curable carrier composition.
16. A coating according to any of the claims 1 or 2, wherein the hydrophobic curable carrier composition contains at least one hydrophobic moiety which is an alkyl, fluoroalkyl, fluoroalkylsilane, alkylsilane, siloxane, di-methyl siloxane, disilazane, alkylidizilazane, or any modifications or combinations thereof.
17. A coating according to any of the claims 1 or 2, wherein the hydrophilic curable carrier composition contains at least one hydrophilic moiety which is an alcohol, an epoxy, a urethane, an acrylate, a thiol or any modification or combination thereof.
18. A coating according to any of the claims 1 or 2, wherein the hydrophobic or hydrophilic curable carrier composition is a physical mixture of different hydrophobic or hydrophilic curable compositions carrying different moieties.
19. A coating according to claim 2 wherein the microstructuring agent is a precipitated silica, unprecipitated silica, hydrophilic fumed silica, hydrophobic fumed silica, colloidal silica, treated colloidal silica, silicates, treated silicates, PTFE micropowder, metal nanopowders, metal oxides, inorganic nanopowders, oxides, sulfides, nanoclays, hyperbranched polymers or bohemite or any modifications or combinations thereof.
20. A coating according to claim 2, wherein the microstructuring agent is a physical mixture of different microstructuring agents.
21. A coating according to claim 2, wherein the microstructuring agent has a particle or an agglomerate size ranging from 0.1 to 50 micrometers.

22. A coating according to claim 2, wherein the microstructuring agent is in a concentration of between 0.1% to 20% by weight in the hydrophobic or hydrophilic curable carrier composition.

Figure 1

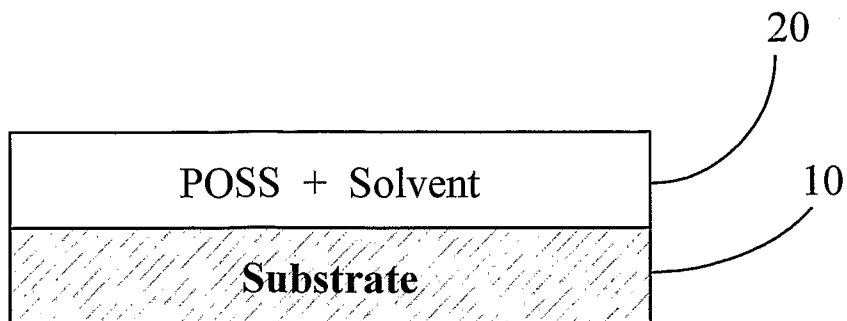


Figure 2

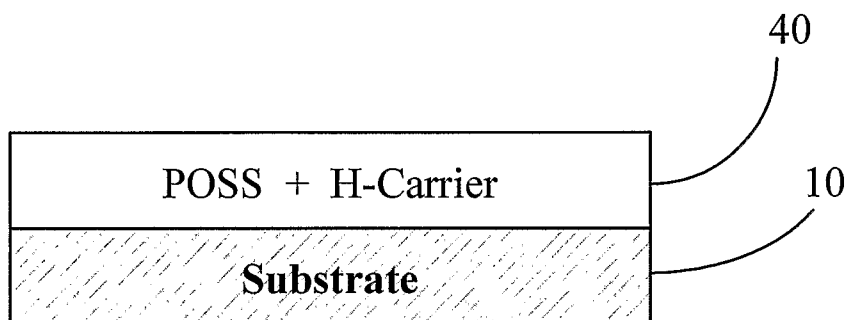


Figure 3

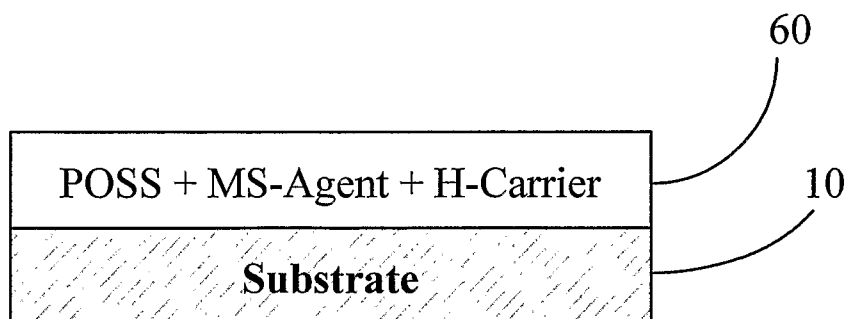


Figure 4

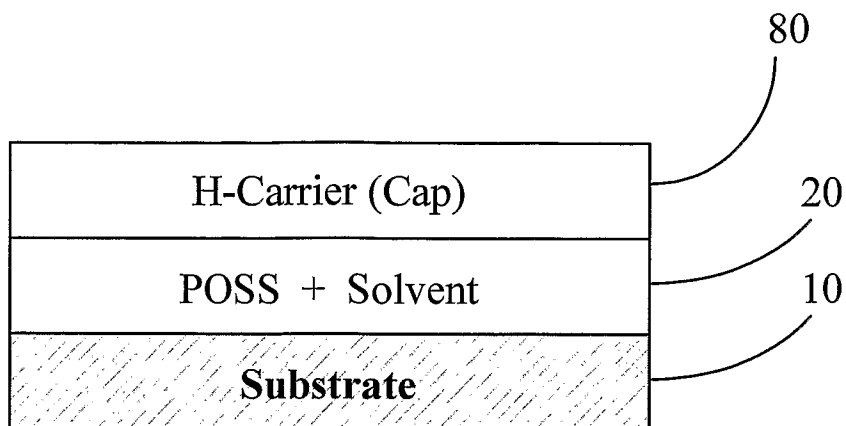


Figure 5

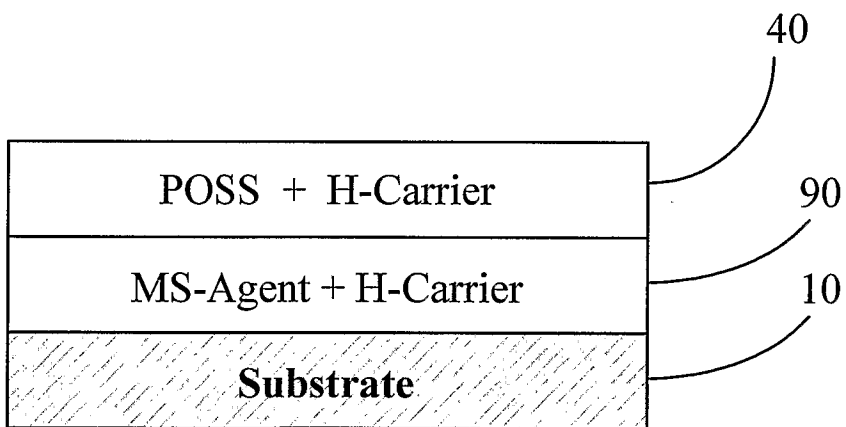


Figure 6

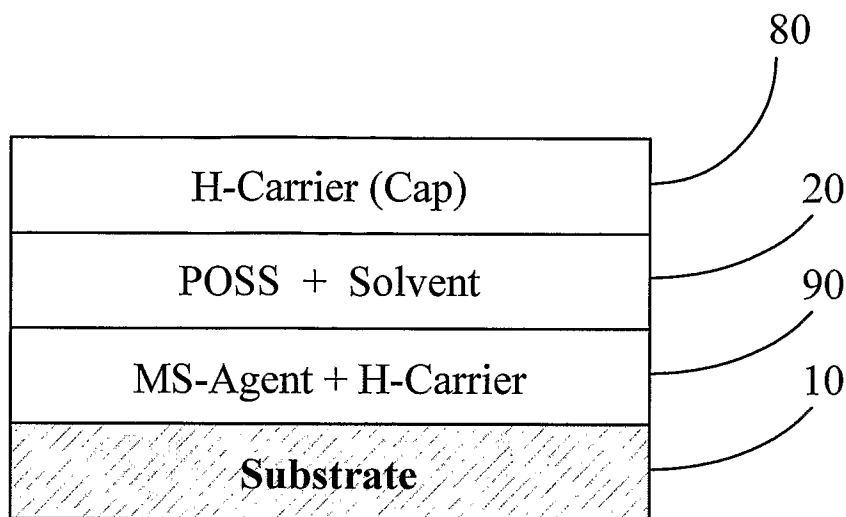


Figure 7

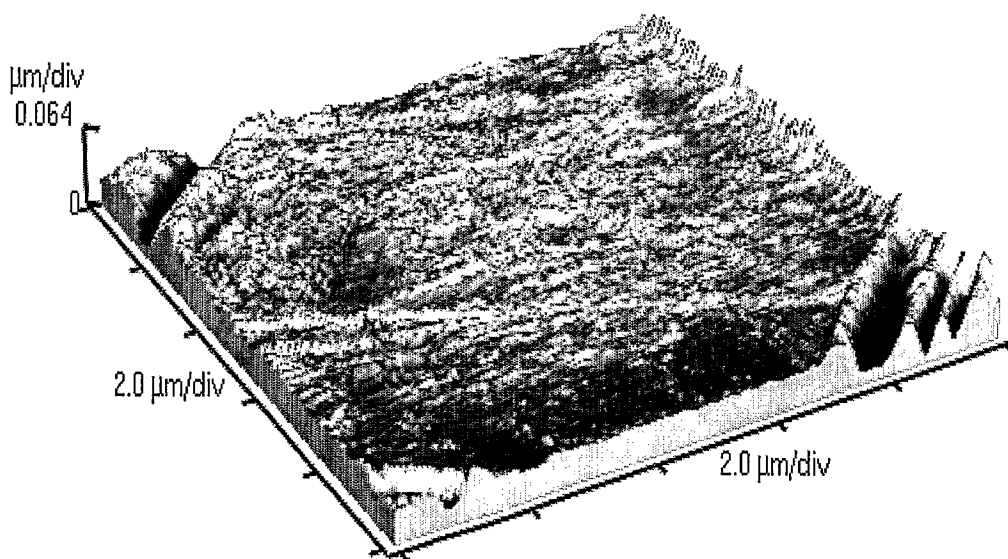


Figure 8

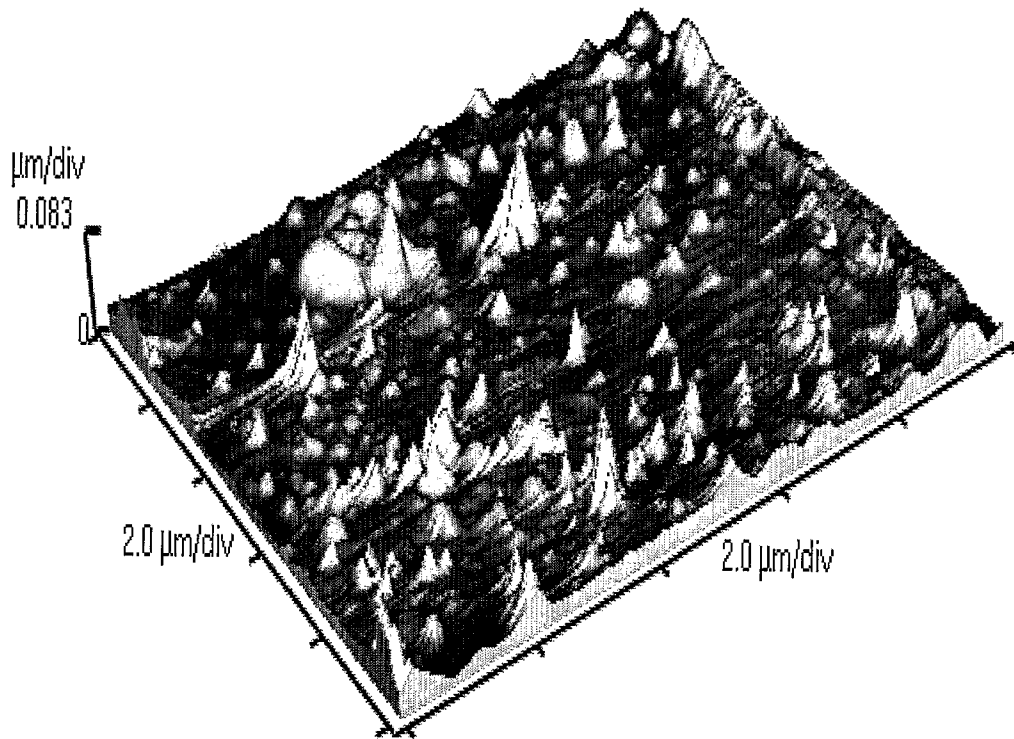


Figure 9

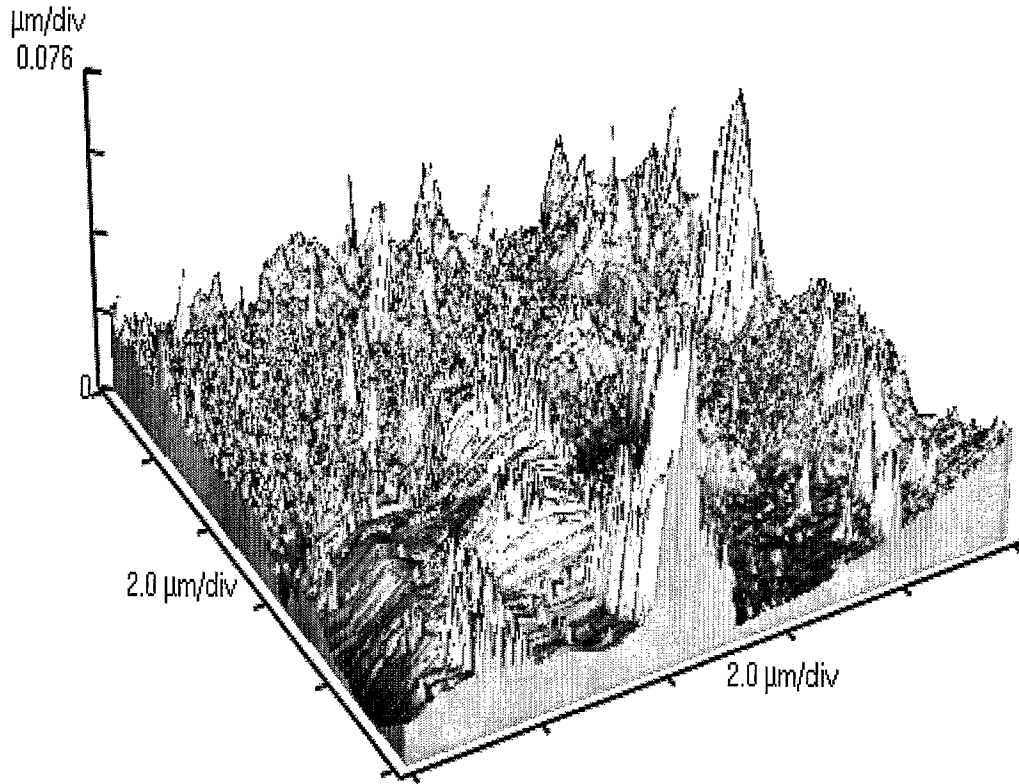


Figure 10

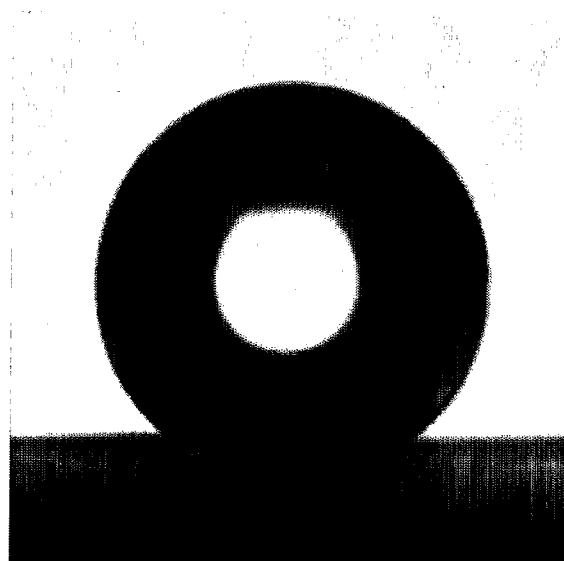


Figure 11

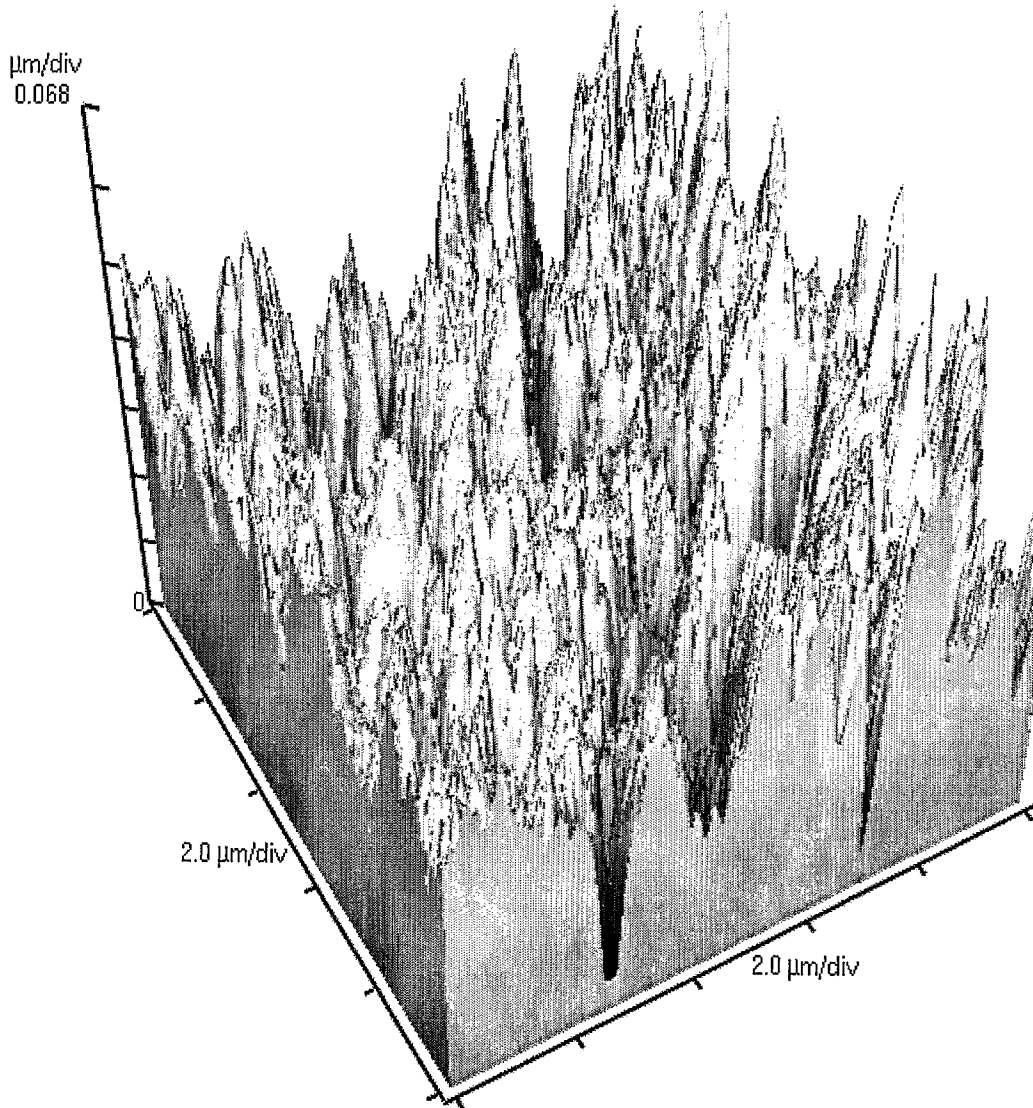


Figure 12

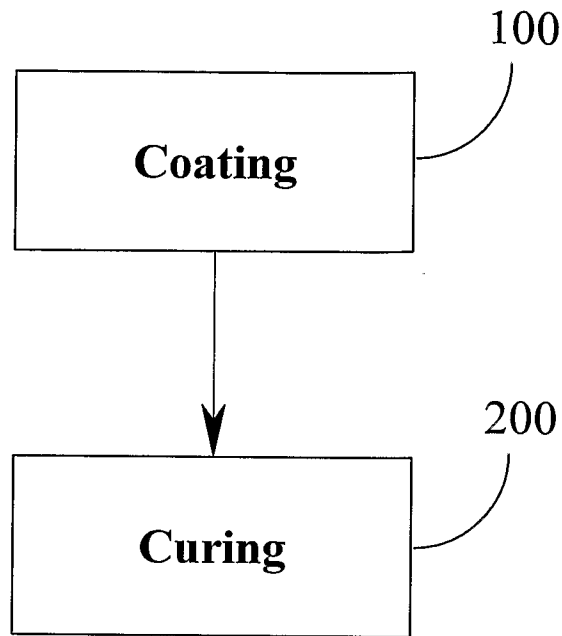


Figure 13

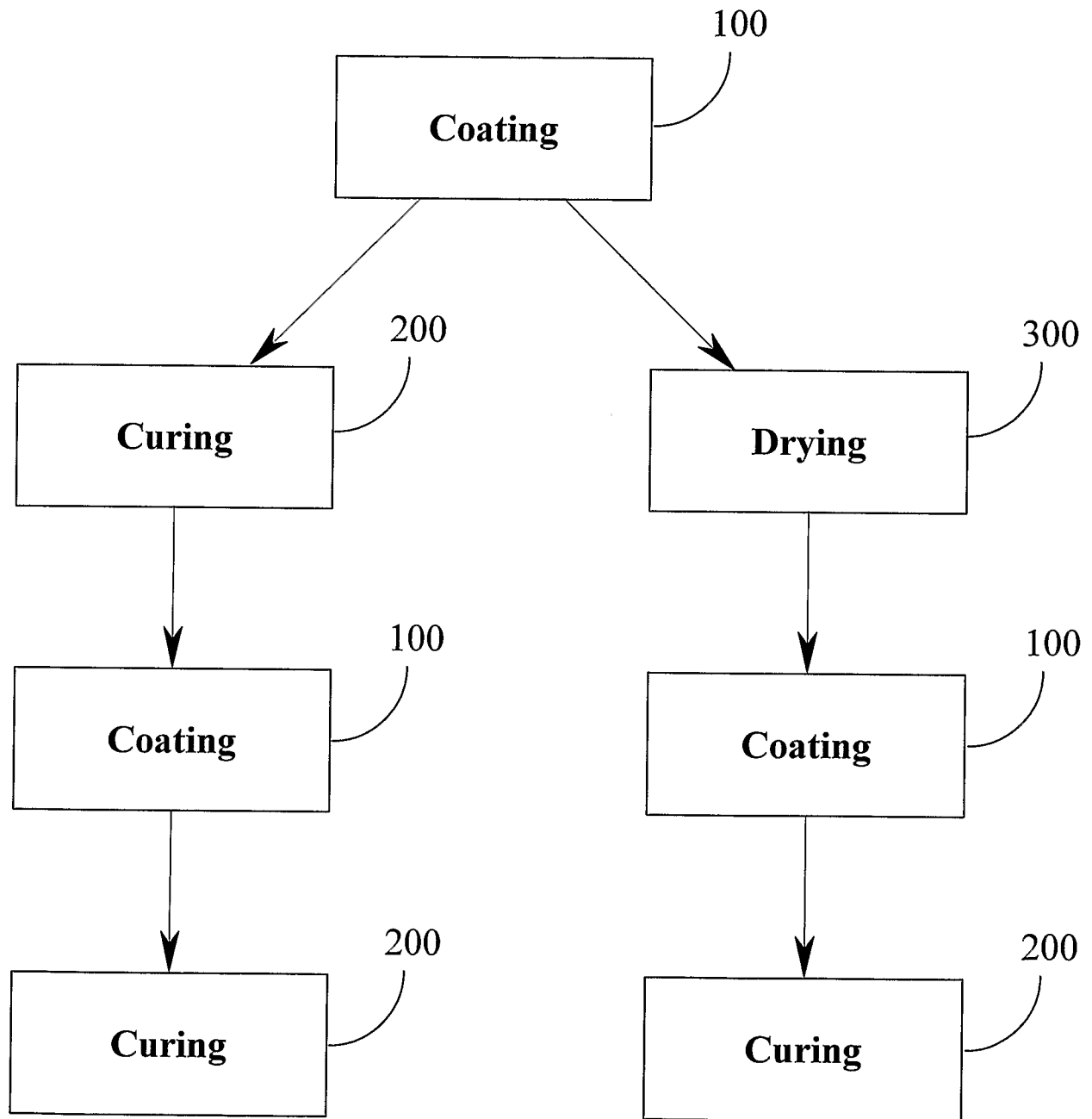


Figure 14

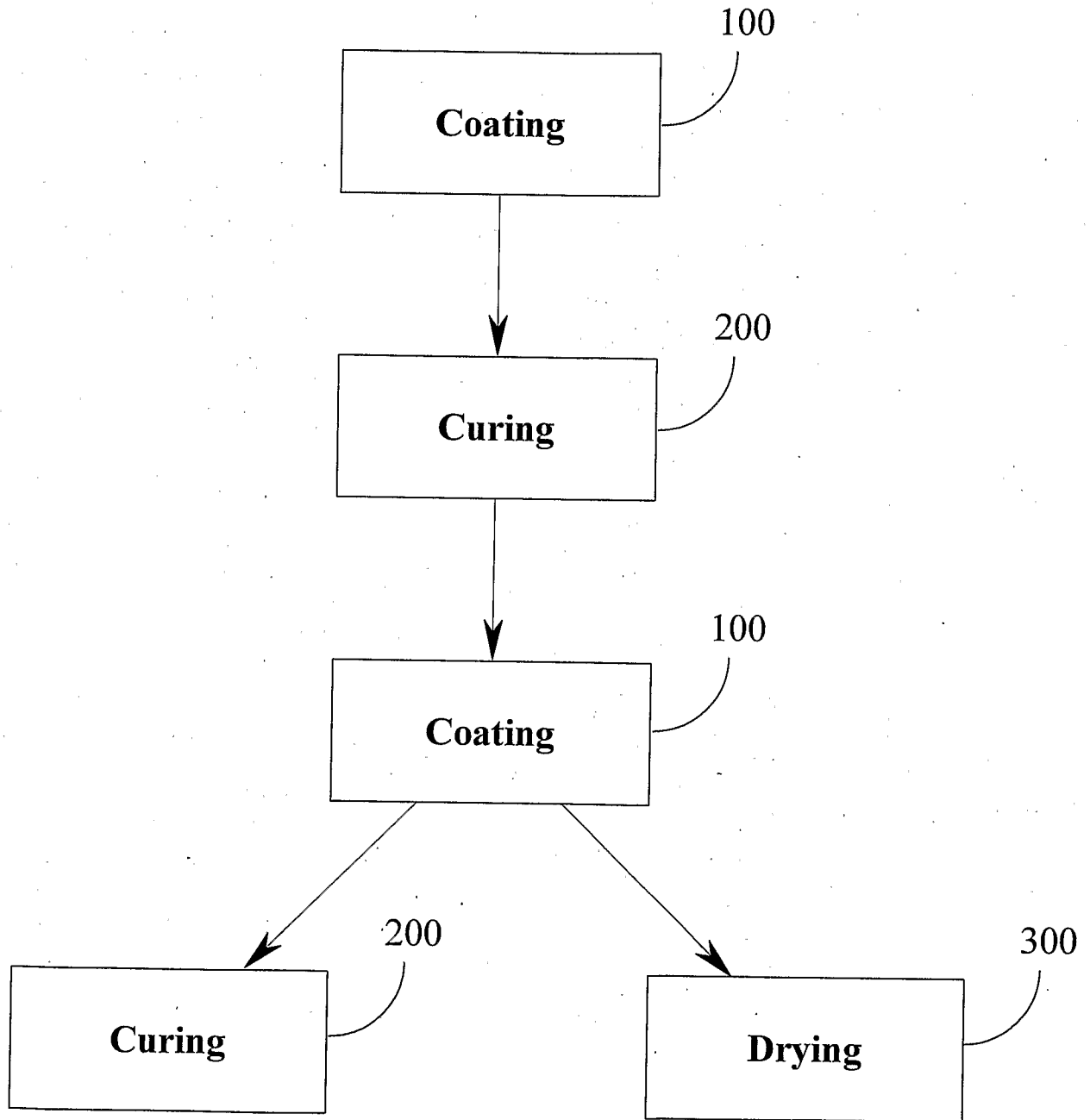


Figure 15

