



- (51) International Patent Classification:
B29C 59/02 (2006.01) *B08B 17/06* (2006.01)
B29C 59/04 (2006.01) *A01G 25/02* (2006.01)
- (21) International Application Number: PCT/IL2014/050001
- (22) International Filing Date: 1 January 2014 (01.01.2014)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
61/751,859 12 January 2013 (12.01.2013) US
61/765,772 17 February 2013 (17.02.2013) US
61/819,603 5 May 2013 (05.05.2013) US
61/846,323 15 July 2013 (15.07.2013) US
- (72) Inventors; and
(71) Applicants : **MOR, Elad** [IL/IL]; 21/3 Erez Street, 7680400 Mazkeret Batya (IL). **OFIR, Yuval** [IL/IL]; 21/7 Elyahu Hanavi Street, 7172234 Modi'in (IL).
- (74) Agents: **LUZZATTO & LUZZATTO** et al.; LUZZATTO, Kfir, P.O. Box 5352, 8415202 Beer Sheva (IL).
- (81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

[Continued on next page]

(54) Title: SUPER-HYDROPHOBIC SURFACES IN LIQUID-COMPRISING SYSTEMS

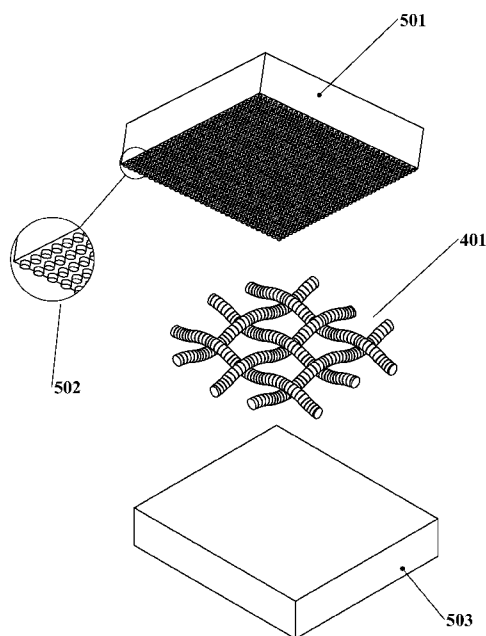


Fig. 5

(57) Abstract: A method for providing a patterned surface, comprises: a) imprinting/thermally-embossing an article with a nano/micro size pattern; b) optionally weaving said textured article into a mesh structure; c) optionally imprinting/thermally-embossing the mesh with nano/micro size pattern; d) applying the mesh to a surface having a softening point lower than the softening point of said textured article; e) applying a pressure onto said mesh, while heating said surface to a temperature equal to or above its softening point, thereby to create a nano/micro pattern on said surface; and f) optionally using the low softening point surface as a mold.

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG). **Published:**

— with international search report (Art. 21(3))

SUPER-HYDROPHOBIC SURFACES IN LIQUID-COMPRISING SYSTEMS

Field of the Invention

The present invention relates to the field of pressure and/or flow rate reduction, and the prevention of sediments and/or damages that are normally caused by the presence of liquids in liquid-comprising systems. More particularly, the invention relates to the field of super-hydrophobic surfaces provided in liquid-comprising systems, such as irrigation systems and drippers.

Background of the Invention

In liquid-comprising systems, such as irrigation systems, there are potential damages inflicted by liquid flow in the system and/or stagnant liquid, since they often contain substances that cling to the walls, for example, plant nutrients, pesticides, accumulation of suspended solids, chemical precipitations like scale and Iron that can be found in water, depending on water quality.

One example of such irrigation network is a water system that comprises drippers that regulate the amount of emitted water, and therefore are also referred to as “emitters”. When a system that comprises emitters is clogged, it is often caused by the presence of different materials and/or contaminants in the water that flows through the system, such as organic agents, grit, and algae. When a certain amount of sediment is accumulated, the drippers can become unusable. Of course the damage can be inflicted on every part of the water system that comes in contact with water. Such damages can cause changes in flow rate, pressure, sectional areas, etc.

One known method for removing sediments is using a flow of acid through the channel, but of course eventually the acid can also harm the channel itself, furthermore the acid can pollute the ground and can found the way to pollute the growths also. Using acid flow and other chemical treatments are described in "Drip system operation and maintenance, recommended procedures for a drip irrigation system", NETAFIM USA, 2010, - <http://www.netafimusa.com/files/literature/agriculture/otherliterature/maintenance/A099Subsurface-Drip-System-Ops.pdf>.

In further description, such systems are sometimes referred to as "water systems" for they are very common, but of course the reference to water can be replaced with any other fluid – liquid or vapor, and does not mean to limit the invention only to water or in any other way.

An example of a water system is an emitters-comprising system, wherein the emitters comprise a water flow and pressure reduction channel – a "labyrinth channel" or "labyrinth", through which water that enter the emitter must flow through to reach the emitter's outlet.

The labyrinth channel is a high resistance flow channel along which pressure of fluid that flows through the emitter drops relatively rapidly along the labyrinth channel, from a relatively high pressure which prevails substantially at or near the emitter inlet, to a relatively low discharge pressure, usually a gauge pressure equal to about zero, substantially at or near the emitter's outlet. The labyrinth channel generally comprises a tortuous "obstacle" flow-path that generates turbulence flow in the labyrinth, to reduce pressure and discharge of fluid by the emitter. The problem that is related to the flow in the labyrinth is that particles are intended to be caught in the turbulent stream, flow in circles and may cause blockages. Nowadays the solution for this problem

is a 'Cascade Labyrinth' that uses a wider water passages, as presented in DRIP IRRIGATION, NaanDanJain [<http://aquadrop.ru/upload/user/file/catalog/NaandanJain.pdf>]

When pressure drops along the channel, it naturally limits the length of the channel, since there is a minimum value of the pressure that allows the system to function properly. According to known art, irrigation systems are limited in length, depends on emitters spacing and channel diameter. Another disadvantage caused by pressure dropping along the channel is inconsistency distribution of fluid.

However, experience has revealed that pressure-compensating drip-emitters may get clogged during operation when they are exposed to low quality water with suspended solids and chemical precipitates. Damaging substances are sometimes formed inside the water network, even if the incoming water were initially clean of them, because certain environmental condition, common in water systems, induce the formation of those substances, like algae. Such organic agents can clog the emitter. Thus, even if the flow path through the emitter is sufficient to pass grit alone, it may not pass the grit if algae are present.

Accordingly, there is a need for a device and method that prevent and/or reduce the clinging of different materials on the walls of a water system and permits enhanced flow through the emitter of organic materials, grit and algae, to reduce the amount of obstruction and the tendency of emitter clogging.

In another embodiment, specific surfaces of marine vessels can be converted to be superhydrophobic and therefore prevent biological fouling (i.e. Biofouling), undesirable accumulation of micro-organisms, algae and diatoms, plants, and animals on the surfaces.

Nowadays, irrigation systems are designed to reduce scale and algae clogging by comprising complex emitters, which increases the cost of the product. Even the best irrigation systems suffer from scale and algae clogging and they are very sensitive to water quality. Some of the problems in irrigation systems are detailed in “Drip system operation and maintenance, recommended procedures for a drip irrigation system”, NETAFIM USA, 2010, pp. 8 & pp. 10-14 - <http://www.netafimusa.com/files/literature/agriculture/otherliterature/maintenance/A099Subsurface-Drip-System-Ops.pdf>.

Another problem that drip irrigation systems deal with is the potential risk of root intrusion into the drippers. This problem occurs more on the permanent sub-surface drip systems (SSD) where roots grow into the buried emitters. For annual crops such as lettuce, root intrusion is commonly minimized by avoiding water stress during the growing season, and at the end of the season the roots and plants are killed by acid injection. For some trees and vines, an active program of chemigation with TRIFLURALIN 5 (TREFLAN) is the only way of control. This herbicide only kills the root tips of the plants without killing the plants, themselves. Some emitters have the chemical TREFLAN impregnated into them. [Subsurface Drip Irrigation systems. Netafim Irrigation Equipment and Drip systems S.A.]

Another field wherein the use of drippers is common is metals extraction. Many mines are provided with drippers for a “heap leaching” process – a process comprising series of chemical reactions that absorbs specific minerals and then re-separate them after their separation from other earth materials. The chemicals are added through drip systems. Since the concentration of particles in the water is relatively high in this process, it is crucial to use a special labyrinth design (e.g. Cascade Labyrinth) and/or perform a flushing process very often.

The present invention relates to the manufacture and use of super-hydrophobic structures for preventing damages to liquid-comprising systems, but before addressing the manufacturing and uses of super-hydrophobic surfaces, it is important to present the definition of a super-hydrophobic surface: The definition of the amount of rejection between a surface and a liquid or a vapor material is determined by the contact angle (also known as – wetting angle), which is measured through the liquid/vapor, where its interface meets a solid surface.

Super-hydrophobic surfaces have a contact angle larger than 150 degrees. This type of surface repels liquid/vapor materials by leaving a layer of air between the surface and said materials. The repulsion between a fluid and a surface prevents friction between them and allows, among other things, a higher velocity in the contact point of the material and the surface. The repulsion and the ability of a fluid to maintain high velocity are in direct link with the angle and they increase when the contact angle is enlarged.

Super-hydrophobic surfaces can be manufactured by using different methods, one of which is imprinting a desired pattern on a surface to create small-dimensional structures provided with gaps between them. The gaps naturally host a gas component, such as air, and provide isolation when the fluid comes in contact with a super-hydrophobic surface. Such isolation provides the necessary repelling between the fluid and the surface. As used herein, the term "imprinting" should be read in its broad meaning, to also include "thermally-embossing".

The imprinting method can be replaced with any other method which will produce a super-hydrophobic surface, like lithography, etching, burn by laser beams or any other burn device, adding material to the surface, or any other method used to form a small-dimension structural surface.

Another suitable process for super-hydrophobic imprint is injection-compression molding (ICM) process, hot punching, etc.

When referring to a small-dimension structural surface, it means that the dimensions of each small structure comprising the surface are of nano/micro-meter size. Such structures may relate to imprinting features having dimensions of less than 100 μm , preferably less than 50 μm , or more preferably less than 25 μm .

Super-hydrophobic nano/micro-meter imprinting, may relate to imprinting features having peak-to-peak post dimensions of less than 200 μm , preferably 1 to 100 μm , more preferably 25 to 100 μm for the micro structure and 500 to 10 nm to the nano structure and can also relate to imprinting features having post height dimensions being less than 300 μm , preferably 1 μm to 150 nm, more preferably 1 to 80 μm for the micro structure and 500 to 10 nm to the nano structure. Super-hydrophobic nano/micro-meter imprinting may further relate to imprinting features having post diameter dimensions being less than 300 μm , preferably 1 μm to 150 nm, more preferably 1 to 80 μm for the micro structure and 500 to 10 nm to the nano structure. All super-hydrophobic nano/micro-meter imprinting features dimensions above, refer to the final processed dimensions.

When imprinting, the surface being imprinted with the micro/nano-meter pattern may be non-planar on a macroscopic scale. The concept of a macroscopic scale may be defined as the length scale where objects are measurable and observable with the naked eye of a person with normal vision. More specifically, the macroscopic scale may be defined as a length above approximately 1 millimeter.

According to known art, micro/nano-structures can be placed on/in a surface through paint, coating or by adding a plastic film "carrying" the structures. By imprinting directly onto the surface (or indirectly; onto a mold surface which defines the surface topography) the structures can be made directly, or indirectly, in a way which is integrated with the existing production methods.

As used herein, the term "textured article" should be read in its broad meaning, for all the structures (articles) that can undergo imprinting or a thermal-embossing process and carry a micro/nano-structures.

Lithography encompasses many different types of surface preparation in which a design is transferred from a master onto a substrate surface, allowing multiple copies to be made. Methods closest to the original meaning of the term involve contact between an inked stamp and the substrate, with micrometer-sized features being standard and the newly established nano-imprint lithography (NIL) allowing smaller patterns to be produced. In photolithography a photoactive polymer layer is irradiated through a mask followed by developing stages where either the exposed or unexposed polymer is removed, leaving a positive or negative image of the mask on the surface. Photolithography can be subdivided into different categories depending on the radiation used: UV, X-ray, e-beam, interference lithography, Bosch etch, etc. It is also possible to use a laser or particle beam to etch the surface directly or to expose a photo resist layer, but this is relatively slow. The patterned surface is then either used as is, or used as a mask on the substrate for deposition or etching. Lithography is useful for generating super-hydrophobic surfaces where the shape of the features and the pattern is well-defined.

All the above technologies are limited and cannot generate patterns and structures with undercuts, relative to the main substrate surface (e.g.

Parting surface). An example is shown in Fig. 1B for structure 106 that cannot be produced with the technologies describe above, e.g. e-beam, interference lithography, Bosch etch, etc.

Nowadays, to achieve a tubular structure provided with an inner super-hydrophobic surface or any other topography, first the super-hydrophobic surface needs to be produced (e.g. inner mold) and only then transformed into a tubular structure. Then the inner mold is dissolved, (example shown in US 8,047,235). That fact indicates a time-consuming process that includes at least two steps in the manufacturing process, wherein each step requires different equipment.

Irrigation systems can work for hours, or be turned off for several days when there is no evaporation of the remaining water. In any case there is constantly flowing or still water in the system, and the contact angle is crucial for the rejection of undesired remaining water. Furthermore, water flow systems absorb pressure hammering, known as 'water hammering' during operation, including the opening and closing of the system's valves.

All these operation conditions and in addition surface imprinting inhomogeneity, can lead to micro and nano droplets condensation as well as capillary waves that can destabilize the composite solid-liquid-air interface, thus reducing the contact angle.

Nosonovsky & Bhushan [Hierarchical roughness makes superhydrophobic surfaces stable. *Microelectron. Eng.* 84, 382–386., Hierarchical roughness optimization for biomimetic superhydrophobic surfaces. *Ultramicroscopy* 107, 969–979. Multiscale dissipative mechanisms and hierarchical surfaces: friction, superhydrophobicity, and biomimetics. Heidelberg, Germany: Springer.] identified mechanisms that lead to destabilization of the composite solid-liquid-air interface, namely capillary waves,

condensation and accumulation of nanodroplets, and surface inhomogeneity. These mechanisms are scale dependent, with different characteristic length scales. To effectively resist these scale-dependent mechanisms, a multiscale (hierarchical) roughness is required. High asperities resist capillary waves, while nanobumps prevent nanodroplets from filling the valleys between asperities and pin the triple line in the case of a hydrophilic spot. A number of artificial roughness-induced hydrophobic surfaces have been fabricated with hierarchical structures using electrodeposition, nanolithography, colloidal systems and photolithography [Bahador Farshchian & Sunggook Park. 2012 Deformation behavior in 3D molding: experimental and simulation studies. Del Campo, A. & Greiner, C. 2007 SU-8: a photoresist for high-aspect-ratio and 3D submicron lithography. *J. Micromech. Microeng.* 17, R81–R95.].

Nowadays, there is no single-step, mass production solution for hierarchical structures with full nano structure cover upon the micro structure, including the micro structure side walls. The overall area of the micro structure side wall can reach 25 to 70 percent of the original super hydrophobic hierarchical substrate area and depends on the post density, i.e., a large surface area is exposed to composite solid–liquid–air interface instability.

Other properties of the super-hydrophobic surface are self-cleaning and self-drying, which help to avoid scale and dirt buildup on tube inner surface after water emptying, which can be a suitable technique for avoiding root insertion into the irrigation system. The water emptying can be done with compressed air, for example using a compressor to pump compressed air through the pipes. Nowadays irrigation water systems are designed to keep the surfaces always wet, to avoid scale and dirt build up.

It is an object of the present invention to provide a device and method that overcome the drawbacks of the prior art.

It is another object of the invention to provide an improved device and method for preventing and/or reducing damages involved in fluid-comprising systems, such as irrigation pipes, drip emitters, drip tape emitters, or any other fluid-transport system, by using super-hydrophobic surfaces.

Other objects and advantages of the invention will become apparent as the description proceeds.

Summary of the Invention

A method for providing a patterned surface, comprises:

- a) imprinting/thermally-embossing an article with a nano/micro size pattern;
- b) optionally weaving said textured article into a mesh structure;
- c) optionally imprinting/thermally-embossing the mesh with a nano/micro size pattern;
- d) applying the mesh structure to a surface having a softening point lower than the softening point of said textured article;
- e) applying a pressure onto said mesh structure, while heating said surface to a temperature equal to or above its softening point, thereby to create a nano/micro pattern on said surface; and
- f) optionally using the low softening point surface as a mold.

According to one embodiment of the invention there is provided a method in which pressure is applied using a patterned surface, thereby creating additional patterning on the surface that is not in contact with the mesh structure.

In an embodiment of the invention the nano/micro-patterned surface is hydrophobic and in another embodiment it has a wetting angle greater than 140° , preferably above 150° .

The surface to be patterned can be a part of a liquid conduit such as a pipe, e.g., a watering system pipe.

Also encompassed by the invention are patterned surfaces whenever manufactured by the method of the invention, as well as devices comprising a patterned surface such as liquid conduits (e.g., pipes).

Further encompassed by the invention is a method for modifying a surface, characterized by creating a hydrophobic surface using heat and/or pressure.

The invention is further directed to a device, selected from a conduit, pipe, emitter or device with hydrophobic surface, characterized by a wetting angle greater than 140° , preferably above 150° , whenever manufactured by the method of the invention.

A device which is a folding conduit or pipe the internal surface area of which was changed with heat and/or pressure using an imprinting/thermal-embossing belt device.

Brief Description of the Drawings

In the drawings:

Fig. 1A schematically shows a drop of liquid on top of a super-hydrophobic surface, and the contact angle between them;

Fig. 1B is an enlarged view of the contact angle of Fig. 1A;

Fig. 2A schematically shows the velocity profile of a fluid inside a tubular structure, wherein there is no slip between the fluid and the surface;

Fig. 2B schematically shows the velocity profile of a fluid inside a tubular structure, wherein there is slip between the fluid and the surface;

Fig. 3A shows a schematic illustration of an imprinting process, according to one embodiment of the invention, wherein the surface on which the pattern is imprinted is the surface of a string that goes through a "roll-to-roll" system;

Fig. 3B is an enlarged view of the imprinting roll-to-roll system of Fig. 3A, wherein the un-patterned string goes through rolls that comprise an imprinting surface;

Fig. 3C shows the outcome of the process of Fig. 3A – the patterned string and the resulting surface;

Fig. 4A shows a group of patterned strings in a "criss-cross" shaped array;

Fig. 4B shows a surface with a "criss-cross" shaped pattern, and an enlarge view of the surface;

Fig. 5 shows two surfaces wherein one of them is an imprinted surface which is made of a material with a relatively high melting and/or softening point, comprising a nano-structural surface, and the other is a surface made of a material with a relatively low melting and/or softening point;

Fig. 6 illustrates the positioning of a group of strings between a patterned surface and another surface;

Fig. 7A shows the final result of an imprinting process of a nano-structural surface and a grid structure, according to another embodiment of the invention.

Fig. 7B is an enlarged view of Fig. 7A, showing the nano-structural surface and the grid structure;

Fig. 8A and Fig. 8B illustrate a method for imprints flat substrate with super-hydrophobic structure;

Fig. 9 (A and B) illustrates the implementation of the imprinting method for imprinting flat substrates with super-hydrophobic structure as described in Figs. 8A and 8B, in a folding irrigation or in generally 'folding conduits;

Fig. 10 (A and B) describes the forming and imprinting of a labyrinth foil;

Fig. 11 illustrates another possible process, according to another embodiment of the invention, providing a super-hydrophobic structure comprising a nano-structural surface and a grid imprint, by using a rotational device;

Fig. 12A illustrates another possible process, according to another embodiment of the invention, providing a super-hydrophobic structure comprising a nano-structural surface and a grid imprint, by using a dip coating process;

Fig. 12B and Fig. 12C are enlarged views, showing the polymer during the process of Fig. 12A;

Fig. 13A and Fig. 13B show one possible de-molding process after the process of Fig. 12A;

Fig. 14A shows an exemplary use of a super hydrophobic structure in a dripper; and

Fig. 14B shows an exemplary super-hydrophobic structure, suitable to be used in the dripper of Fig. 12A.

Detailed Description of the Invention

The invention relates to a device comprising super-hydrophobic surfaces as inside walls in fluid-comprising systems and in liquid conduits, for preventing and/or decreasing sediments of different materials which can cause problems such as pressure, flow, or sectional area changes, and for improving the flow through a channel, allowing the use of longer channels than usual, among many other advantages which will be revealed in the following description. The invention further relates to methods for manufacturing a device that comprises inner super-hydrophobic surfaces. The invention relates also to a method for the mass production of hierarchical super-hydrophobic structures.

Super-hydrophobic surfaces have a contact angle larger than 150 degrees. This surface repels liquid/vapor materials by leaving a layer of air between the surface and the material. Fig. 1A shows a hierarchical super-hydrophobic surface 101, composed from microstructure 104, with a drop of liquid 102 on top of it, wherein the contact angle 103 between them is larger than 150 degrees. Fig. 1B is an enlarged view of the contact angle of Fig. 1A, with detailed view on the nanostructures 105 and nanostructure 106 having undercuts 107, relative to the main parting substrate surface.

According to one embodiment of the invention, the super-hydrophobic surfaces are used in irrigation systems, as inside walls or as any other part that comes in contact with the irrigation water and substances.

The velocity of a fluid inside a tubular structure is schematically illustrated in Figs. 2A and 2B, wherein the velocity profile shown in Fig. 2A is an example of a state wherein there is no slip between the fluid and the surface 201, and therefore the velocity of the contact point 202 is zero, and Fig. 2B is an example of a state wherein there is slip between the fluid and the surface 203, and therefore the velocity of the contact points

204 is larger than zero. The magnitude of the velocity in a contact point is determined by the air layer thickness that is influenced by the contact angle, i.e. the amount of friction/slip between a fluid and a surface that it comes in contact with. Some consequences of slip between the fluid and the surface are: fluid flow resistance is reduced as well as shear between the surface and the boundary fluid layer, anti-dirt sedimentation property due to the slip between the fluid and the surface (for example sand particles that tend to enter to the drip hose/emitter), improved flow rate and pressure uniformity along the pipeline.

Fig. 3A shows a schematic illustration of an imprinting process, according to one embodiment of the invention, wherein the textured article's surface on which the pattern is imprinted is a linear surface, such as a filament (a string). The string 301 goes through a "roll-to-roll" system 302. Such system provides a solution for high-speed, large area, nano-scale patterning with greatly improved throughput. The process includes: un-patterned string 301 that goes through roll-to-roll nano-imprint process between two rolls 303 and 304, and a patterned string 305 with nano-structure imprint. The linear surface can be, e.g., a polymer such as Nylon, Polyester, or metal like aluminum or stainless steel or any combination, i.e. metal string with polymer coating it.

Fig. 3B is an enlarged view of the imprinting roll-to-roll system 302 of Fig. 3A, wherein the un-patterned string 301 goes through the rolls 303 and 304 that comprise a negative (e.g. holes) imprinting surface 306. Fig. 3C shows the outcome of the process of Fig. 3A – the patterned string 305 and the resulting positive (e.g. posts) imprinting surface 307. The string imprinting process is not limited only to roll-to-roll process and can be done with all processes that can change its surface using heat and/or pressure.

The invention also relates to structure comprising an inner surface built to form a micro-structural surface, wherein said inner surface is a nano-structural surface itself, according to one embodiment of the invention. The process for manufacturing such embodiment is described in details over the following description of the drawings.

Fig. 4A shows a group 401 of patterned strings 402 (like the patterned strings 305 with imprinting surface 306 of Fig. 3A, shown in Fig. 4B) in a “criss-cross” shaped array (or – a grid), wherein the pattern on the strings 402 is a result of a nano-structure imprinting. The grid can also be referred to as a mesh net (a micro-mesh net or screen printing net). The nano-structure imprinting on the grid’s strings can also be made after the grid weaving, using soft top and bottom molds that can overcome the grid roughness. One possible process is to spin coat the mesh with epoxy resin, imprint it using heat and/or pressure, and cure the coating. Some other optional disciplines that can use the nano-structure imprinting grid are filtration for producing water repellent filters (e.g. mosquitoes net with self-cleaning properties) and screen printing for producing a mesh with changeable and controlled contact angle.

Fig. 5 shows two surfaces wherein one of them is an imprinted surface 501 which is made of a material with a relatively high melting and/or softening point and can be made from polymer (e.g. Nylon, rubber), metal (e.g. Aluminum, stainless steel), ceramic (e.g. glass, silicon) or combination, comprising a nano-structural surface 502, and the other is a surface 503 made of a material with a relatively low melting and/or softening point (relatively to the first surface 501 and to the group of strings 401). Surface 503 can be a polymer with low melting point like, but not limited, Polypropylene or Polyethylene, which are widely used in the manufacture of pipes for irrigation. The group of strings 401 is suitable to be positioned between surfaces 501 and 503.

Fig. 6 illustrates the positioning of a group of strings 401 between a patterned surface 501 and another surface 503, wherein the surfaces 501 and 503 are pressured one against the other when the group of strings 401 is in the middle. When pressuring the surfaces 501 and 503 while the group of strings 401 is between them, it will cause the softer surface 503 to melt and to be imprinted by the group of strings 401 and to get the shape of the grid 401 and also the shape of the pattern of each patterned string 402, and wherever there are spaces between the strings, the softer surface 503 will be imprinted by the imprinted surface 501.

In order to speed up the process, heat can be applied during the pressuring of the surfaces 501 and 503, as long as the heat will soften or melts the surface with the lower melting and/or softening point 503, but not the group of strings 401 or the patterned surface 501. During the cooling process the 503 surface solidifies and undergoes shrinkage that helps to de-molding the 503 surface from the mold's nanostructure that has been undercut, like nanostructure 106. For example Polyethylene has a shrinkage ratio of 8%.

The final result of the above process, according to another embodiment of the invention, is shown in Fig. 7, wherein the initial surface 503 has become a patterned surface 701 with an imprint of a nano-structural surface 702 and an imprint of a micro-grid structure 703. Fig. 7B is an enlarged view of Fig. 7A, showing the full coverage of nanostructures 702 imprinted on the micro-grid structure 703, including micro-grid side walls.

Although the process is presented with a grid-shaped array of patterned strings, the strings can also be arranged in any other way suitable to the final desired shape of imprint. Furthermore, as used herein, the terms "mesh" or "grid" should be read in its broad meaning, for all the

geometrical compositions that are composed from, at least one textured article.

The patterned surface 701 can be used as a master or mold in production processes like hot stamping, injection processes like injection compression molding, in-mold decoration, hot lamination, and all other processes in which a substrate can change its surface using heat and/or pressure.

Fig. 8A and Fig. 8B illustrate a method for imprints flat substrate with super-hydrophobic structure. Cross-section of imprinting belt device 804, composed of surface 501 and the strings group 401 that are rolled together on the rollers 803. Unprinted foil 503 is loaded and passes through device 804 that presses and/or heats the foil against imprinted surface 501 while the group of strings 401 is between them. The relative linear velocity between 503, 401 and 501, is zero, that means that all surfaces and strings group moving together (Fig. 8B), i.e. the imprint method is carried out in the same static principle that shown in Fig. 6. The imprint process time can be adjusted with the overlap length 801 changing, and can be adapted the foil 503 extrusion production rate. The de-molding angle 802, can be adapted also, for reduction the de-molding force.

Fig. 9B illustrates the implementation of the imprinting method for imprinting flat substrates with a super-hydrophobic structure as described in Figs. 8A and 8B, in a folding irrigation hose (e.g. Drip-Tape hose) or in generally 'folding conduits', flat foil or substrates that are rolled into a pipe shape. Unprinted foil 903 is passed through imprinting belt device 904 (like imprinting belt device 804) that generates heat and/or pressure and, as a result, a super-hydrophobic structure is generated with a single-step production process on the inner side of the foil 902. Then the foil 902 is folded into a folding conduit 901, as described in Fig. 9A.

Fig. 10B describes the forming and imprinting a labyrinth foil 1001. As shown in Fig. 9A and Fig. 9B, unprinted foil 1004, is passed through an imprinting belt device with a unique labyrinth shape 1002 (like imprinting belt device 804) that generates heat and/or pressure and, as a result, a super-hydrophobic structure is generated together with the labyrinth shape 1003, with a single-step process on the inner side of the foil 1001. Then the labyrinth foil 1001 is placed on foil 902 and folded together into folded conduit 901, as shown in Fig. 10A.

Fig. 11 illustrates another possible process, according to another embodiment of the invention, providing a super-hydrophobic structure comprising a nano-structural surface and a micro-grid imprint on the inner tube surface, using a single-step production process. In This process, there is a rotational device 1101 comprising engraving components 1102, which have the same curvature radius as the inner curvature radius of the tube, rotating along the axis 1106 of the device 1101 while in contact with the inner surface of a tubular structure 1103. The rotational device 1101 has the ability to be in a linear relative movement with the tubular structure 1103 are therefore engrave a desired pattern on the surface in contact. The unprinted tube is loaded and passes through the rotational device 1101, using the heat that is generated from the exterior side of tubular 1103 and/or engraving components 1102 pressuring, super-hydrophobic structure 1105 is generated on the inner side of the tube, with single-step production process, and can be placed and executed right after the cold drawing process, tube extrusion process or all other similar processes for creating, dimension or surface modification tubes processes.

Fig. 12A, Fig. 12B and Fig. 12C illustrates another possible process, according to another embodiment of the invention, providing a super-hydrophobic structure comprising a nano-structural surface and a micro-grid imprint on the inner surface of tubes, by a dip coating process under

pressure. This process includes, molten 'polymer bath' 1201 that can be filled with PVC, PTFE, PE, and among other polymers 1202, pressure chamber 1203 and hollow rod 1204 ('rod mold') that can be made from rigid materials or soft and inflatable materials also, with super-hydrophobic structure. Rod 1204 has an air inlet 1206 that is connected to the chamber outside compressed air supply and air outlet hole 1205, that functions as mono-directional valve that enables only air to pass through it during the de-molding process. Rod 1204 is connected to vertical conveyor 1207 that lifts the rod 1204 from the polymer bath 1201 during the coating process.

The dip coating process carried out under pressure production steps includes: attaining the desired pressure inside the pressure chamber 1203, dip coating rod 1204 in the polymer bath 1201 by the vertical conveyor 1207, using controlled withdrawal velocity to obtain a desired thickness and finally the polymer drying process that dries the polymer 1208 on the rod.

In the de-molding process shown in Fig. 13A and Fig. 13B, air pressure is inserted into the rod 1204 using air inlet 1206, and forced to flow through outlet hole 1205, so as to inflate and de-mold the dry polymer 1208 from rod 1204. Another possible technique for de-molding the imprinted tube is by using an inflatable rod mold that can expand before the coating process and to shrink after that the polymer that had solidified (e.g., a soft rod mold made of rubber).

This inner tube surface imprint with a super-hydrophobic structure method is suitable for short and narrow tubes, and can be used for producing smooth labyrinths (i.e. labyrinth without tortuous "obstacles") with high resistance to flow, high durability, very simple design and structure as well as low blockage risk. The smooth labyrinth narrow tube

can be connected to the main irrigation pipes using fit connectors. Another application example is a medical tubing such as catheters and syringe needles.

Fig. 14B shows an exemplary use of a super hydrophobic structure 1401 of Fig. 14A in a dripper 1402 (use in irrigation systems, for example).

All the above description has been provided for the purpose of illustration and is not meant to limit the invention in any way except as per the attached claims.

An experiment was carried out in order to evaluate the feasibility of the method described above to create a super-hydrophobic structure comprising a micro-grid imprint on the inner surface of tubes with single-step production process, using PET film, 200 micron thickness, and a micromesh with string diameter of 16 micron and spacing of 56 micron. According to method shown in Fig. 6, the PET film and the micromesh were pressed in 1.75 kg/cm^2 against 1 mm PE foil and heated up to 120°C for 15 seconds. The results show that the PE foil gets the negative shape of the micromesh.

An experiment was carried out in order to evaluate the feasibility of the method described above to create a super-hydrophobic hierarchical structure comprising a nano-structural surface and a micro-grid imprint on the inner surface of tubes with single-step production process, using a structural surface made from 200 micron thickness PET film with optical grating of 1000 lines/mm and a micromesh with string diameter of 16 micron and spacing of 56 micron. According to the method described in Fig. 6, the PET film and the micromesh were pressed in 1.75 kg/cm^2 against 1 mm PE foil and heated up to 120°C for 15 seconds. The results show that the PE foil gets the negative shape of the micromesh and also

the negative shape of the nanostructure PET film pattern, on top of each post.

Claims

1. A method for providing a patterned surface, comprising:
 - a) imprinting/thermally-embossing an article with a nano/micro size pattern;
 - b) optionally weaving said textured article into a mesh structure;
 - c) optionally imprinting/thermally-embossing the mesh with a nano/micro size pattern;
 - d) applying the mesh structure to a surface having a softening point lower than the softening point of said textured article;
 - e) applying a pressure onto said mesh structure, while heating said surface to a temperature equal to or above its softening point, thereby to create a nano/micro pattern on said surface; and
 - f) optionally using the low softening point surface as a mold.
2. According to one embodiment of the invention there is provided a method in which pressure and/or heat is applied using a patterned surface, thereby creating additional patterning on the surface that is not in contact with the mesh structure.
3. A method according to claim 1, wherein the nano/micro-patterned surface is hydrophobic.
4. A method according to claim 3, wherein the hydrophobic surface has a wetting angle greater than 140° , preferably greater than 150° .
5. A method according to claim 1, wherein the surface to be patterned is part of a liquid conduit.
6. A method according to claim 5, wherein the liquid conduit is a pipe.
7. A method according to claim 6, wherein the pipe is a watering system pipe.

8. A patterned surface whenever manufactured by the method of claim 1.
9. A device comprising a patterned surface as claimed in claim 8.
10. The device of claim 9, which is a liquid conduit.
11. The device of claim 10, which is a pipe.
12. A method for modifying a surface, characterized by creating a hydrophobic surface using heat and/or pressure.
13. A device, selected from a conduit, pipe, emitter or device with hydrophobic surface, whenever manufactured by the method of claim 12.
14. A device which is a folding conduit or pipe the internal surface area of which was changed with heat and/or pressure using an imprinting/thermally-embossing belt device.
15. A device which is a conduit or pipe, the internal surface area of which was changed with heat and/or pressure using engraving components which have the same curvature radius as the inner curvature radius of the conduit or pipe.
16. A device which is a conduit or pipe, the internal surface area of which was created/changed with heat and/or pressure using the expansion or shrinkage ability thereof, or of the mold, to perform the de-molding process.
17. A smooth labyrinth comprised in a hydrophobic narrow tube.
18. A mesh the surface area of which was changed with heat and/or pressure.
19. A drip irrigation emptying system with compressed gas to avoid root insertion.

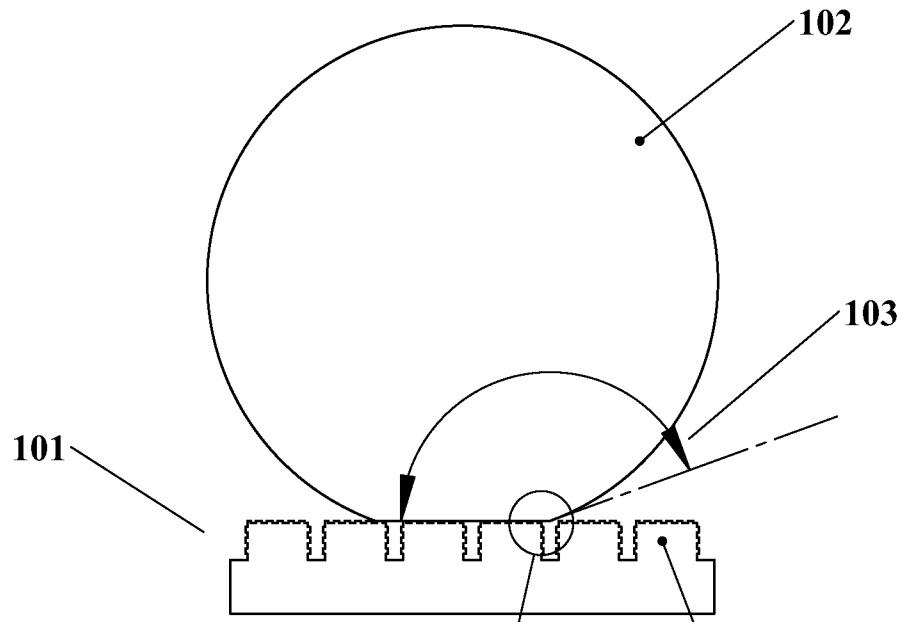


Fig. 1A

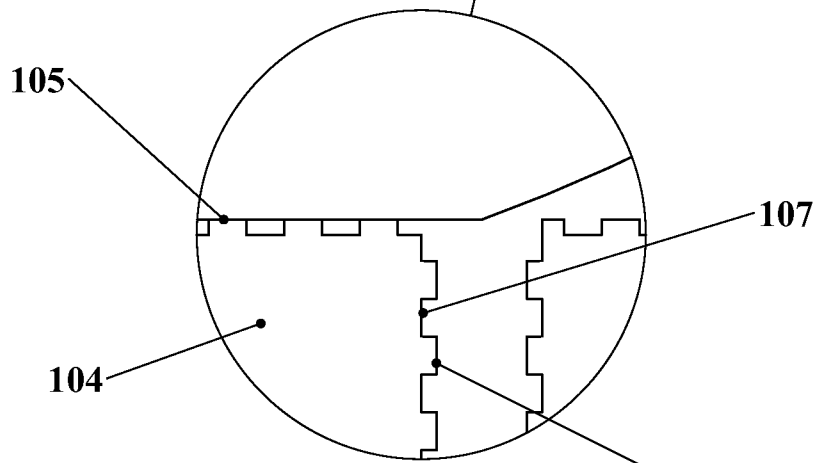


Fig. 1B

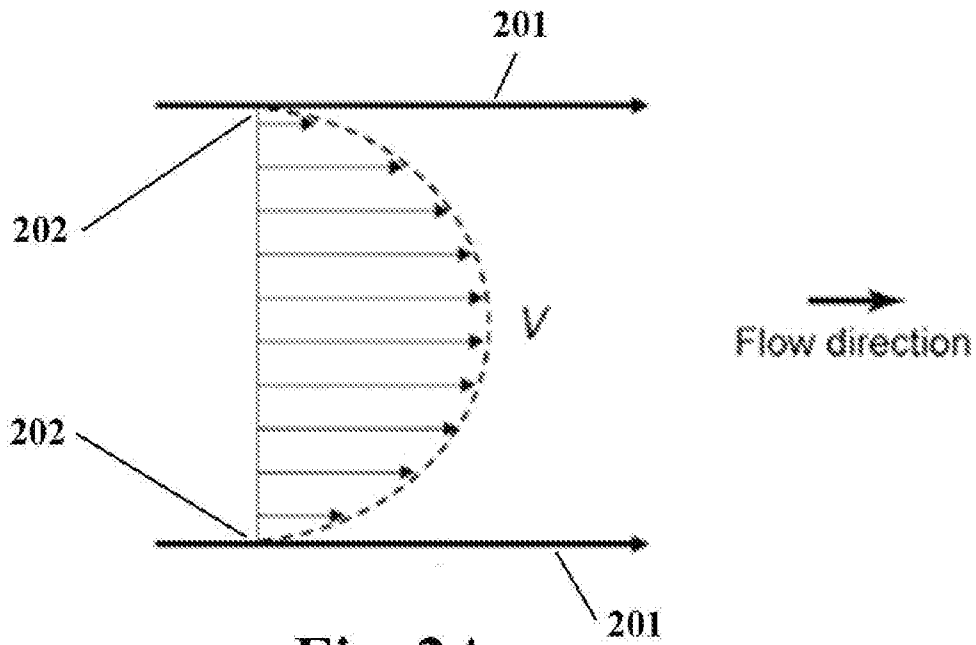


Fig. 2A

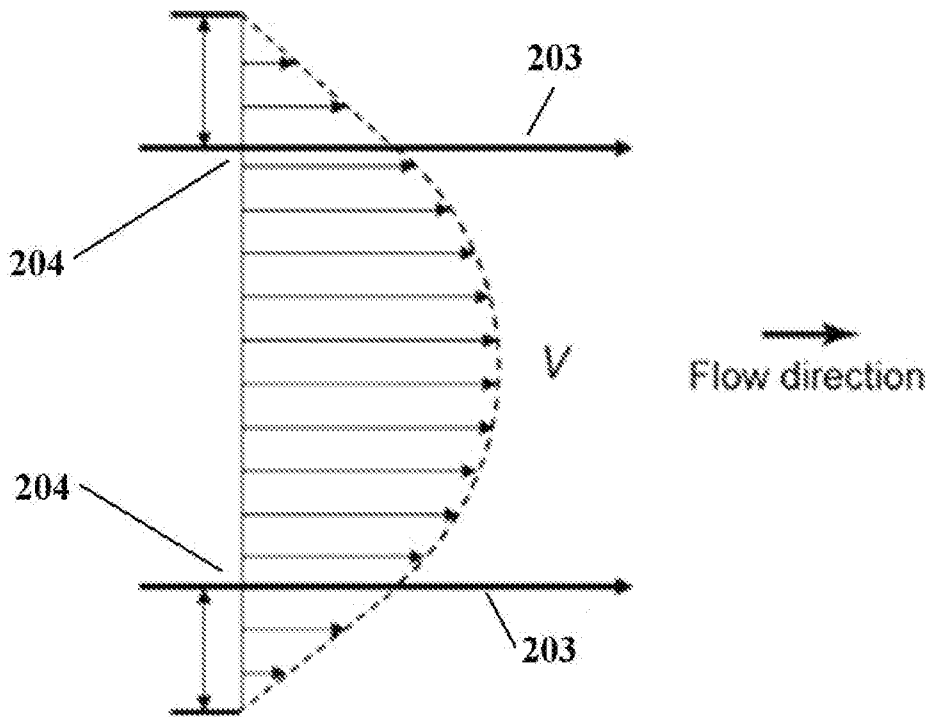


Fig. 2B

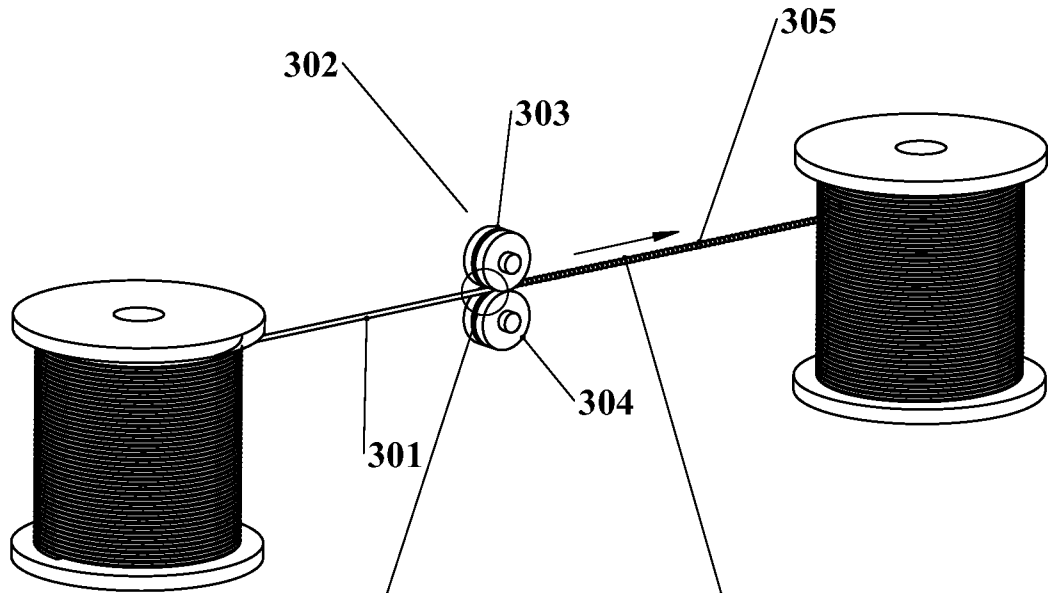


Fig. 3A

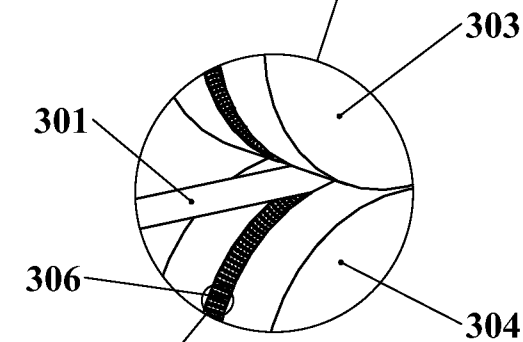


Fig. 3B

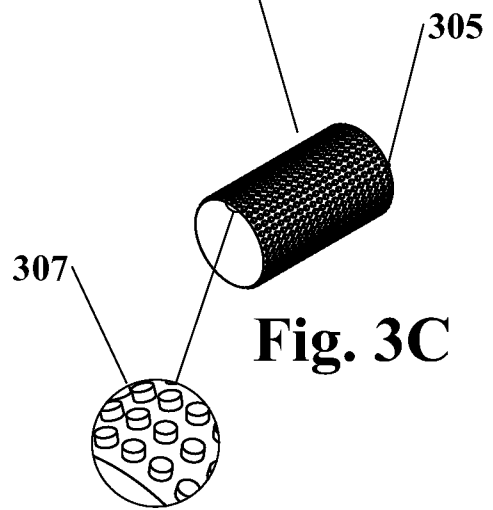


Fig. 3C

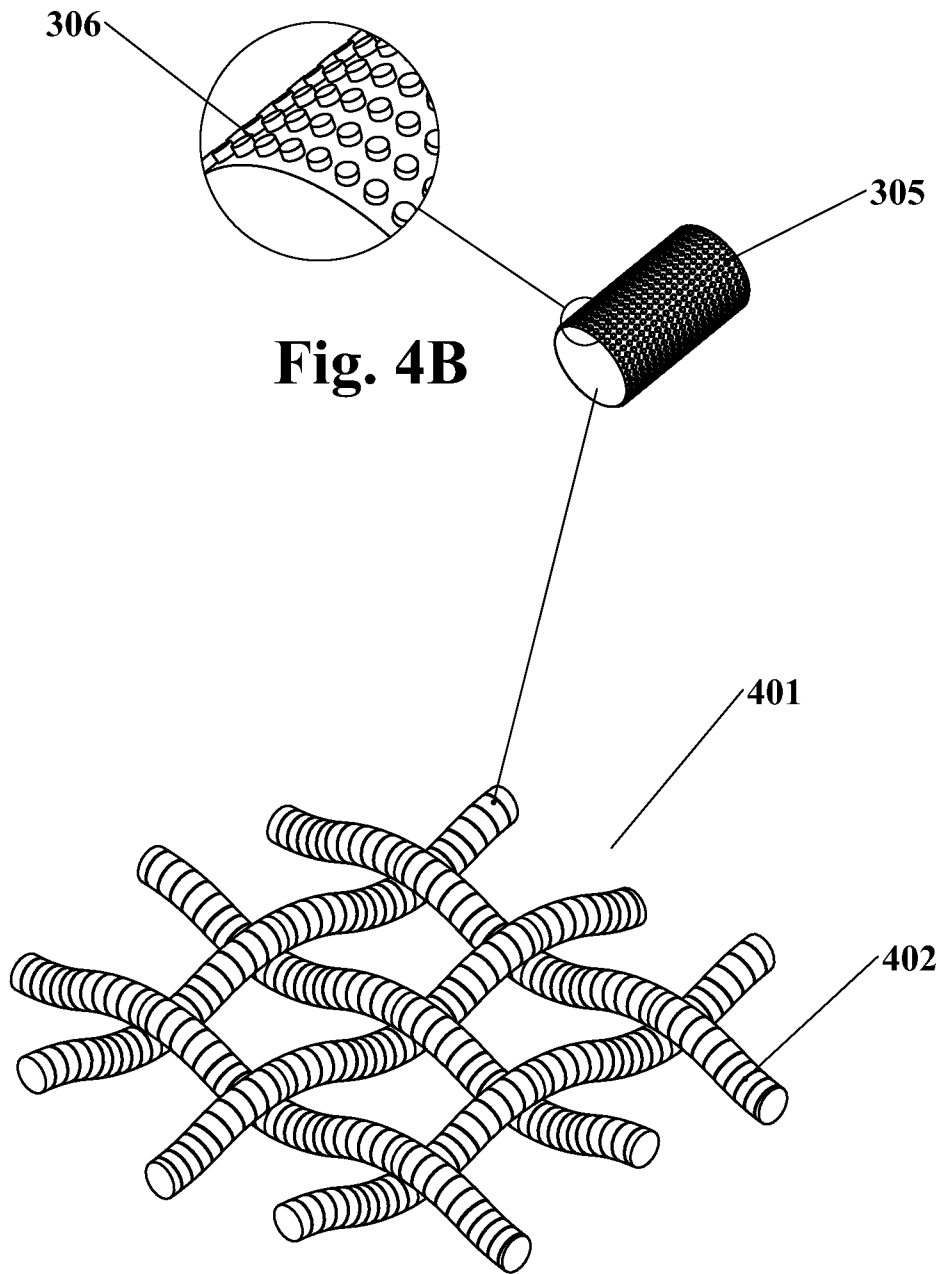


Fig. 4B

Fig. 4A

5/14

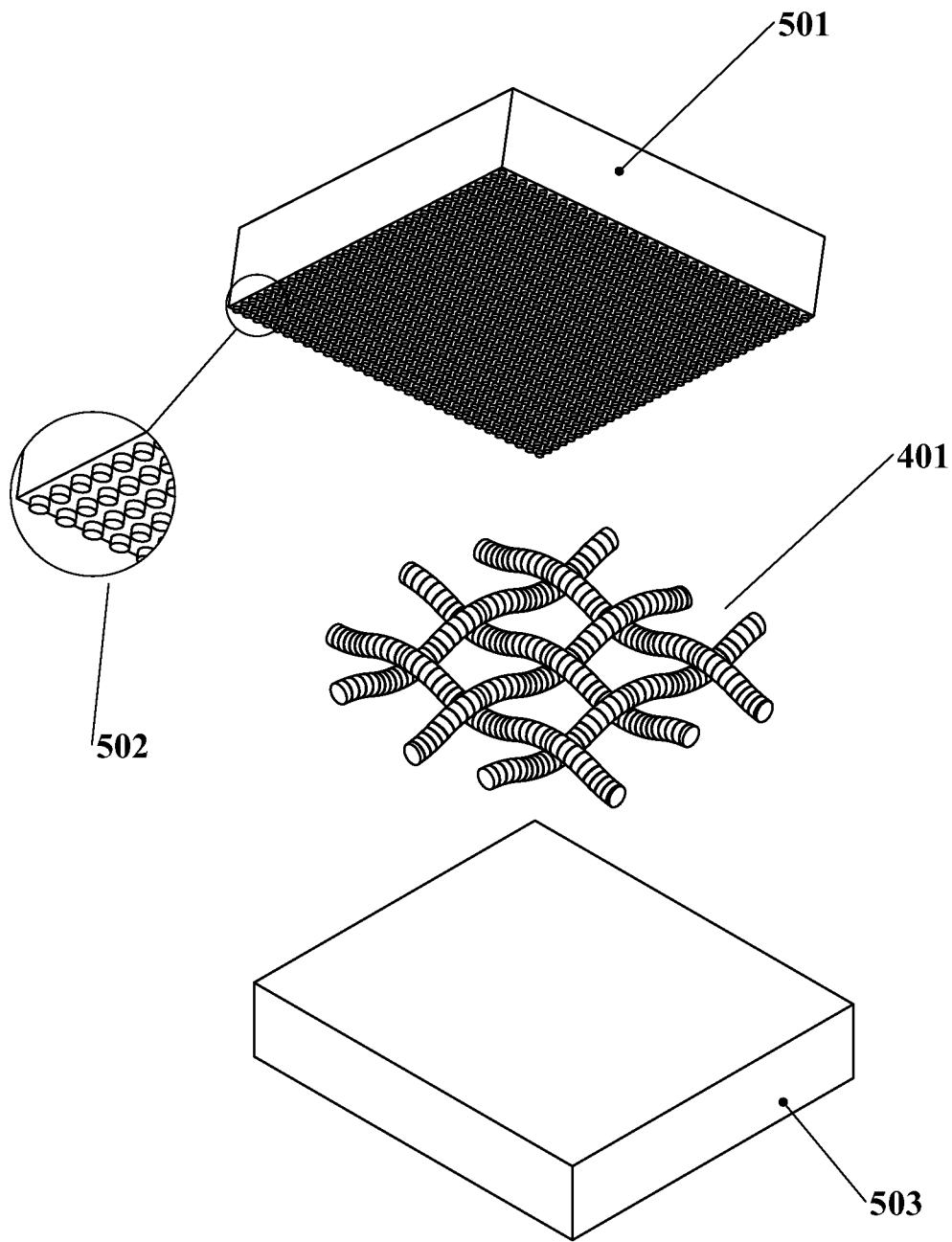


Fig. 5

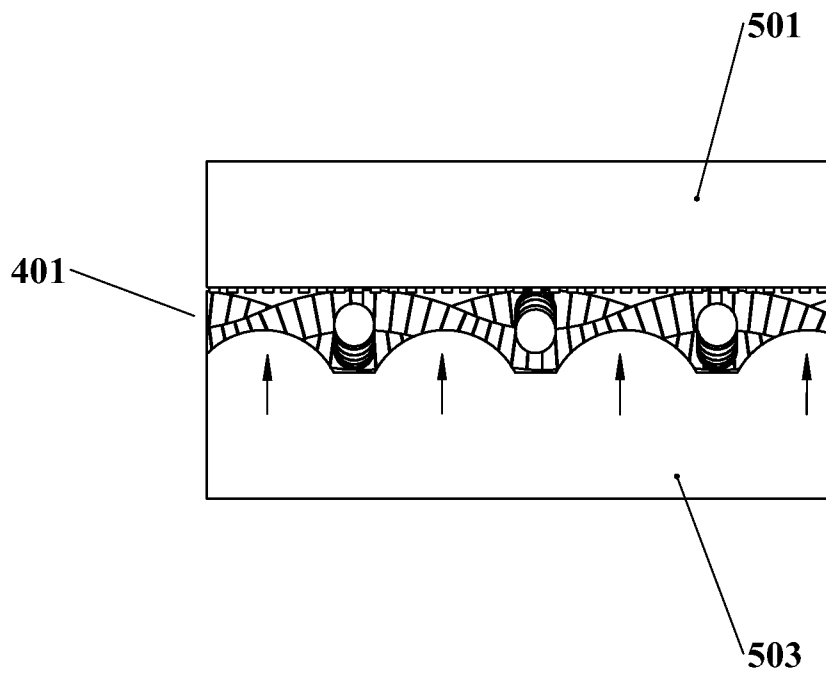


Fig. 6

7/14

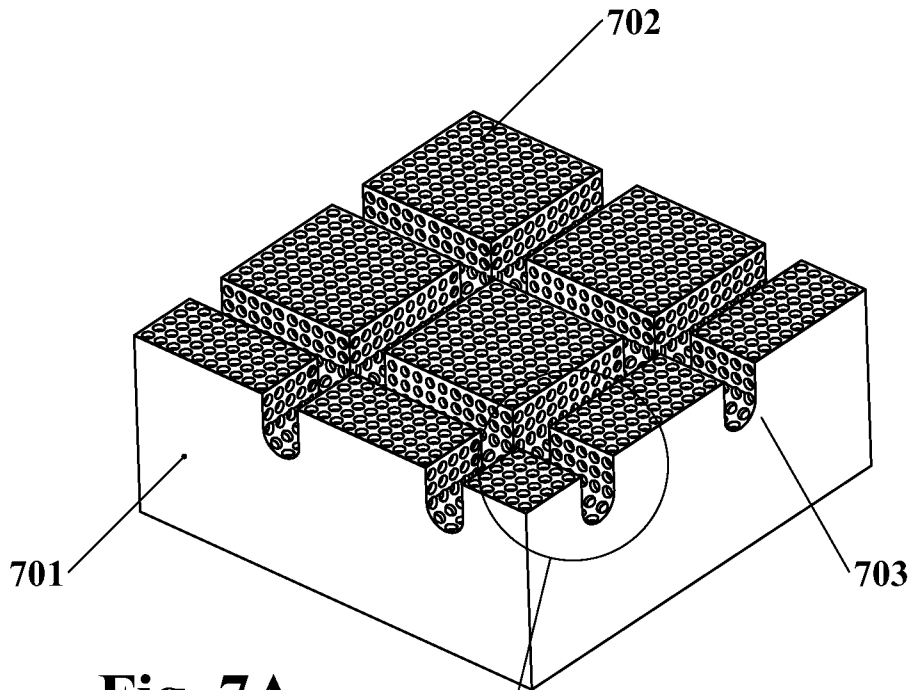


Fig. 7A

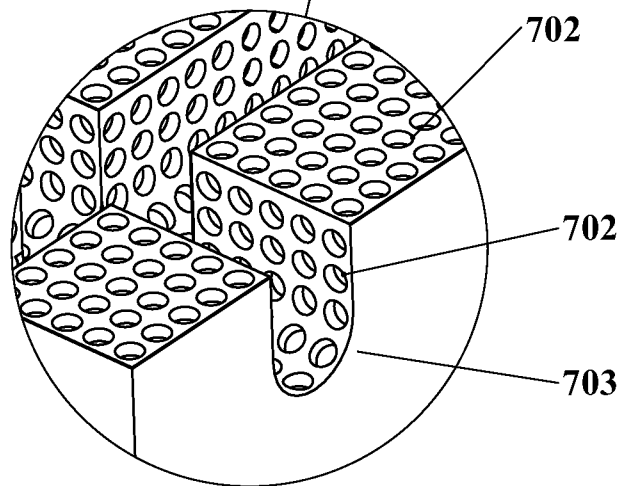
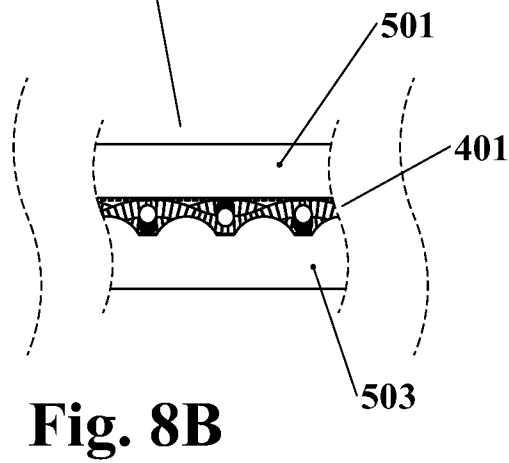
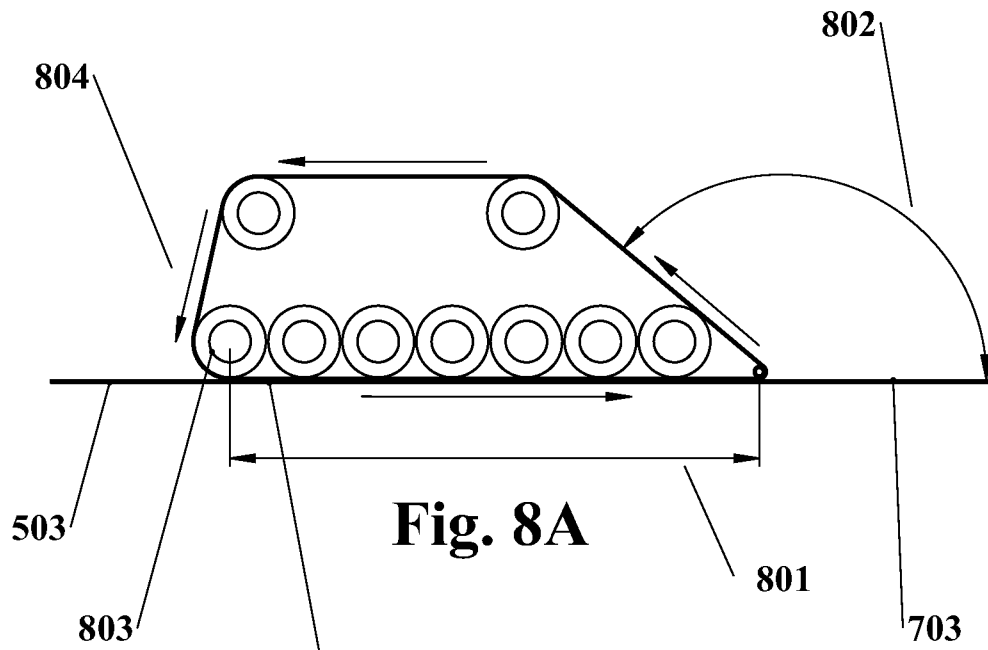


Fig. 7B



9/14

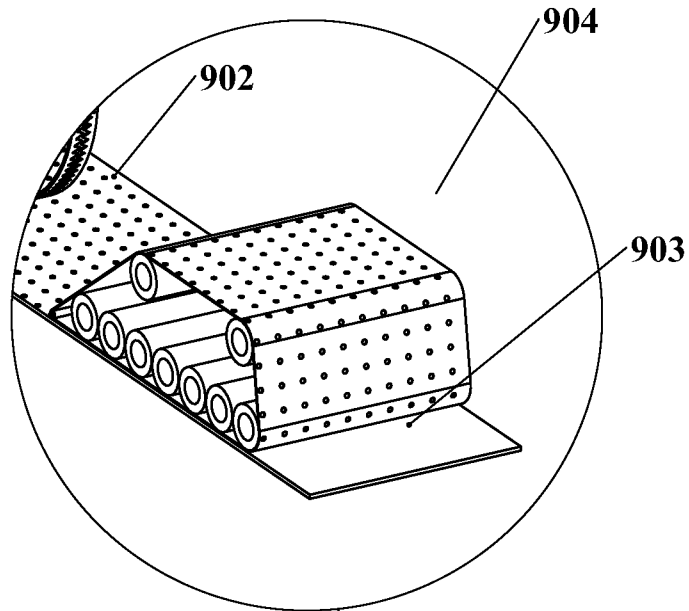


Fig. 9B

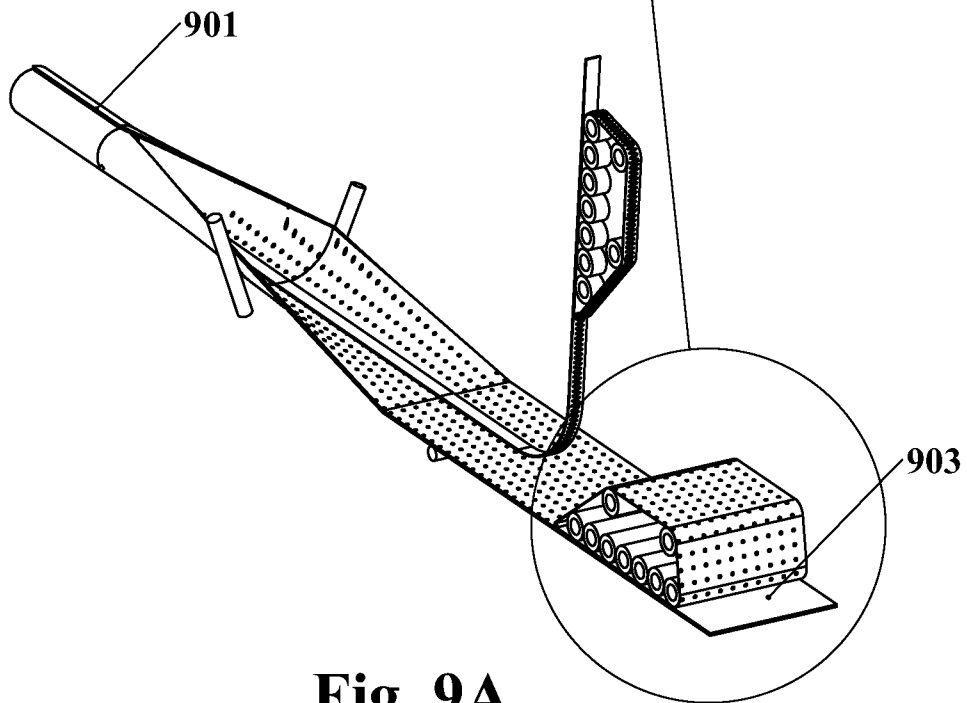


Fig. 9A

10/14

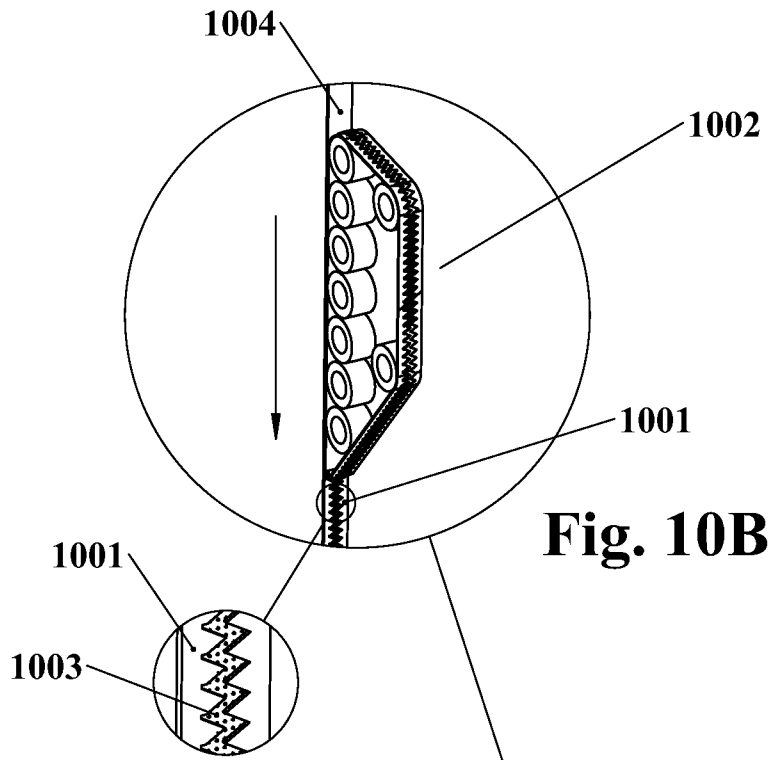


Fig. 10B

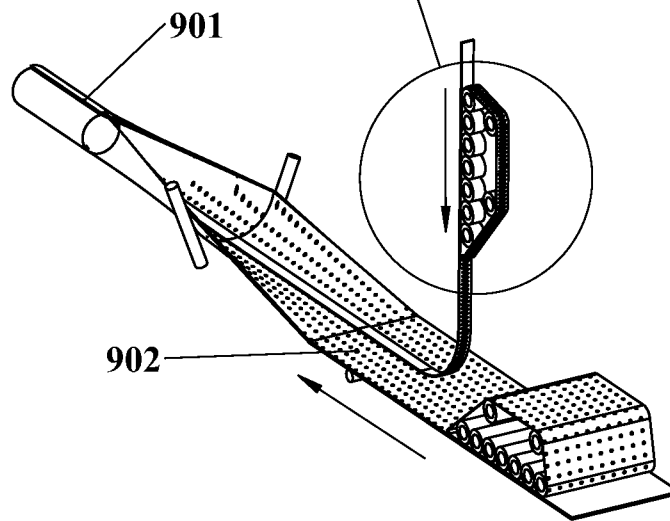


Fig. 10A

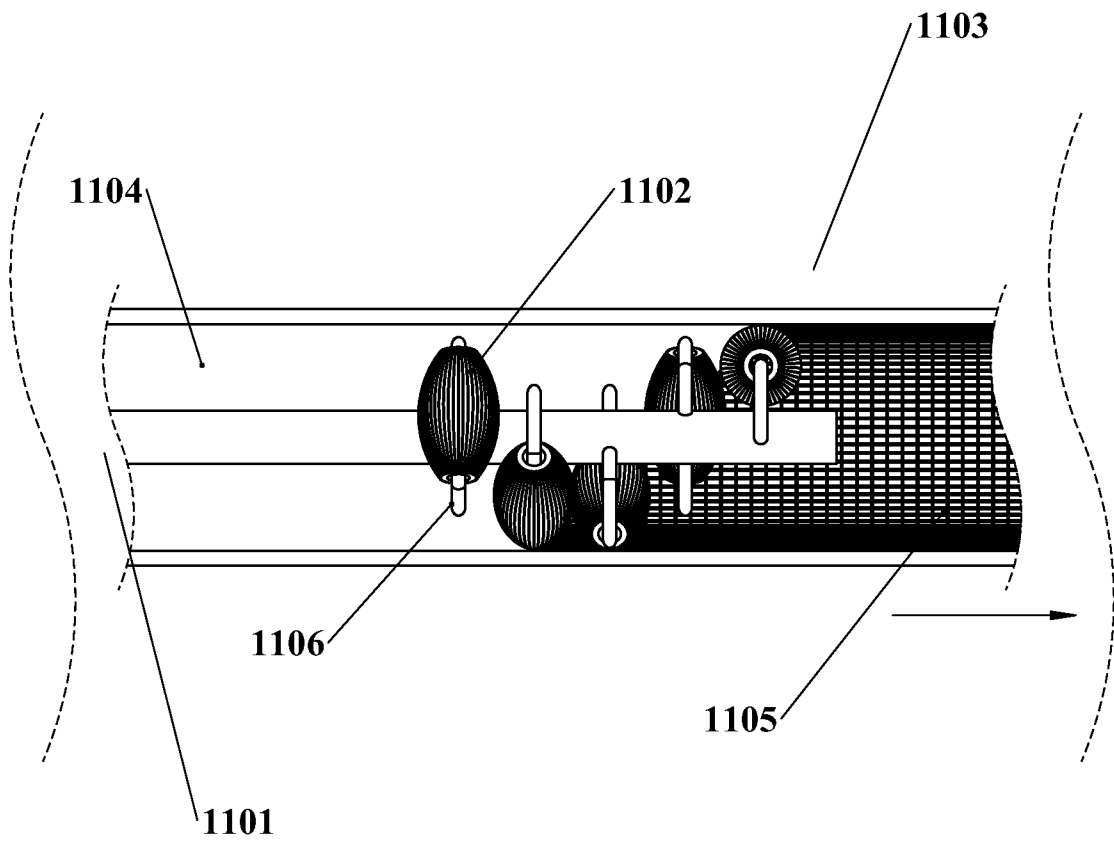


Fig. 11

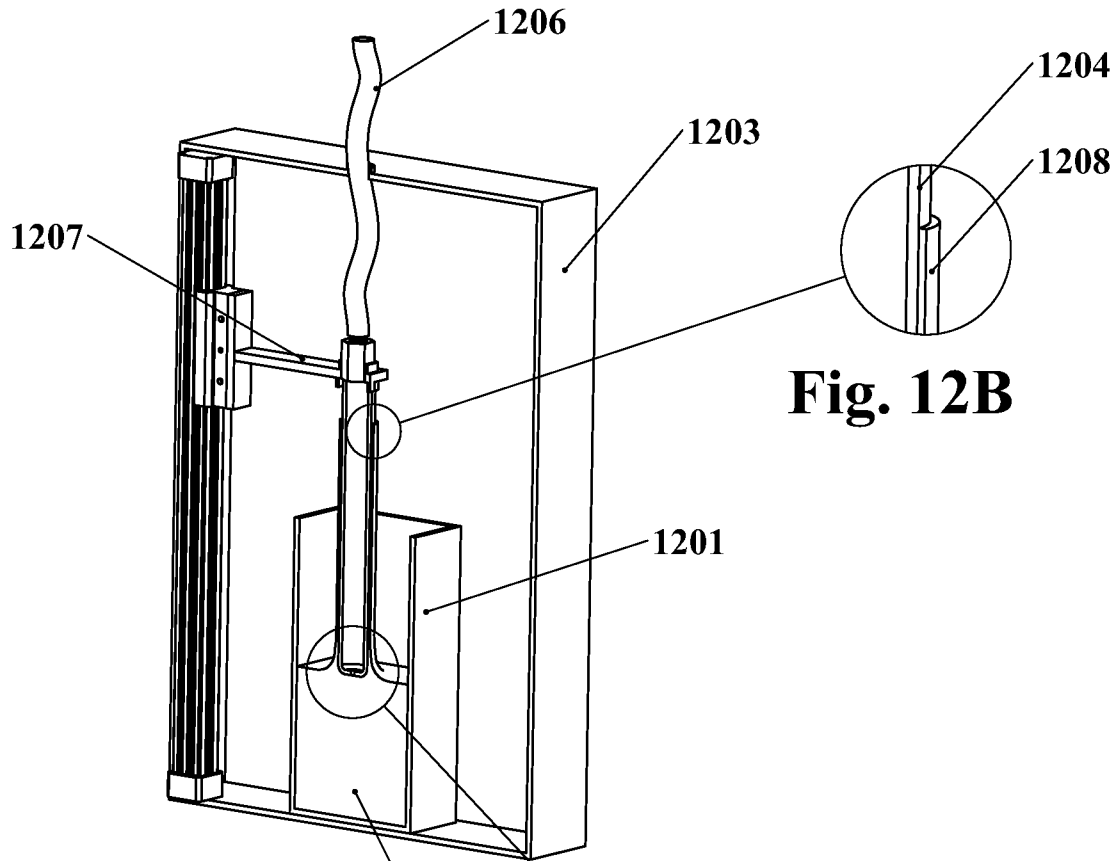


Fig. 12A

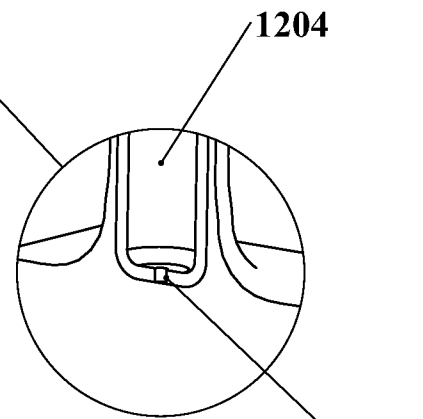


Fig. 12C

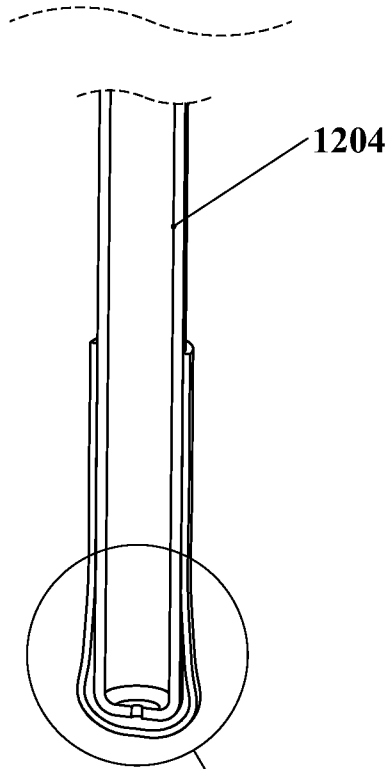


Fig. 13A

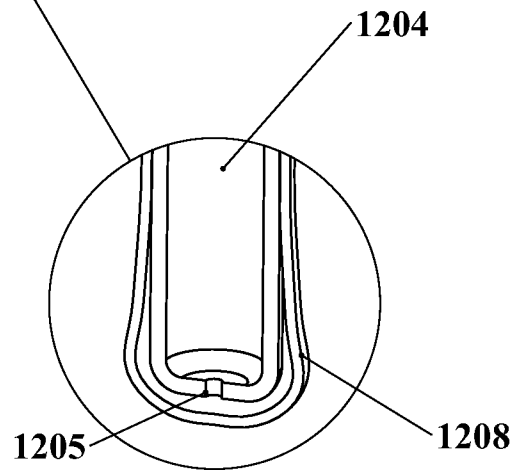


Fig. 13B

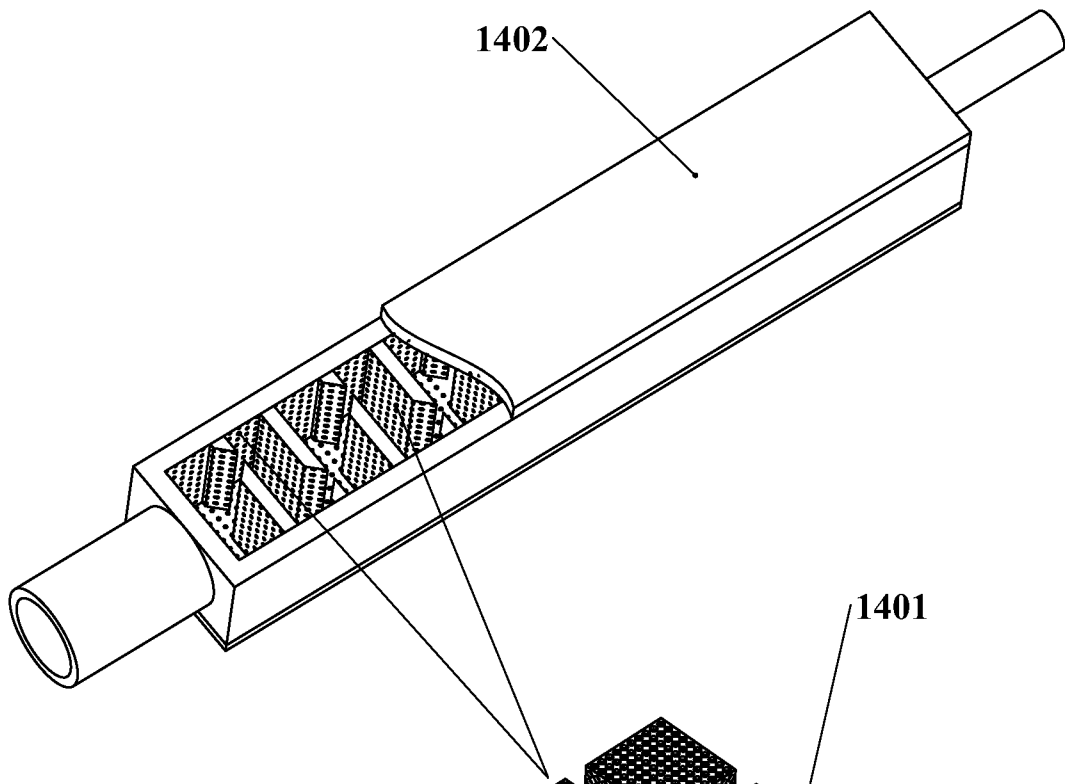


Fig. 14A

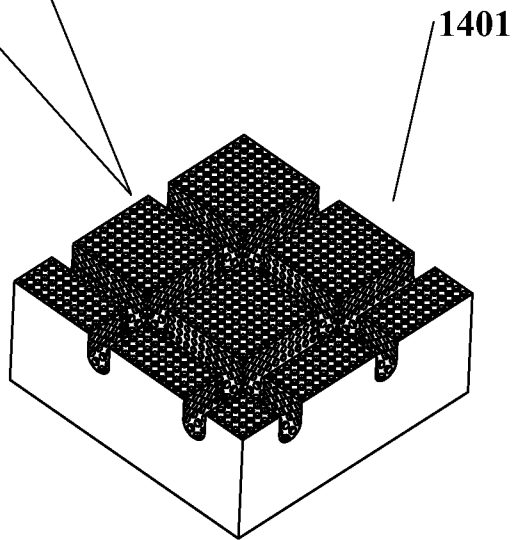


Fig. 14B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL2014/050001

A. CLASSIFICATION OF SUBJECT MATTER
IPC (2014.01) B29C 59/02, B29C 59/04, B08B 17/06, A01G 25/02

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC (2014.01) B08B, B29C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Databases consulted: Esp@cenet, Google Patents, Google Scholar, FamPat database
Search terms used: Superhydrophobic , patterned/textured surface , emboss , mesh , pipe/conduit , lotus effect

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| X | WO 2012118805 A2 RESEARCH FOUNDATION OF THE CITY UNIVERSITY OF NEW YORK 07 Sep 2012 (2012/09/07) Example 1; Figures 7 & 8 ; page 23 lines 4-7 ; page 22 lines 1-14 ; Table 2 , page 23 | 1,3,4,8,9 |
| X | US 3354022 A DETTRE R. H. et al. 21 Nov 1967 (1967/11/21) Examples ; Col. 14 lines 31-37 | 1,3,4,8,9 |
| X | US 6660363 B1 BARTHLOTT W. 09 Dec 2003 (2003/12/09) Col. 2 lines 8-24 , 36-52 , 63-67 ; Example 2 | 1,5-11 |
| Y | | 3,4 |
| X | WO 2012064745 A2 UNIVERSITY OF FLORIDA RESARCH FOUNDATION INC. 18 May 2012 (2012/05/18) page 12 line 20 – page 15 line 4 ; fig. 4 and fig. 5-9 ; table 3 , page 17 | 1,3,4,8 |

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

* 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

| | |
|--|---|
| Date of the actual completion of the international search 20 Mar 2014 | Date of mailing of the international search report 23 Mar 2014 |
|--|---|

| | |
|--|---|
| Name and mailing address of the ISA: Israel Patent Office Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel Facsimile No. 972-2-5651616 | Authorized officer GUTMAN Ariel Telephone No. 972-2-5657816 |
|--|---|

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IL2014/050001

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| E | WO 2014041501 A1 ARIEL - UNIVERSITY RESEARCH AND DEVELOPMENT COMPANY, LTD. 20 Mar 2014 (2014/03/20) The whole document | 1 |

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: 2
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 2 is formulated in a form which does not follow the conventional claiming practice, as laid down in the PCT guidelines 5.01-5.05, 5.15 and 5.16. This creates ambiguities and consequently generates clarity issues which can not enable the reader to determine the subject matter of the claim.

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See extra sheet.

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1,3-11

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet):

* This International Searching Authority found multiple inventions in this international application, as follows:

| | | |
|---------------|---|----------------|
| Invention/s 1 | Refers to a method for creating a patterned surface by imprinting/embossing said surface with a textured article using heat and pressure. | Claim/s 1,3-11 |
| Invention/s 2 | Refers to a method for creating hydrophobic surface by using heat and/or pressure. | Claim/s 12,13 |
| Invention/s 3 | Refers to a device wherein it surface was modified by heat and/or pressure using an imprinting/embossing belt device. | Claim/s 14 |
| Invention/s 4 | Refers to a device wherein it surface was modified by heat and/or pressure using engraving components. | Claim/s 15 |
| Invention/s 5 | Refers to a device wherein it surface was modified by heat and/or pressure using a molding process. | Claim/s 16 |
| Invention/s 6 | Refers to a smooth labyrinth | Claim/s 17 |
| Invention/s 7 | Refers to a mesh wherein it surface was modified by heat and/or pressure. | Claim/s 18 |
| Invention/s 8 | Refers to a drip irrigation emptying system. | Claim/s 19 |

INTERNATIONAL SEARCH REPORT
Information on patent family members

| |
|--|
| International application No. PCT/IL2014/050001 |
|--|

| Patent document cited search report | Publication date | Patent family member(s) | Publication Date |
|-------------------------------------|------------------|-------------------------|------------------|
| WO 2012118805 A2 | 07 Sep 2012 | EP 2681259 A2 | 08 Jan 2014 |
| | | US 2013251948 A1 | 26 Sep 2013 |
| | | WO 2012118805 A2 | 07 Sep 2012 |
| | | WO 2012118805 A3 | 13 Dec 2012 |
| US 3354022 A | 21 Nov 1967 | US 3354022 A | 21 Nov 1967 |
| US 6660363 B1 | 09 Dec 2003 | AT 174837 T | 15 Jan 1999 |
| | | AU 3165595 A | 04 Mar 1996 |
| | | CZ 9700245 A3 | 14 May 1997 |
| | | CZ 295850 B6 | 16 Nov 2005 |
| | | DE 59504640 D1 | 04 Feb 1999 |
| | | DK 0772514 T3 | 23 Aug 1999 |
| | | EP 0772514 A1 | 14 May 1997 |
| | | EP 0772514 B1 | 23 Dec 1998 |
| | | ES 2128071 T3 | 01 May 1999 |
| | | HU T75807 A | 28 May 1997 |
| | | HU 217781 B | 28 Apr 2000 |
| | | JP H10507695 A | 28 Jul 1998 |
| | | PL 318260 A1 | 26 May 1997 |
| | | PL 178053 B1 | 29 Feb 2000 |
| | | US 6660363 B1 | 09 Dec 2003 |
| WO 9604123 A1 | 15 Feb 1996 | | |
| WO 2012064745 A2 | 18 May 2012 | US 2013230695 A1 | 05 Sep 2013 |
| | | WO 2012064745 A2 | 18 May 2012 |
| | | WO 2012064745 A3 | 27 Sep 2012 |
| WO 2014041501 A1 | 20 Mar 2014 | NONE | |