

(19)



(11)

**EP 2 754 618 A1**

(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 153(4) EPC

(43) Date of publication:

**16.07.2014 Bulletin 2014/29**

(51) Int Cl.:

**B65D 25/14** <sup>(2006.01)</sup>      **B65D 65/40** <sup>(2006.01)</sup>  
**B32B 27/06** <sup>(2006.01)</sup>      **A47G 19/02** <sup>(2006.01)</sup>

(21) Application number: **12829733.0**

(86) International application number:

**PCT/KR2012/007177**

(22) Date of filing: **06.09.2012**

(87) International publication number:

**WO 2013/036042 (14.03.2013 Gazette 2013/11)**

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB  
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO  
PL PT RO RS SE SI SK SM TR**

- **JO, Kyoung Sik**  
**Seoul 158-774 (KR)**
- **LEE, Jin Hwan**  
**Ansan-si**  
**Gyeonggi-do 425-020 (KR)**
- **YUN, Tae Kyung**  
**Seoul 138-902 (KR)**
- **LEE, Kwang Ryeol**  
**Seoul 137-060 (KR)**
- **MOON, Myoung Woon**  
**Seoul 136-130 (KR)**
- **KIM, Seong Jin**  
**Seoul 151-847 (KR)**

(30) Priority: **08.09.2011 KR 20110091338**

(71) Applicants:

- **CJ Cheiljedang Corporation**  
**Jung-gu**  
**Seoul 100-400 (KR)**
- **Korea Institute of Science and Technology**  
**Seoul 136-130 (KR)**

(74) Representative: **Mounteney, Simon James**

**Marks & Clerk LLP**  
**90 Long Acre**  
**London**  
**WC2E 9RA (GB)**

(72) Inventors:

- **SONG, Eun Kyung**  
**Goyang-si**  
**Gyeonggi-do 411-764 (KR)**

(54) **FOOD CONTAINER HAVING NANOSTRUCTURED HYDROPHOBIC SURFACE AND MANUFACTURING METHOD THEREOF**

(57) The present invention relates to a food container made of a plastic material and having a nano-structured hydrophobic surface, including: a plurality of nano-structures formed on a surface of the food container; and a first hydrophobic thin film coated on an upper side of the surface, on which the nano-structures are formed, and a

manufacturing method thereof. According to the present invention, it is possible to provide the food container having the nano-structured hydrophobic surface capable of having excellent gas blocking performance, as well as hydrophobicity, and the manufacturing method thereof.

**EP 2 754 618 A1**

**Description****[Technical Field]**

5 **[0001]** The present invention relates to a food container and a manufacturing method thereof, and more particularly, to a food container having a nano-structured hydrophobic surface having hydrophobicity and a gas blocking property, and a manufacturing method thereof.

**[Background Art]**

10 **[0002]** Recently, a food container, which is used for storing food and the like, is mainly formed of a plastic material, such as polypropylene (PP) or polyethylene terephthalate (PET) by reason of manufacturing easiness and a low cost.

**[0003]** A plastic material having relatively low surface energy is a hydrophilic material having a contact angle of 50 to 80° with respect to pure water.

15 **[0004]** A fact that a surface has hydrophilicity means that the surface prefers a contact with water to a contact with air, and water attached to the surface has a wide contact area with the surface and is not well separated from the surface. That is, food is stably attached to the surface.

**[0005]** In a case where an attachment degree of food is high, a stain is generated on a surface of the food container even after the food is removed, and further, there is a problem in that food residue is left on the surface of the food container by the stable contact between the surface of the food container and the food.

20

**[Disclosure]****[Technical Problem]**

25 **[0006]** An object of the present invention is to provide a food container having a nano-structured hydrophobic surface capable of preventing a stain generated due to a contact of food containing water with a surface of the food container, decreasing food residual left on the surface of the food container, and preventing a harmful influence from the food container by minimizing a contact area of food and the food container, and a manufacturing method thereof.

30

**[Technical Solution]**

**[0007]** In order to achieve the aforementioned object, the present invention provides a food container made of a plastic material and having a nano-structured hydrophobic surface, including: a plurality of nano-structures formed on a surface of the food container; and a first hydrophobic thin film coated on an upper side of the surface, on which the nano-structures are formed.

35

**[0008]** Further, the food container may further include a gas blocking film formed between the surface of the food container and the first hydrophobic thin film.

**[0009]** Further, the food container may further include a second hydrophobic thin film formed between the surface of the food container and the gas blocking film.

40

**[0010]** Further, the nano-structure may have any one shape among a nano-pillar shape, a nano-rod shape, a nano-dot shape, and a nano-wire shape.

**[0011]** Further, the nano-structure may have a width of 1 to 100 nm and a height of 1 to 1000 nm.

**[0012]** Further, a contact angle of the first hydrophobic thin film may be equal to or larger than 90°, and contact angle hysteresis of the first hydrophobic thin film may be less than 30°.

45

**[0013]** Further, a sum of a thickness of the first hydrophobic thin film and a thickness of the gas blocking film may be a half of a height of the nano-structure or lower.

**[0014]** Further, a sum of a thickness of the first hydrophobic thin film, a thickness of the gas blocking film, and a thickness of the second hydrophobic thin film may be a half of a height of the nano-structure or lower.

50

**[0015]** Further, the first hydrophobic thin film is formed of hexamethyldisiloxane

**[0016]** Further, the gas blocking film may be formed of silicon oxide.

**[0017]** Further, the second hydrophobic thin film may be formed of hexamethyldisiloxane

**[0018]** Further, the gas blocking film and the first and second hydrophobic thin films may be discontinuously combined.

**[0019]** Further, the gas blocking film and the first and second hydrophobic thin films may be continuously combined according to a continuous change in mutual chemical composition.

55

**[0020]** A method of manufacturing a food container having a nano-structured hydrophobic surface of the present invention includes: forming a plurality of nano-structures on a surface of the food container formed of a plastic material; and coating a first hydrophobic thin film on an upper side of the surface, on which the nano-structures are formed.

**[0021]** Further, the method may further include coating a gas blocking film on the upper side of the surface, on which the nano-structures are formed, between the forming of the plurality of nano-structures and the coating of the first hydrophobic thin film.

5 **[0022]** Further, the method may further include coating a second hydrophobic thin film on the upper side of the surface, on which the nano-structures are formed, between the forming of the plurality of nano-structures and the coating of the gas blocking film.

**[0023]** Further, the nano-structure may have any one shape among a nano-pillar shape, a nano-rod shape, a nano-dot shape, and a nano-wire shape.

**[0024]** Further, the nano-structure may have a width of 1 to 100 nm and a height of 1 to 1000 nm.

10 **[0025]** Further, a contact angle of the first hydrophobic thin film may be equal to or larger than 90°, and contact angle hysteresis of the first hydrophobic thin film may be less than 30°.

**[0026]** Further, a sum of a thickness of the first hydrophobic thin film and a thickness of the gas blocking film may be a half of a height of the nano-structure or lower.

15 **[0027]** Further, a sum of a thickness of the first hydrophobic thin film, a thickness of the gas blocking film, and a thickness of the second hydrophobic thin film may be a half of a height of the nano-structure or lower.

**[0028]** Further, the first hydrophobic thin film may be formed of hexamethyldisiloxane Further, the gas blocking film may be formed of silicon oxide.

**[0029]** Further, the second hydrophobic thin film may be formed of hexamethyldisiloxane

**[0030]** Further, the gas blocking film and the first and second hydrophobic thin films may be discontinuously combined.

20 **[0031]** Further, the gas blocking film and the first and second hydrophobic thin films may be continuously combined according to a continuous change in mutual chemical composition.

#### **[Advantageous Effects]**

25 **[0032]** As described above, according to the present invention, it is possible to provide the food container having the nano-structured hydrophobic surface capable of preventing a stain generated due to a contact of food containing water with a surface of the food container, decreasing food residual left on the surface of the food container, and preventing a harmful influence from the food container by minimizing a contact area of food and the food container, and a manufacturing method thereof.

30 **[0033]** Further, according to the present invention, it is possible to provide the food container having the nano-structured hydrophobic surface capable of having excellent gas blocking performance, as well as hydrophobicity, by additionally forming the gas blocking film, and the manufacturing method thereof.

#### **[Description of Drawings]**

35 **[0034]**

FIG. 1A is a diagram illustrating a food container having a nano-structured hydrophobic surface according to a first exemplary embodiment of the present invention.

40 FIG. 1B is a diagram illustrating a method of manufacturing the food container illustrated in FIG. 1A.

FIG. 2A is a diagram illustrating a food container having a nano-structured hydrophobic surface according to a second exemplary embodiment of the present invention.

FIG. 2B is a diagram illustrating a method of manufacturing the food container illustrated in FIG. 2A.

45 FIG. 3A is a diagram illustrating a food container having a nano-structured hydrophobic surface according to a third exemplary embodiment of the present invention.

FIG. 3B is a diagram illustrating a method of manufacturing the food container illustrated in FIG. 3A.

FIG. 4 is a graph illustrating a static contact angle between water, vinegar, and soy sauce measured according to a time of oxygen plasma processing performed on the food container.

50 FIG. 5A is a graph illustrating a dynamic contact angle of water according to a time of oxygen plasma processing performed on the food container.

FIG. 5B is a graph illustrating a dynamic contact angle of vinegar according to a time of oxygen plasma processing performed on the food container.

FIG. 5C is a graph illustrating a dynamic contact angle of soy sauce according to a time of oxygen plasma processing performed on the food container.

55 **[Best Mode]**

**[0035]** Other detailed matters of the exemplary embodiments are included in the detailed description and the drawings.

**[0036]** Various advantages and features of the present disclosure and methods accomplishing thereof will become apparent from the following detailed description of exemplary embodiments with reference to the accompanying drawings. However, the present invention is not limited to the exemplary embodiments set forth below, and may be embodied in various other forms. The present exemplary embodiments are for rendering the description of the present invention complete and are set forth to provide a complete understanding of the scope of the invention to a person with ordinary skill in the technical field to which the present invention pertains, and the present invention will only be defined by the scope of the claims. Like reference numerals indicate like elements throughout the specification.

**[0037]** Hereinafter, a food container having a nano-structured hydrophobic surface and a method of manufacturing the same according to the present invention will be described with reference to the exemplary embodiment of the present invention and the drawings for describing the exemplary embodiment of the present invention.

**[0038]** FIG. 1A is a diagram illustrating a food container having a nano-structured hydrophobic surface according to a first exemplary embodiment of the present invention.

**[0039]** Referring to FIG. 1A, a food container 100 having a nano-structured hydrophobic surface (hereinafter, referred to as a "food container") according to a first exemplary embodiment of the present invention includes a plurality of nano-structures 20 and a first hydrophobic thin film 30.

**[0040]** The food container 100 is formed of a plastic material, such as polypropylene (PP), polyethylene terephthalate (PET), polyethylene (PE), polystyrene (PS) and the like.

**[0041]** In order to solve a problem (the food container 100 has hydrophilicity, so that food is attached to the food container 100) of the food container 100 formed of the plastic material, the food container 100 according to the exemplary embodiment is formed of the plurality of nano-structures 20 on a surface thereof.

**[0042]** That is, an air membrane is stably positioned in a space between the respective nano structures 20, so that the surface of the food container 100 has a very small contact area with food 60 containing water. Accordingly, the surface of the food container 100 has the hydrophobicity.

**[0043]** Further, in order to improve the hydrophobicity of the surface of the food container 100, a first hydrophobic thin film 30 may be coated on an upper side of the surface of the food container 100, on which the nano-structures are formed.

**[0044]** The first hydrophobic thin film 30 may be implemented by a material, which has low surface energy to have hydrophobicity, and may be preferably implemented by hexamethyldisiloxane (HMDSO), but may also adopt polytetrafluoroethylene (PTFE) or alkyl keton dimer (AKD), which is a conventionally well-known hydrophobic thin film.

**[0045]** Further, in the food container 100 in the present exemplary embodiment, a contact angle of a water drop, which is in contact with the first hydrophobic thin film 30, is 90° or more through the forming of the nano-structures 20 and the first hydrophobic thin film 30, and contact angle hysteresis is also less than 30°.

**[0046]** A contact angle is defined as an angle between a liquid surface and a solid surface in a liquid and a solid which are in contact with each other, and is generally represented by an angle formed between a tangent line from a contact point of a droplet and a solid leaded to a droplet surface and the solid surface. The contact angle is used as a criterion indicating wettability of the solid surface.

**[0047]** That is, as a contact angle is small, hydrophilicity is large, and as a contact angle is large, hydrophobicity is large.

**[0048]** Contact angle hysteresis may be defined by a difference between an advancing contact angle, at which a liquid starts to move forward from the surface, and a receding contact angle, at which the liquid starts to move backward from the surface, and the fact that a value of the contact angle hysteresis is large means that a liquid is not well detached from a surface, and the fact that a value of the contact angle hysteresis is small means that a liquid is well detached from a surface.

**[0049]** Accordingly, as described above, the contact angle of the first hydrophobic thin film 30 may be formed to be 90° or greater to achieve hydrophobicity, and the contact angle hysteresis may be formed to be less than 30°, thereby making the food 60 be well detached from the surface of the food container 100.

**[0050]** Here, the shape of the nano-structure 20 may be variously implemented, and an example thereof may include any one of a nanopillar shape, a nanorod shape, a nanodot shape, and a nanowire shape.

**[0051]** Further, a width of the nano-structure 20 may be set to be 1 to 100 nm, and a height thereof may be set to be 1 to 1000 nm.

**[0052]** FIG. 1B is a diagram illustrating a method of manufacturing the food container illustrated in FIG. 1A. That is, a method of manufacturing the food container 100 according to the first exemplary embodiment of the present invention includes a food container preparing step S100, a nano-structure forming step S110, and a first hydrophobic thin film coating step S120.

**[0053]** First, in the food container preparing step S100, the food container 100, which is formed of a plastic material and has a flat surface, is prepared.

**[0054]** Then, the nano-structure forming step S110 of forming the plurality of nano-structures 20 on the surface of the food container 100 is performed.

**[0055]** In the nano-structure forming step S110, dust on the surface of the food container 100 is removed by using a nitrogen gun (not shown). Then, the food container 100 is positioned within a chamber of Radio Frequency-Chemical

Vapor Deposition (RF-CVD) equipment (not shown), and a vacuum state is formed.

[0056] A vacuum pressure within the chamber of the RF-CVD equipment is adjusted to a predetermined value by using a pump and the like, and plasma processing starts on the surface of the food container 100.

5 [0057] To this end, after oxygen gas is inserted into the chamber, a plasma state is generated by RF-power. Then, the plurality of nano-structures 20 is formed on the surface of the food container 100 by a chemical reaction between the food container 100 and oxygen plasma.

[0058] As the time of the oxygen plasma processing on the food container 100 is increased, a height of the nano-structure 20 is increased, and a width thereof is decreased. That is, the sharper and longer nano-structure is formed.

[0059] Next, the first hydrophobic thin film coating step S 120 is performed.

10 [0060] In the first hydrophobic thin film coating step S120, after the oxygen plasma processing performed in the nano-structure forming step S110 is completed, a first hydrophobic thin film forming material in a gas state is inserted into the chamber of the RF-CVD equipment. Then, the plasma state is generated by the RF-power again, so that the first hydrophobic thin film forming material in the gas state may be deposited on the surface of the food container 100 in which the nano-structures 20 are formed. Accordingly, the first hydrophobic thin film 30 is finally coated on the surface  
15 of the food container 100.

[0061] For example, when hexamethyldisiloxane (HMDSO) gas is inserted as the first hydrophobic thin film forming material, the first hydrophobic thin film 30 made of plasma polymerized HMDSO (pp-HMDSO) may be formed. The first hydrophobic thin film 30 made of plasma polymerized HMDSO (pp-HMDSO) has low surface energy to have hydrophobicity.

20 [0062] It is possible to manufacture the food container having hydrophobicity through the aforementioned manufacturing method, and thus it is possible to prevent a phenomenon in that liquid-state food is attached to the surface of the food container, thereby preventing a phenomenon in that a stain is generated on the surface of the food container and minimizing the amount of food left on the surface of the food container.

25 [0063] Further, it is possible to minimize a contact area between the food and the food container, thereby preventing harmful ingredients from being transferred from the food container to the food.

[0064] FIG. 2A is a diagram illustrating a food container having a nano-structured hydrophobic surface according to a second exemplary embodiment of the present invention.

30 [0065] Referring to FIG. 2A, a food container 200 having a nano-structured hydrophobic surface (hereinafter, referred to as a "food container") according to a second exemplary embodiment of the present invention includes a plurality of nano-structures 20, a first hydrophobic thin film 30, and a gas blocking film 40.

[0066] That is, the present exemplary embodiment is different from the first exemplary embodiment in that the gas blocking film 40 is further included, so that the present exemplary embodiment will be described based on the gas blocking film 40, and descriptions overlapping those of the first exemplary embodiment will be omitted.

35 [0067] The gas blocking film 40 is formed between the surface of the food container 200 and the first hydrophobic thin film 30.

[0068] Further, the first hydrophobic thin film 30 is coated on the surface of the food container 200 in which the gas blocking film 40 is formed.

40 [0069] The gas blocking film 40 is inserted between the food container 200 and the first hydrophobic thin film 30, so that the food container 200 according to the exemplary embodiment of the present invention may have excellent gas blocking performance. Accordingly, food stored inside the food container 200 may be preserved for a long time.

[0070] In this case, the gas blocking film 40 has a high thin film density, so that the gas blocking film 40 may be silicon oxide having excellent gas blocking performance.

45 [0071] Further, in a case where a sum of a thickness  $h_3$  of the first hydrophobic thin film 30 and a thickness  $h_4$  of the gas blocking film 40 is set to be excessively large, a space between the nano-structures 20 is decreased, thereby causing a problem in that hydrophobicity deteriorates, so that the sum of the thickness  $h_3$  of the first hydrophobic thin film 30 and the thickness  $h_4$  of the gas blocking film 40 may be set to be a half of a height  $h_2$  of the nano-structure 20 or smaller.

50 [0072] FIG. 2B is a diagram illustrating a method of manufacturing the food container illustrated in FIG. 2A. That is, a method of manufacturing the food container 200 according to the second exemplary embodiment of the present invention includes a food container preparing step S200, a nano-structure forming step S210, a gas blocking film coating step S220, and a first hydrophobic thin film coating step S230.

[0073] The food container preparing step S200 and the nano-structure forming step S210 are identically performed to those aforementioned the first exemplary embodiment.

[0074] Next, differently from the first exemplary embodiment, in the present exemplary embodiment, the gas blocking film coating step S220 is performed before the first hydrophobic thin film coating step S230.

55 [0075] In gas blocking film coating step S220, the gas blocking film 40 is coated on the surface of the food container 200 in which the nano-structures 20 are formed.

[0076] The process may be performed within the chamber of the RF-CVD equipment using plasma.

[0077] For example, the gas blocking film 40 has a high thin film density, so that the gas blocking film 40 may be silicon

oxide having excellent gas blocking performance.

[0078] Then, the first hydrophobic thin film coating step S230 of coating the first hydrophobic thin film 30 on the gas blocking film 40 is performed.

[0079] The first hydrophobic thin film coating step S230 may be identically performed to that described in the first exemplary embodiment.

[0080] Here, the gas blocking film coating step S220 and the first hydrophobic thin film coating step S230 may be discontinuously or continuously performed.

[0081] According to the discontinuous process, the plasma state is released after the gas blocking film 40 is formed, and the plasma state is generated again after confirming that gas for coating the first hydrophobic thin film 30 stably flows into the chamber to coat the first hydrophobic thin film 30.

[0082] Accordingly, the gas blocking film 40 and the first hydrophobic thin film 30 are discontinuously combined so as to prevent mutual composition from being continuously changed.

[0083] In the meantime, according to the continuous process, the plasma state is continuously maintained even after the gas blocking film 40 is formed, and gas flowing into the chamber is continuously changed from gas forming the gas blocking film 40 to gas forming the first hydrophobic thin film 30.

[0084] According to the continuous process, it is possible to form a thin film structure in which composition is gradually changed from the gas blocking film 40 to the first hydrophobic thin film 30. That is, as another expression, it is possible to form a thin film structure in which thin films are continuously connected.

[0085] The continuous process may be used for reducing a time consumed for changing gas in a factory performing mass production, and has an effect in that difference in stress applied to the thin films is released during discontinuous deposition.

[0086] According to the aforementioned process, the nano-structures 20, the gas blocking film 40, and the first hydrophobic thin film 30 are sequentially positioned on the surface of the food container 200 as a result.

[0087] FIG. 3A is a diagram illustrating a food container having a nano-structured hydrophobic surface according to a third exemplary embodiment of the present invention.

[0088] Referring to FIG. 3A, a food container 300 having a nano-structured hydrophobic surface (hereinafter, referred to as a "food container") according to a third exemplary embodiment of the present invention includes a plurality of nano-structures 20, a first hydrophobic thin film 30, a gas blocking film 40, and a second hydrophobic thin film 50.

[0089] That is, the present exemplary embodiment is different from the second exemplary embodiment in that the second hydrophobic thin film 50 is further included, so that the present exemplary embodiment will be described based on the second hydrophobic thin film 50, and descriptions overlapping those of the second exemplary embodiment will be omitted.

[0090] The second hydrophobic thin film 50 is formed between a surface of the food container 300 and the gas blocking film 40. That is, the second hydrophobic thin film 50 is first coated on the surface of the food container 300, and then the gas blocking film 40 is formed on the second hydrophobic thin film 50.

[0091] Further, after the gas blocking film 40 is coated, and then the first hydrophobic thin film 30 is coated on the gas blocking film 40.

[0092] Accordingly, the second hydrophobic thin film 50, the gas blocking film 40, and the first hydrophobic thin film 30 are sequentially positioned on the nano-structures 20 of the food container 300.

[0093] When the gas blocking film 40 having flexibility is directly coated on the food container 300, there is a problem in that strong residual stress is left, and the second hydrophobic thin film 50 positioned at the lowermost side serves as a buffer thin film (buffer layer) for releasing the problem.

[0094] The second hydrophobic thin film 50 may be formed of the same material as that of the first hydrophobic thin film 30. Accordingly, the second hydrophobic thin film 50 may also be implemented by hexamethyldisiloxane (HMDSO), but may also adopt polytetrafluoroethylene (PTFE) or alkyl keton dimer (AKD), which is a conventionally well-known hydrophobic thin film.

[0095] Further, in a case where a sum of a thickness  $h_3$  of the first hydrophobic thin film 30, a thickness  $h_4$  of the gas blocking film 40, and a thickness  $h_5$  of the second hydrophobic thin film 50 is set to be excessively large, a space between the nano-structures 20 is decreased, thereby causing a problem in that hydrophobicity deteriorates, so that the sum of the thickness  $h_3$  of the first hydrophobic thin film 30, the thickness  $h_4$  of the gas blocking film 40, and a thickness  $h_5$  of the second hydrophobic thin film 50 may be set to be a half of a height  $h_2$  of the nano-structure 20 or smaller.

[0096] FIG. 3B is a diagram illustrating a method of manufacturing the food container illustrated in FIG. 3A. That is, a method of manufacturing the food container 300 according to the third exemplary embodiment of the present invention includes a food container preparing step S300, a nano-structure forming step S310, a second hydrophobic thin film coating step S320, a gas blocking film coating step S330, and a first hydrophobic thin film coating step S340.

[0097] The food container preparing step S300 and the nano-structure forming step S310 are identically performed to those aforementioned the first and second exemplary embodiments.

[0098] Next, differently from the second exemplary embodiment, in the present exemplary embodiment, the second

hydrophobic thin film coating step S320 is performed before the gas blocking film coating step S330.

[0099] In the second hydrophobic thin film coating step S320, the second hydrophobic thin film 50 is coated on the surface of the food container 300 in which the nano-structures 20 are formed, which may be performed by the same method as that of the first hydrophobic thin film coating step S120 in the aforementioned first exemplary embodiment.

[0100] Then, the gas blocking film coating step S330 and the first hydrophobic thin film coating step S340 are sequentially performed equally to those of the second exemplary embodiment.

[0101] In the gas blocking film coating step S330, the gas blocking film 40 is coated on the second hydrophobic thin film 50, and in the first hydrophobic thin film coating step S340, the first hydrophobic thin film 30 is coated on the gas blocking film 40.

[0102] Here, the second hydrophobic thin film coating step S320, the gas blocking film coating step S330, and the first hydrophobic thin film coating step S340 may be discontinuously performed similar to the second exemplary embodiment, or may be continuously performed.

[0103] According to the discontinuous process, the plasma state is released after the second hydrophobic thin film 50 is formed, the plasma state is generated again after confirming that gas coated on the gas blocking film 40 stably flows into the chamber to form the gas blocking film 40, the plasma state is released after forming the gas blocking film 40, and the plasma state is generated again after confirming that gas coated on the first hydrophobic thin film 30 stably flows into the chamber to coat the first hydrophobic thin film 30.

[0104] Accordingly, the second hydrophobic thin film 50, the gas blocking film 40, and the first hydrophobic thin film 30 are discontinuously combined so as to prevent mutual composition from being continuously changed.

[0105] In the meantime, according to the continuous process, the plasma state is continuously maintained even after the second hydrophobic thin film 50 is formed, and gas flowing into the chamber is continuously changed from gas forming the second hydrophobic thin film 50 to the gas forming the gas blocking film 40. Further, the plasma state is continuously maintained even after the gas blocking film 40 is formed, and gas flowing into the chamber is continuously changed from gas forming the gas blocking film 40 to gas forming the first hydrophobic thin film 30.

[0106] According to the continuous process, it is possible to form a thin film structure in which composition is gradually changed from the second hydrophobic thin film 50 to the first hydrophobic thin film 30 via the gas blocking film 40. That is, as another expression, it is possible to form a thin film structure in which thin films are continuously connected.

[0107] The continuous process may be used for reducing a time consumed for changing gas in a factory performing mass production, and has an effect in that difference in stress applied to the thin films is released during discontinuous deposition.

[0108] FIG. 4 is a graph illustrating a static contact angle between water, vinegar, and soy sauce measured according to a time of oxygen plasma processing performed on the food container. In this case, an x-axis indicates a time of oxygen plasma processing performed before coating the hydrophobic thin film and the gas blocking film, and a y-axis indicates a static contact angle measured in a state where a corresponding liquid droplet is stopped.

[0109] An experiment is performed by using a polypropylene (PP) sheet, which is a plastic material widely used as the food container.

[0110] In order to form the nano-structures on a surface of the PP sheet, dust on the surface of the PP sheet is first clearly blown by using a nitrogen gun for one minute, and then the PP sheet is positioned within the chamber of the Radio Frequency-Chemical Vapor Deposition (RF-CVD) equipment (not shown), and a vacuum state is formed.

[0111] A vacuum pressure within the chamber is decreased with high vacuum of 10-6 mtorr by using a rotary pump and a turbo pump, and then plasma processing starts to be performed on the surface of the PP sheet. To this end, after inserting oxygen gas into the chamber, the plasma state is formed by RF-power. Then, the plurality of nano-structures 20 is formed on the surface of the PP sheet by chemical reaction between the PP sheet and the oxygen plasma.

[0112] Then, the second hydrophobic thin film 50, the gas blocking film 40, the first hydrophobic thin film 30 are sequentially coated. In this case, the first hydrophobic thin film 30 and the second hydrophobic thin film 50 are formed of pp-hexamethyldisiloxane (pp-HMDSO), and the gas blocking film 40 is formed of silicon oxide.

[0113] Further, the first hydrophobic thin film 30 and the second hydrophobic thin film 50 are coated with a thickness of 30 nm, and the gas blocking film 40 is coated with a thickness of 30 nm.

[0114] As can be seen in the graph illustrated in FIG. 4, as the time of the oxygen plasma processing is increased, the contact angle is increased. That is, it can be seen that hydrophobicity of the surface of the PP sheet is improved.

[0115] FIG. 5A is a graph illustrating a dynamic contact angle of water according to a time of oxygen plasma processing performed on the food container, FIG. 5B is a graph illustrating a dynamic contact angle of vinegar according to a time of oxygen plasma processing performed on the food container, and FIG. 5C is a graph illustrating a dynamic contact angle of soy sauce according to a time of oxygen plasma processing performed on the food container. In this case, an x-axis indicates a time of oxygen plasma processing performed before coating the hydrophobic thin film and the gas blocking film, and a y-axis indicates a dynamic contact angle.

[0116] Particularly, in order to recognize the contact angle hysteresis, an advancing contact angle and a receding contact angle of a corresponding liquid droplet are separately illustrated.

[0117] A fact that the contact angle hysteresis is small means that even though a surface is slightly inclined, the liquid easily flows down on the surface. That is, it means that as the contact angle hysteresis is small, the liquid is not attached to the surface. As can be seen in FIGS. 5A to 5C, as a time of the oxygen plasma processing is increased, the contact angle hysteresis of water, vinegar, and soy sauce is decreased.

[0118] It will be appreciated by those skilled in the art that the present invention described above may be implemented into other specific forms without departing from the technical spirit thereof or essential characteristics. Thus, it is to be appreciated that exemplary embodiments described above are intended to be illustrative in every sense, and not restrictive. The scope of the present invention is represented by the claims to be described below rather than the detailed description, and it is to be interpreted that the meaning and scope of the claims and all the changes or modified forms derived from the equivalents thereof come within the scope of the present invention.

**[Description of Main Reference Numerals of Drawings]**

**[0119]**

20: Nano-structure	30: First hydrophobic thin film
40: Gas blocking film	50: Second hydrophobic thin film
60: Food	100, 200, 300: Food container

**Claims**

1. A food container made of a plastic material and having a nano-structured hydrophobic surface, comprising:  
 a plurality of nano-structures formed on a surface of the food container; and  
 a first hydrophobic thin film coated on an upper side of the surface, on which the nano-structures are formed.
2. The food container of claim 1, further comprising:  
 a gas blocking film formed between the surface of the food container and the first hydrophobic thin film.
3. The food container of claim 2, further comprising:  
 a second hydrophobic thin film formed between the surface of the food container and the gas blocking film.
4. The food container of claim 1, wherein the nano-structure has any one shape among a nano-pillar shape, a nano-rod shape, a nano-dot shape, and a nano-wire shape.
5. The food container of claim 1, wherein the nano-structure has a width of 1 to 100 nm and a height of 1 to 1000 nm.
6. The food container of claim 1, wherein a contact angle of the first hydrophobic thin film is equal to or larger than 90°, and contact angle hysteresis of the first hydrophobic thin film is less than 30°.
7. The food container of claim 2, wherein a sum of a thickness of the first hydrophobic thin film and a thickness of the gas blocking film is a half of a height of the nano-structure or lower.
8. The food container of claim 3, wherein a sum of a thickness of the first hydrophobic thin film, a thickness of the gas blocking film, and a thickness of the second hydrophobic thin film is a half of a height of the nano-structure or lower.
9. The food container of claim 1, wherein the first hydrophobic thin film is formed of hexamethyldisiloxane
10. The food container of claim 2, wherein the gas blocking film is formed of silicon oxide.
11. The food container of claim 3, wherein the second hydrophobic thin film is formed of hexamethyldisiloxane
12. The food container of claim 3, wherein the gas blocking film and the first and second hydrophobic thin films are discontinuously combined.



13. The food container of claim 3, wherein the gas blocking film and the first and second hydrophobic thin films are continuously combined according to a continuous change in mutual chemical composition.

5 14. A method of manufacturing a food container having a nano-structured hydrophobic surface, comprising:

forming a plurality of nano-structures on a surface of the food container formed of a plastic material; and coating a first hydrophobic thin film on an upper side of the surface, on which the nano-structures are formed.

10 15. The method of claim 14, further comprising:

coating a gas blocking film on the upper side of the surface, on which the nano-structures are formed, between the forming of the plurality of nano-structures and the coating of the first hydrophobic thin film.

15 16. The method of claim 15, further comprising:

coating a second hydrophobic thin film on the upper side of the surface, on which the nano-structures are formed, between the forming of the plurality of nano-structures and the coating of the gas blocking film.

20 17. The method of claim 14, wherein the nano-structure has any one shape among a nano-pillar shape, a nano-rod shape, a nano-dot shape, and a nano-wire shape.

18. The method of claim 14, wherein the nano-structure has a width of 1 to 100 nm and a height of 1 to 1000 nm.

25 19. The method of claim 14, wherein a contact angle of the first hydrophobic thin film is equal to or larger than 90°, and contact angle hysteresis of the first hydrophobic thin film is less than 30°.

20. The method of claim 15, wherein a sum of a thickness of the first hydrophobic thin film and a thickness of the gas blocking film is a half of a height of the nano-structure or lower.

30 21. The method of claim 16, wherein a sum of a thickness of the first hydrophobic thin film, a thickness of the gas blocking film, and a thickness of the second hydrophobic thin film is a half of a height of the nano-structure or lower.

22. The method of claim 14, wherein the first hydrophobic thin film is formed of hexamethyldisiloxane

35 23. The method of claim 15, wherein the gas blocking film is formed of silicon oxide.

24. The method of claim 16, wherein the second hydrophobic thin film is formed of hexamethyldisiloxane

40 25. The method of claim 16, wherein the gas blocking film and the first and second hydrophobic thin films are discontinuously combined.

45 26. The method of claim 16, wherein the gas blocking film and the first and second hydrophobic thin films are continuously combined according to a continuous change in mutual chemical composition.

FIG. 1A

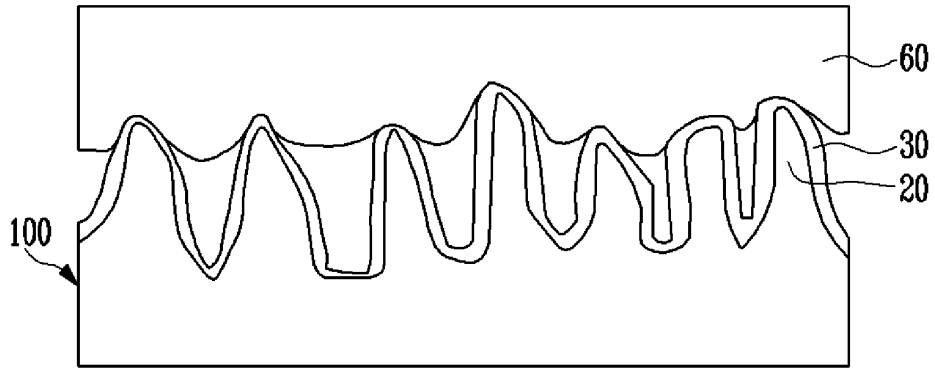


FIG. 1B

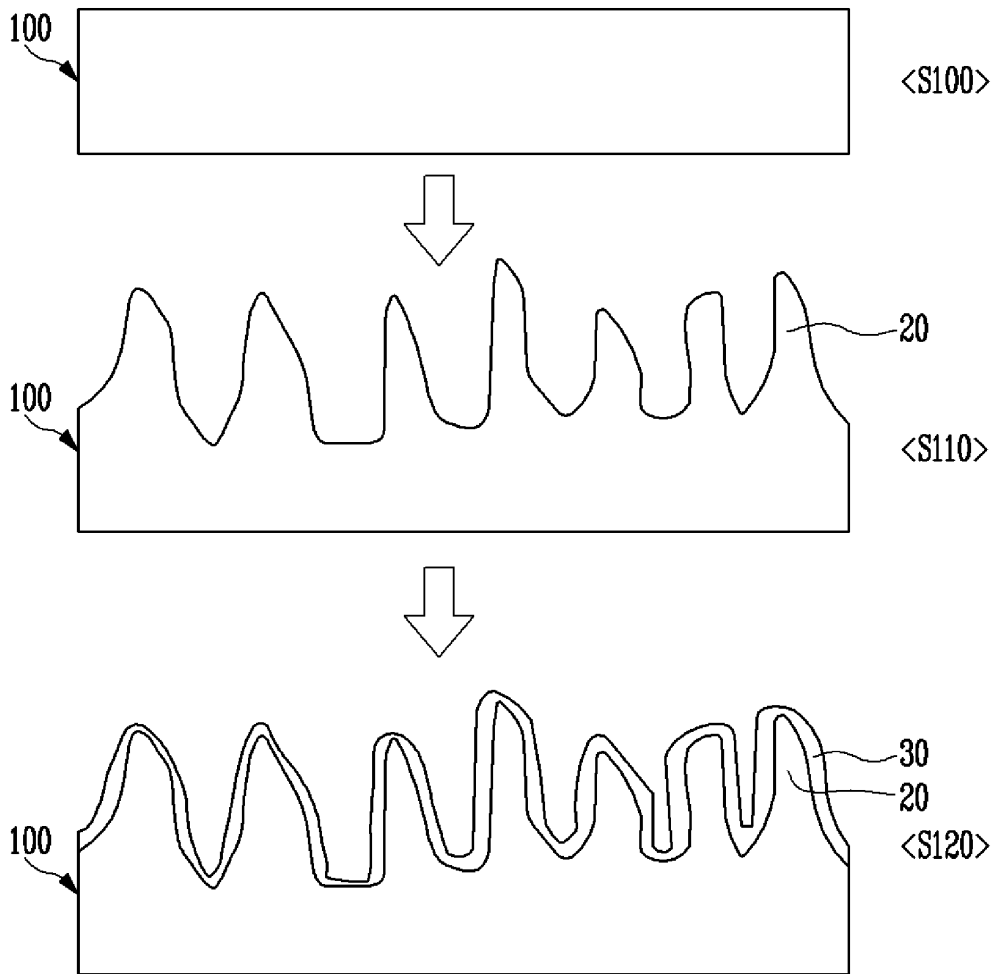


FIG. 2A

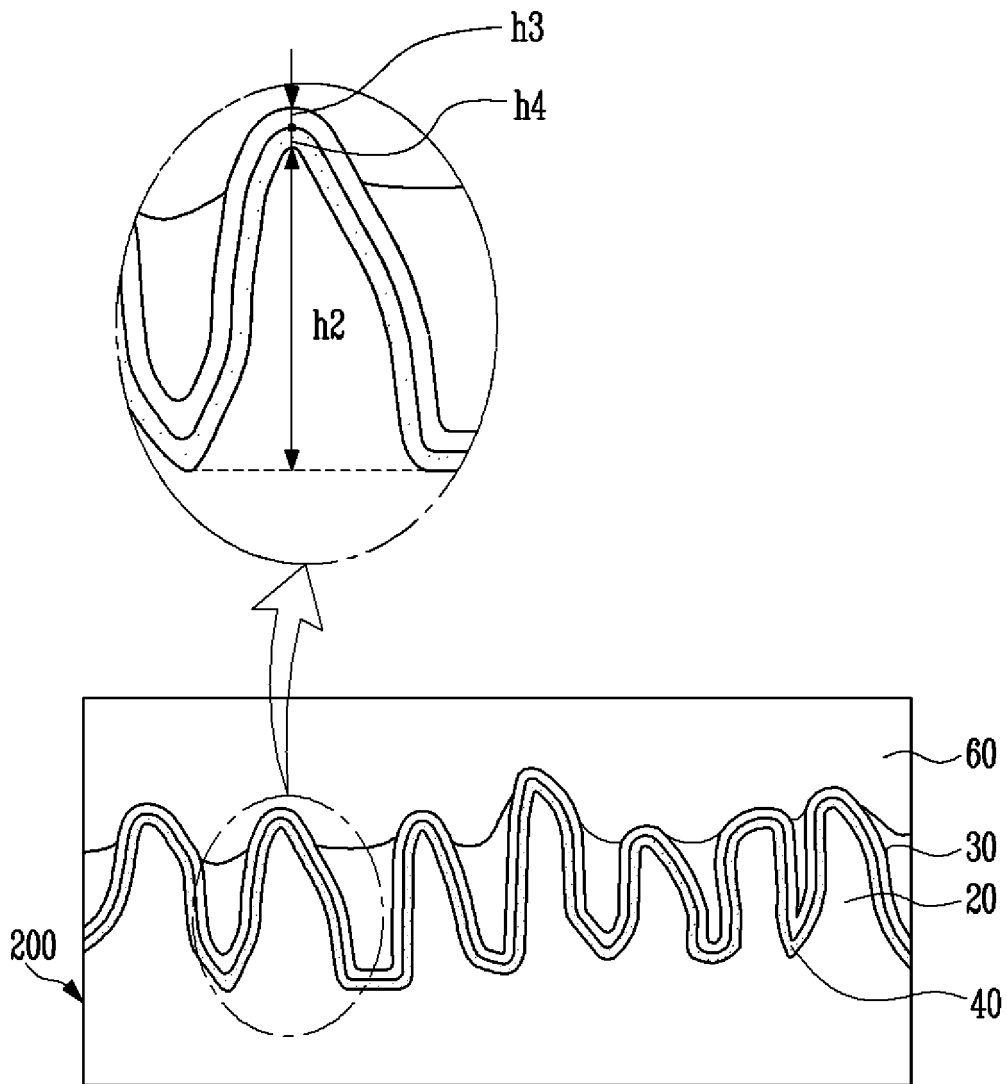


FIG. 2B

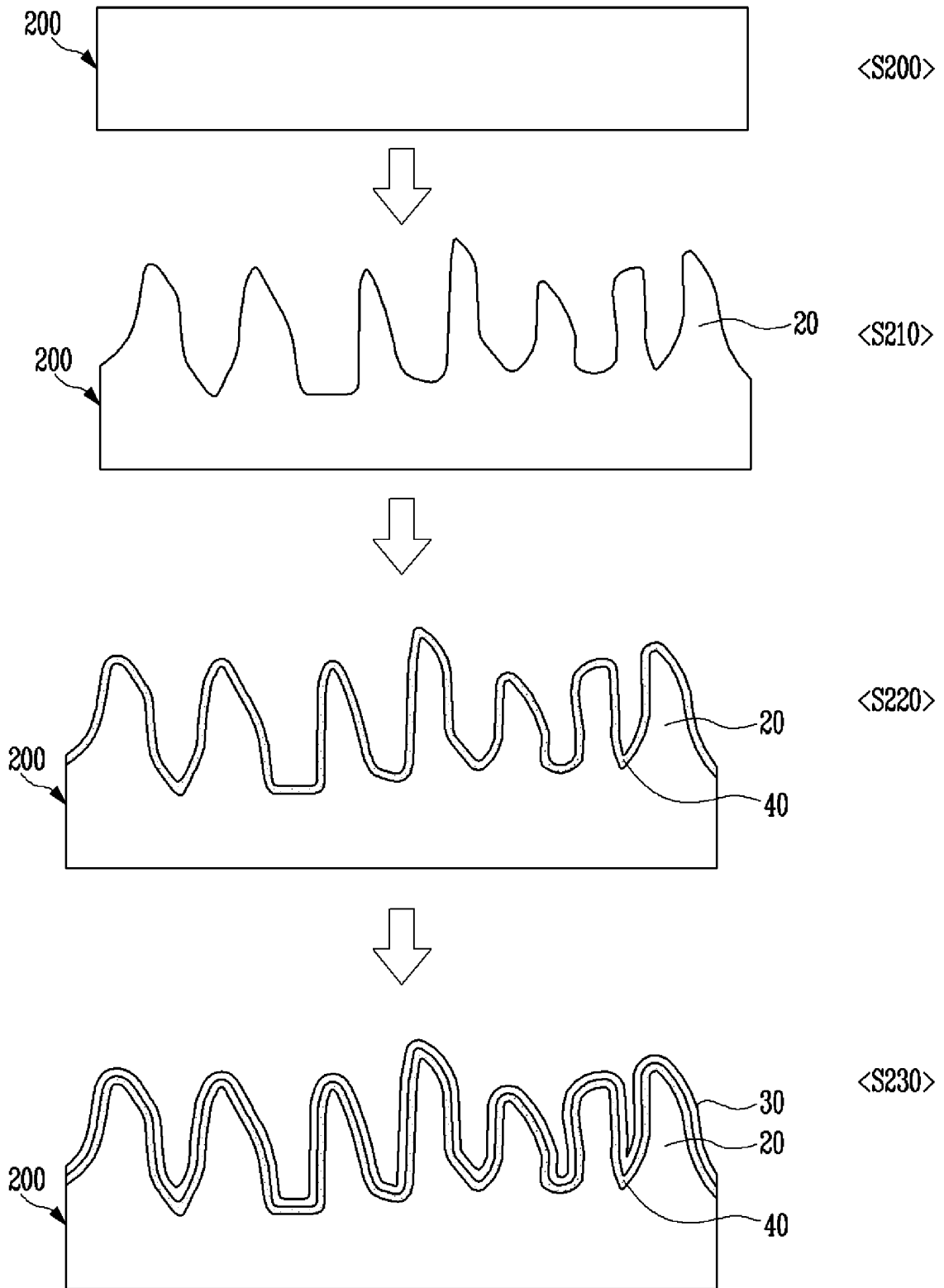


FIG. 3A

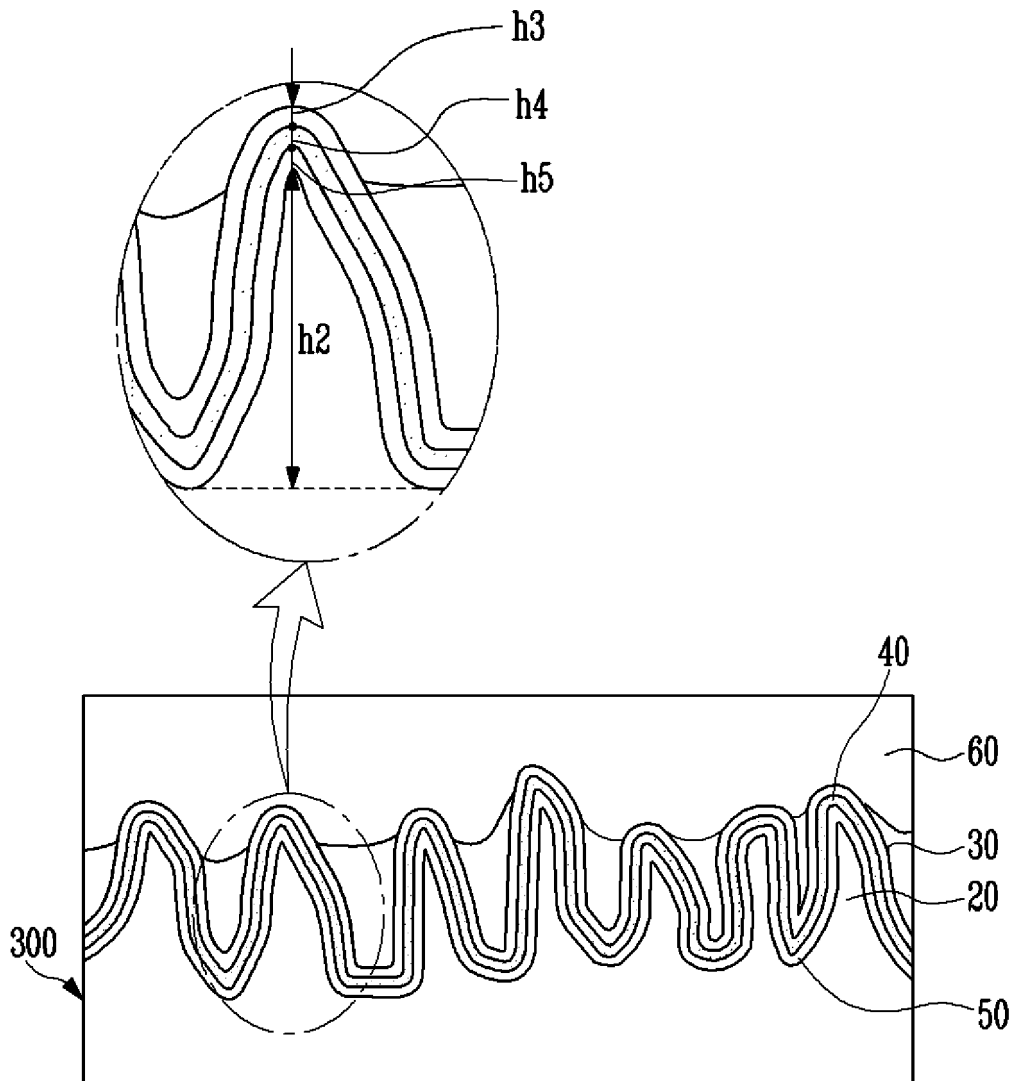


FIG. 3B

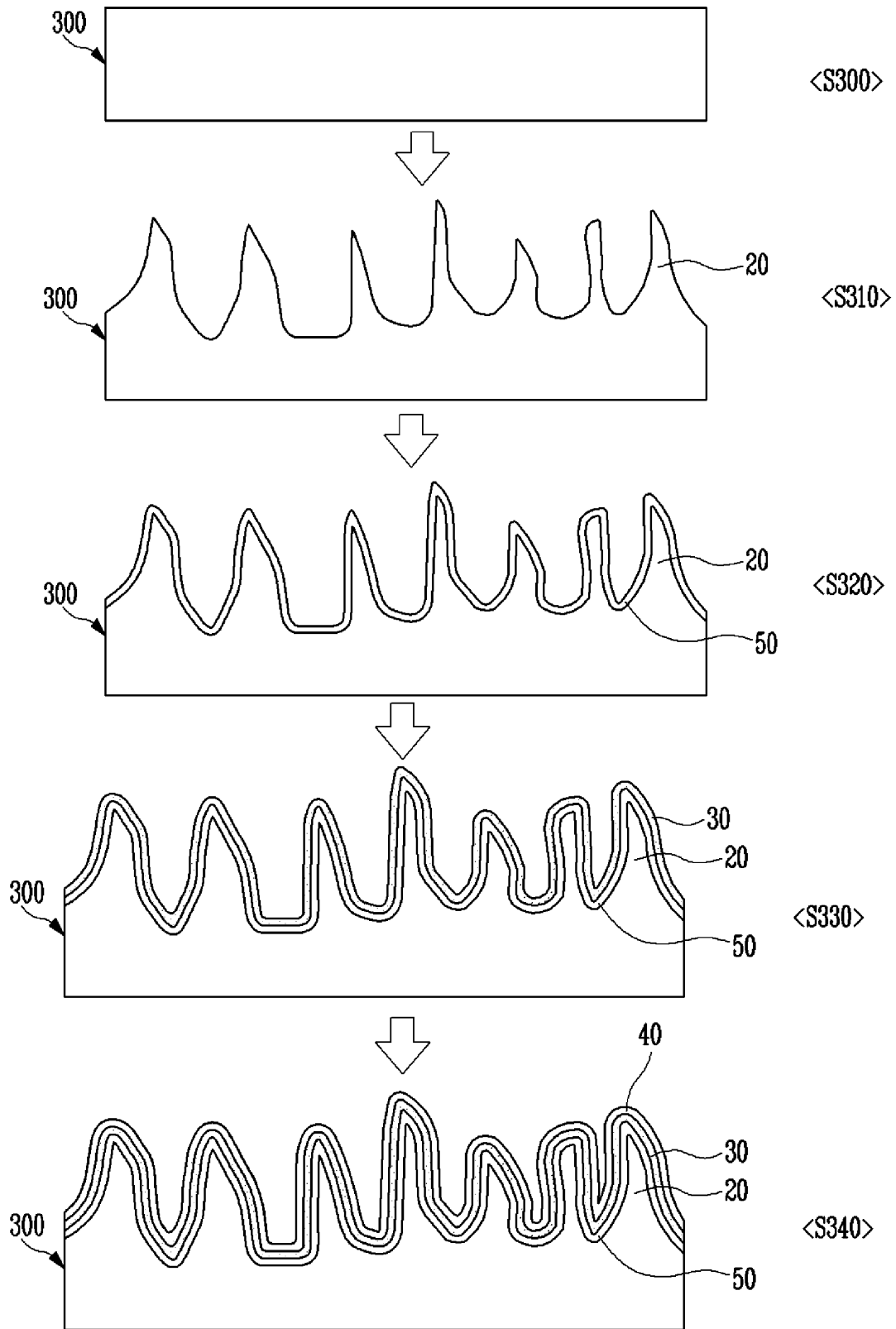


FIG. 4

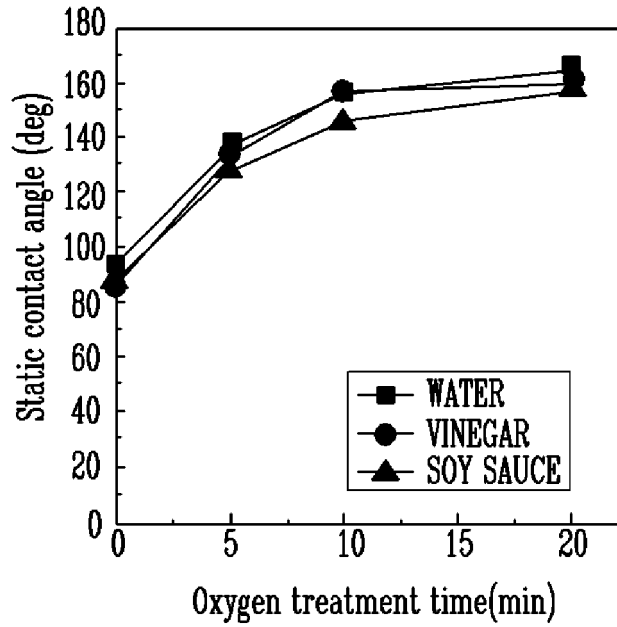


FIG. 5A

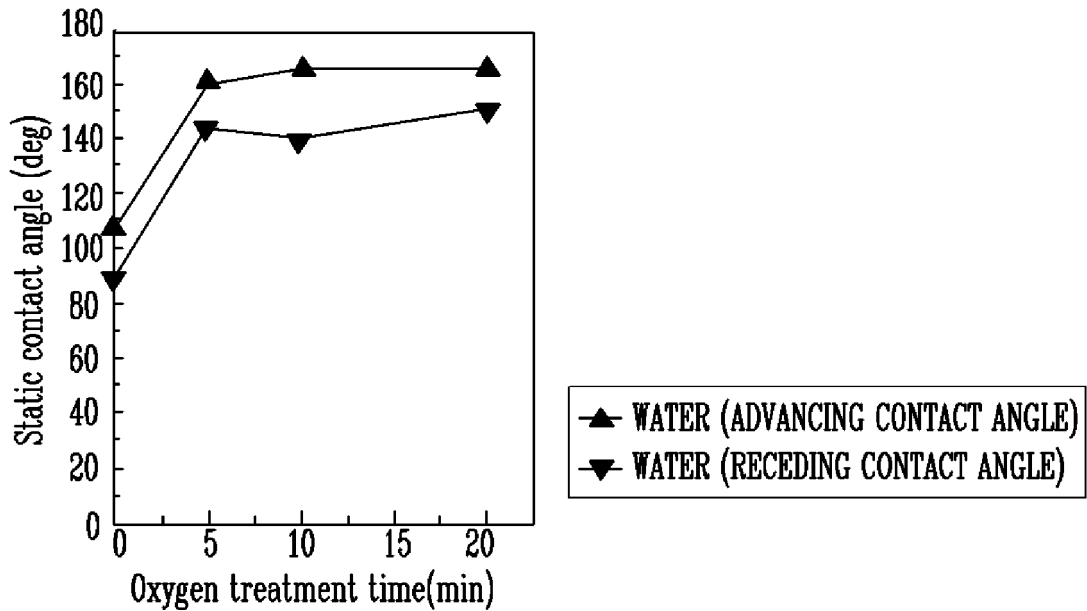


FIG. 5B

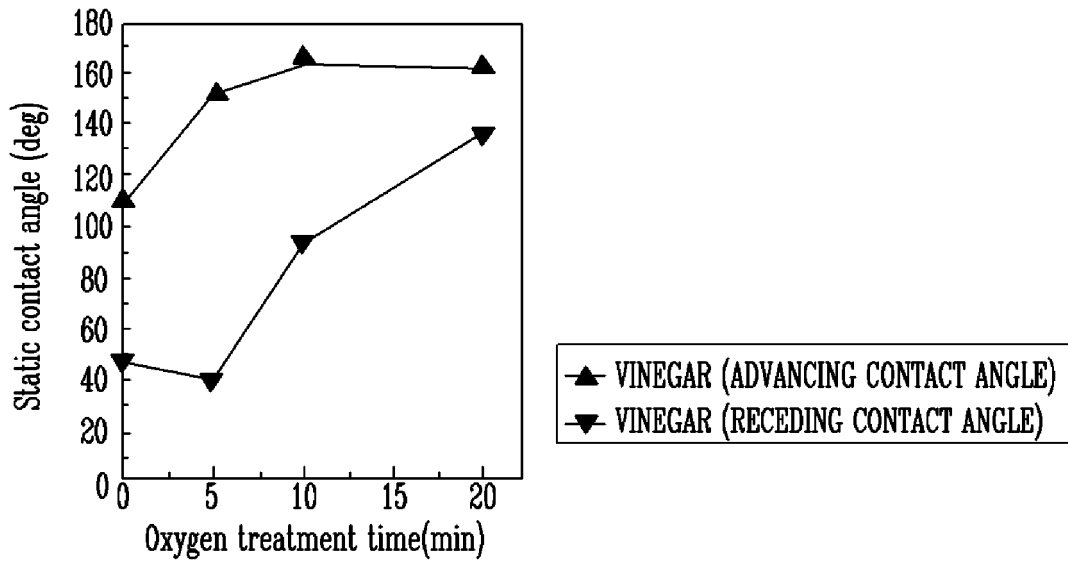
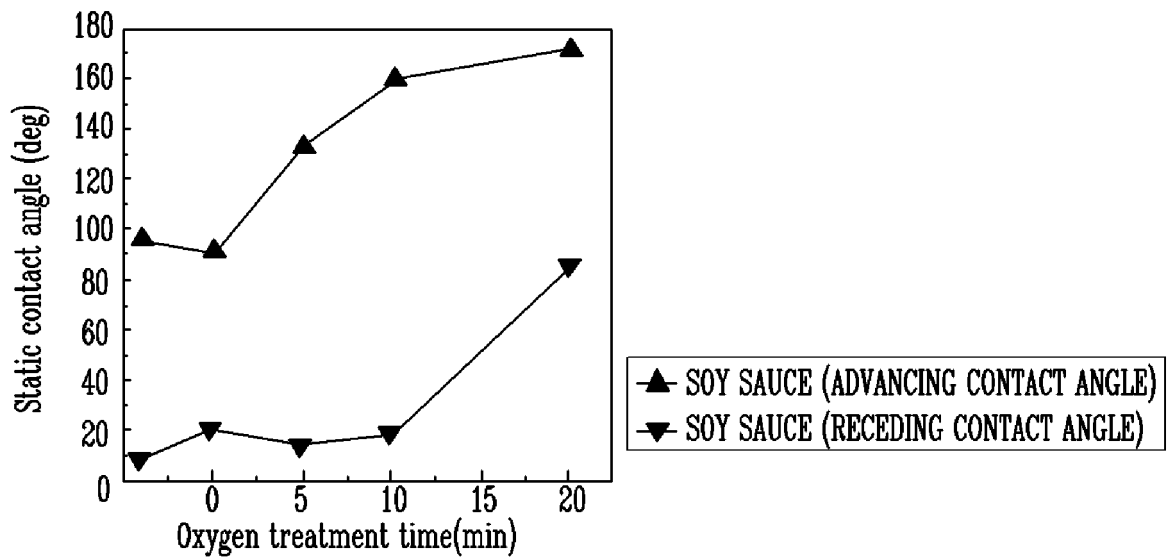


FIG. 5C





INTERNATIONAL SEARCH REPORT

International application No.

**PCT/KR2012/007177**

5

A. CLASSIFICATION OF SUBJECT MATTER  
**B65D 25/14(2006.01)i, B65D 65/40(2006.01)i, B32B 27/06(2006.01)i, A47G 19/02(2006.01)i**  
 According to International Patent Classification (IPC) or to both national classification and IPC

10

B. FIELDS SEARCHED  
 Minimum documentation searched (classification system followed by classification symbols)  
 B65D 25/14; B65D 65/40; B32B 27/06; B32B 1/02; B32B 17/06; C23C 16/515; B65D 90/04; A47G 19/02

15

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
 Korean Utility models and applications for Utility models: IPC as above  
 Japanese Utility models and applications for Utility models: IPC as above

20

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 eKOMPASS (KIPO internal) & Keywords: container, coating, CVD, nano structure, HMDSO

20

C. DOCUMENTS CONSIDERED TO BE RELEVANT

25

30

35

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006-0024508 A1 (D'URSO, BRIAN R.; SIMPSON, JHON T.) 02 February 2006 See abstract, page 2 paragraphs [0019]-[0028], claims 1-13 and figure 2.	1-26
Y	US 2003-0044552 A1 (KOMADA, MINORU) 06 March 2003 See page 1, paragraph [0006] - page 2, paragraph [0027] and figures 2, 14.	1-26
A	EP 1388594 A2 (SCHOTT, GLAS et al.) 11 February 2004 See page 9, paragraph [0071] - page 10, paragraph [0083] and figure 3.	1-26
A	US 5736207 A (WALTHER, MARTEN et al.) 07 April 1998 See abstract, column 4, line 36 - column 5, line 57 and figure 3.	1-26

40

Further documents are listed in the continuation of Box C.  See patent family annex.


45

\* Special categories of cited documents:  
 "A" document defining the general state of the art which is not considered to be of particular relevance  
 "E" earlier application or patent but published on or after the international filing date  
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
 "O" document referring to an oral disclosure, use, exhibition or other means  
 "P" document published prior to the international filing date but later than the priority date claimed  
 "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
 "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

50

Date of the actual completion of the international search <b>24 JANUARY 2013 (24.01.2013)</b>	Date of mailing of the international search report <b>24 JANUARY 2013 (24.01.2013)</b>
--	---

55

Name and mailing address of the ISA/KR  Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer  Telephone No.
---	---

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.

PCT/KR2012/007177

5

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member	Publication date
US 2006-0024508 A1	02.02.2006	AU 2005-283033 A1	16.03.2006
		AU 2005-327910 A1	31.08.2006
		CA 2575145 A1	16.03.2006
		CA 2575197 A1	31.08.2006
		CA 2575197 C	12.05.2009
		EP 1778412 A1	02.05.2007
		EP 1791794 A2	06.06.2007
		JP 2008-508181 A	21.03.2008
		JP 2008-508181 T	21.03.2008
		JP 2008-508182 A	21.03.2008
		KR 10-2007-0044436 A	27.04.2007
		KR 10-2007-0044437 A	27.04.2007
		MX 2007001050 A	16.04.2007
		US 2006-0024478 A1	02.02.2006
		US 2006-0289380 A1	28.12.2006
		US 2007-0281130 A1	06.12.2007
		US 2008-0080816 A1	03.04.2008
		US 2008-296252 A1	04.12.2008
		US 7150904 B2	19.12.2006
		US 7258731 B2	21.08.2007
		US 7697807 B2	13.04.2010
		US 7697808 B2	13.04.2010
		US 8241508 B2	14.08.2012
WO 2006-028603 A2	16.03.2006		
WO 2006-028603 A3	16.03.2006		
WO 2006-091235 A1	31.08.2006		
WO 2009-052027 A2	23.04.2009		
WO 2009-052027 A3	23.04.2009		
US 2003-0044552 A1	06.03.2003	JP 03-678361 B2	03.08.2005
		JP 04-191668 B2	03.12.2008
		JP 2003-053873 A	26.02.2003
		JP 2005-096466 A	14.04.2005
		US 2006-0029757 A1	09.02.2006
		US 6905769 B2	14.06.2005
US 7306852 B2	11.12.2007		
EP 1388594 A2	11.02.2004	AU 2003-229285 A1	12.12.2003
		AU 2003-229286 A1	12.12.2003
		AU 2003-229287 A1	12.12.2003
		AU 2003-232621 A1	12.12.2003
		AU 2003-233770 A1	12.12.2003
		AU 2003-233771 A1	12.12.2003
		AU 2003-233772 A1	12.12.2003
		AU 2003-236789 A1	12.12.2003
		AU 2003-237678 A1	12.12.2003
		AU 2003-237688 A1	12.12.2003
		AU 2003-238400 A1	12.12.2003
		AU 2003-239757 A1	12.12.2003

Form PCT/ISA/210 (patent family annex) (July 2009)

EP 2 754 618 A1

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.

PCT/KR2012/007177

5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55

Patent document cited in search report	Publication date	Patent family member	Publication date
		AU 2003-239758 A1	12.12.2003
		AU 2003-239758 A8	12.12.2003
		AU 2003-242577 A1	12.12.2003
		AU 2003-245890 A1	12.12.2003
		CA 2484023 A1	04.12.2003
		CA 2484824 A1	04.12.2003
		CA 2484844 A1	04.12.2003
		CN 1495285 A	12.05.2004
		CN 1495285 C0	12.03.2008
		CN 1552943 A	08.12.2004
		CN 1552943 C0	16.04.2008
		CN 1656246 A	17.08.2005
		CN 1656246 C0	20.08.2008
		CN 1656250 A	17.08.2005
		CN 1656250 C0	19.11.2008
		EP 1365043 A1	26.11.2003
		EP 1365043 B1	05.04.2006
		EP 1367145 A1	03.12.2003
		EP 1367145 B1	17.05.2006
		EP 1388593 A2	11.02.2004
		EP 1388593 A3	25.08.2004
		EP 1388594 A3	25.08.2004
		EP 1388594 B1	06.01.2010
		EP 1415018 A1	06.05.2004
		EP 1415018 B1	15.10.2008
		EP 1507723 A1	23.02.2005
		EP 1507723 B1	15.03.2006
		EP 1507884 A1	23.02.2005
		EP 1507885 A1	23.02.2005
		EP 1507886 A1	23.02.2005
		EP 1507887 A2	23.02.2005
		EP 1507887 B1	09.07.2008
		EP 1507889 A1	23.02.2005
		EP 1507890 A1	23.02.2005
		EP 1507891 A1	23.02.2005
		EP 1507893 A1	23.02.2005
		EP 1507894 A1	23.02.2005
		EP 1507894 B1	14.12.2005
		EP 1507895 A1	23.02.2005
		EP 1507895 B1	21.07.2010
		EP 1537253 A1	08.06.2005
		EP 1537254 A1	08.06.2005
		JP 2004-003026 A	08.01.2004
		JP 2004-003027 A	08.01.2004
		JP 2004-068159 A	04.03.2004
		JP 2004-538176 A	24.12.2004
		JP 2005-526613 A	08.09.2005
		JP 2005-526675 A	08.09.2005
		JP 2005-526911 A	08.09.2005
		JP 2005-526912 A	08.09.2005

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.

PCT/KR2012/007177

5

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member	Publication date
		JP 2005-526913 A	08.09.2005
		JP 2005-526914 A	08.09.2005
		JP 2005-526915 A	08.09.2005
		JP 2005-527079 A	08.09.2005
		JP 2005-527080 A	08.09.2005
		JP 2005-531688 A	20.10.2005
		JP 2005-534804 A	17.11.2005
		JP 4386832 B2	09.10.2009
		JP 4388804 B2	09.10.2009
		JP 4426790 B2	03.03.2010
		JP 4512485 B2	14.05.2010
		JP 4567442 B2	13.08.2010
		JP 4636875 B2	03.12.2010
		JP 4654027 B2	24.12.2010
		JP 4889073 B2	22.12.2011
		JP 4977316 B2	20.04.2012
		US 2003-0219547 A1	27.11.2003
		US 2003-0232150 A1	18.12.2003
		US 2004-0142184 A1	22.07.2004
		US 2004-0247948 A1	09.12.2004
		US 2005-0118428 A1	02.06.2005
		US 2005-0223988 A1	13.10.2005
		US 2005-0227002 A1	13.10.2005
		US 2005-0229850 A1	20.10.2005
		US 2005-0233077 A1	20.10.2005
		US 2006-0086320 A1	27.04.2006
		US 2006-0099340 A1	11.05.2006
		US 2006-0150909 A1	13.07.2006
		US 7109070 B2	19.09.2006
		US 7399500 B2	15.07.2008
		US 7699933 B2	20.04.2010
		US 7810448 B2	12.10.2010
		US 7926446 B2	19.04.2011
		US 7931955 B2	26.04.2011
		WO 03-014415 A1	20.02.2003
		WO 03-099688 A1	04.12.2003
		WO 03-100115 A1	04.12.2003
		WO 03-100116 A1	04.12.2003
		WO 03-100117 A1	04.12.2003
		WO 03-100118 A2	04.12.2003
		WO 03-100118 A3	04.12.2003
		WO 03-100119 A1	04.12.2003
		WO 03-100120 A2	04.12.2003
		WO 03-100121 A2	04.12.2003
		WO 03-100121 A3	04.12.2003
		WO 03-100122 A2	04.12.2003
		WO 03-100124 A1	04.12.2003
		WO 03-100125 A1	04.12.2003
		WO 03-100126 A1	04.12.2003
		WO 03-100127 A1	04.12.2003

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.

**PCT/KR2012/007177**

5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55

Patent document cited in search report	Publication date	Patent family member	Publication date
		WO 03-100128 A1	04.12.2003
		WO 03-100129 A1	04.12.2003
US 5736207 A	07.04.1998	CA 2161362 A1	28.04.1996
		CA 2161362 C	16.01.2007
		EP 0709485 A1	01.05.1996
		EP 0709485 B1	28.10.1998
		JP 08-318590 A	03.12.1996
		JP 4050800 B2	20.02.2008
		US 5900285 A	04.05.1999