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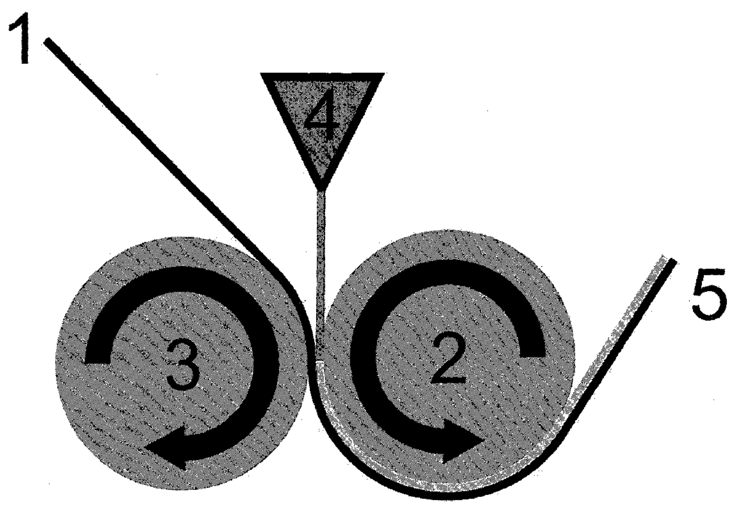

Figure 1

(57) Abstract: A method for producing a high aspect ratio micro- or nanostructured thermoplastic polymer foil, or a nanostructured thermoplastic polymer coating on a carrier foil, comprising at least one high aspect ratio nanostructured surface area, is disclosed. The method comprises applying a high aspect ratio nanostructured surface on an extrusion coating roller and maintaining the temperature of the roller below the solidification temperature of the thermoplastic material. A thermoplastic foil and a thermoplastic coating made by the method is also disclosed.

WO 2015/144174 A1

METHOD AND APPARATUS FOR PRODUCING A HIGH ASPECT RATIO NANOSTRUCTURED FOIL BY EXTRUSION COATING OR EXTRUSION CASTING

FIELD OF THE INVENTION

The present invention relates to a method and apparatus for manufacturing foils with a thermoplastic surface comprising high-aspect ratio micro or nanostructures

BACKGROUND OF THE INVENTION

In biotechnological, medical and consumer applications, it is desirable to apply functional structures e.g. nanostructures, to defined areas of articles for use as functional surfaces, altering the properties of the surface relative to that of an unstructured surface. Examples of desirable functions are self-cleaning or super repellent surfaces. A method of producing such articles independently of the overall macro-geometry is desirable, in particular if such articles are mass produced at a relative low price as many of these articles must be disposable or low cost reusable products, e.g. toys or packaging material.

The most commonly used method for making controlled micro or nanostructures in thermoplastic surfaces are variotherm injection molding type processes. By melting a thermoplastic material and injecting it into a heated mold under high pressure, the surface of the mold will be replicated, thereby generating a micro or nanostructures polymeric replica. The most common application of this is CD/DVD/Blu-Ray manufacturing, where a polymeric replica may be made in a few seconds. However, the molding of high aspect ratio structures, where the width is low and the depth is high, is challenging using these types of processes due to the rapid cooling of the melt surface upon injection into the cold mold. One solution to this problem have been to vary the temperature of the mold during the process in a variotherm process where the mold is heated above the solidification temperature during melt injection and subsequently cooled below the solidification temperature in order to make the polymeric part solidify so it can be removed from the mold. This, however, increases the cycle times considerably.

Embossing processes are closely related to the variotherm injection molding types of process, where a solid thermoplastic substrate, typically a foil, is being heated while in contact with a master structure made by conventional lithographic means.

the master structure typically consist of a nickel or silicon or silicone (PDMS) shim or stamp. After heating and shaping of the surface topography of the substrate to be the inverse of the master structure, the master and substrate is cooled below the solidification temperature of the substrate, and the substrate may be removed. Typical processing throughputs of these types of processes are. cm2 per heating/cooling cycle which typically takes from 10 s and up to several minutes depending on the apparatus, giving a productivity on the order of 10-100 cm2/s equaling 0.001-0.01 m2/s.

Some reports of high speed replication have been given, but only for low aspect ratio structures, typically decorative or diffractive structures.

For many applications these throughput rates are several orders of magnitude to slow. Applications such as functionalized foils for food packaging, coating of windows, ships or car windshields with self cleaning surfaces all require throughputs on the order of 1 m2/s or higher in order to be economically feasible.

Due to the abovementioned problems with the state-of-the-art, it would be desirable to have a technological solution, where high aspect ratio micro or nanostructures may be formed in foils at low cost at high throughput rates. It would further be advantageous if this solution could provide micro or nanostructures of a high quality and it would be a further advantage if the micro or nanostructured area could cover the whole area of the manufactured foil.

To overcome the abovementioned problems of state-of-the-art an invention providing the technological solution with the abovementioned desired properties is here presented.

What we propose is to use an extrusion coating or casting type technology to coat or produce generic foils with a thin layer of a thermoplastic material, which is micro or nanostructured during the coating process.

Extrusion coating is a process where a carrier foil is moved between two rollers, a cooling roller and a counter roller, respectively. A polymeric melt is applied between the foil and the cooling roller in a continuous process. Upon contact with the cooling roller, the thermoplastic melt solidifies, and upon contact with the carrier foil, the thermoplastic melt is adhered to the carrier foil. The result is a carrier foil coated with a thin layer of a thermoplastic material.

Extrusion casting is a process where a thermoplastic melt is moved between two rollers, a cooling roller and a counter roller, respectively. The thermoplastic melt is applied between the foil and the cooling roller in a continuous process. Upon contact with the cooling roller, the thermoplastic melt solidifies forming a thermoplastic foil. Extrusion casting is essentially the same process as extrusion coating, where the carrier foil is omitted, and extrusion coating will be descriptive to both the extrusion coating and the extrusion casting processes in this description, unless specifically stated.

We have invented a process that may produce micro or nanostructured thermoplastic coatings by micro or nanostructuring the cooling roller and by carefully choosing the extrusion coating process parameters. This process may enable production at high throughput rates. So far throughput rates of up to 0.5 m2/s have been demonstrated in pilot production setup, and using full scale production equipment, rates of 5-10 m2/s may be achieved. In order for the process to work, micro or nanostructured cooling rollers are required. We have therefore also developed a method for micro or nanostructuring cooling rollers.

The novelty and inventive step of the invention is realized by the surprisingly high throughput and surface quality of the process, as well as the ability of the process to make continuous areas of micro or nanostructures without significant seam lines and the ability to cover the whole area of the manufactured foil.

OBJECT OF THE INVENTION

It may be seen as an object of the present invention to provide an improved method for producing large areas of foil with micro or nanostructured thermoplastic coating at either a throughput rate larger than today's state-of-the-art, at a substantially lower cost than the cost associated with today's state-of-the-art processes, or with a substantially better quality of replication of the micro or nanostructures than state-of-the-art processes.

It is a further object of the invention to enable production of spatially continuous micro or nanostructures without visible seam lines.

It is a further object of the present invention to provide an alternative to the prior art.

DESCRIPTION OF THE INVENTION

The invention here presented regards the process of manufacturing of a micro or nanostructured polymer coating applied onto carrier foils by the use of a micro or nanostructured roller. One embodiment of the technique is shown in figure 1. A carrier foil (1) is passed between the micro or nanostructured roller (2) and a counter roller (3). A thermoplastic melt is deposited between the micro or nanostructured roller (2) and the carrier foil (1). The micro or nanostructured roller is kept at a temperature below the solidification temperature of thermoplastic melt. The micro or nanostructured roller and the counter roller rotates as indicated by the arrows, thereby moving the carrier foil while laminating the thermoplastic melt to the carrier foil. Upon contact between the thermoplastic melt (4) and the micro or nanostructured roller (2), a simultaneous cooling and shaping of the thermoplastic melt occurs, thereby forming a micro or nanostructured and solid thermoplastic coating which is laminated to the carrier foil, thereby forming a carrier foil comprising a micro or nanostructured thermoplastic coating (5). The rotational velocity of the rollers time the width of the foil equals the throughput of the process or the rate of which micro or nanostructured surface is produced. Typical widths of rollers are from 10's of cm to several meters, and typical rotational velocities are from 10 to 300 meter/minute. The applicants have demonstrated successful production of both micro and nanostructured thermoplastic coatings with rotational velocities up to 60 m/min, on a roller 50 cm wide, resulting in a production rate of 30 m2/min or 0.5 m2/s.

Another embodiment is shown in figure 2. A thermoplastic melt is (1) is passed between the micro or nanostructured roller (2) and a counter roller (3). The micro or nanostructured roller is kept at a temperature below the solidification temperature of thermoplastic melt. The micro or nanostructured roller and the counter roller rotates as indicated by the arrows, thereby moving the thermoplastic melt. Upon contact between the thermoplastic melt (1) and the micro or nanostructured roller (2), a simultaneous cooling and shaping of the thermoplastic melt occurs, thereby forming a micro or nanostructured and solid thermoplastic foil (4). The rotational velocity of the rollers time the width of the foil equals the throughput of the process or the rate of which micro or nanostructured surface is produced. Typical widths of rollers are from 10's of cm to several meters, and typical rotational velocities are from 10 to 300 meter/minute. The applicants have demonstrated successful production of high aspect ratio micro and nanostructured thermoplastic foils with rotational velocities up to 60 m/min, on a roller 50 cm wide, resulting in a production rate of 30 m2/min or 0.5 m2/s.

The roller may be made by different techniques. One technique for manufacturing such a micro or nanostructured roller is by the application of a thin layer of liquid ceramic material precursor solution, directly on the surface of a conventional high surface roughness roller, allowing the solvent of the liquid ceramic precursor solution to evaporate in order to form a ductile film of ceramic material precursor, structuring the film of ductile ceramic material precursor by a mechanical process such as embossing, curing it to a film of structured solid ceramic material and using it for the purpose of the disclosed invention. Another method for manufacturing the micro or nanostructured roller is a shim approach, where shims containing the micro or nanostructure are mounted on the roller by means of welding, gluing, taping, magnetism or other means. The shims are typically manufactured by conventional lithographic means, such as deep UV lithography, photolithography, electron beam lithography, electroplating, dry or wet etching, step-and-repeat nano imprint lithography, embossing or by other means to make a micro or nanostructured surface. The shims typically consists of thin nickel or silicon plates cut out in the desired shape, and may be placed in close vicinity to each other in order to cover most of the surface area of the roller. This method, however, will make visible seam lines between the individual shims, which will typically have a width of minimum 10-100 μm, depending on the precision of the cutting and mounting tools used.

The invention relates to a method for producing a nanostructured thermoplastic polymer coating on a carrier foil comprising at least one high aspect ratio nanostructured surface area, said method comprising at least the following steps:

- providing an initial extrusion coating roller for an industrial polymer extrusion coating process using a thermoplastic material

- applying a high aspect ratio nanostructured surface on the said extrusion coating roller thereby forming a high aspect ratio nanostructured extrusion coating roller

- maintaining the temperature of the said high aspect ratio nanostructured extrusion coating roller below the solidification temperature of the said thermoplastic material

- moving a carrier foil between the rotating high aspect ratio nanostructured extrusion coating roller and a rotating counter pressure roller at a given velocity corresponding to the rotational velocity of the rotating high aspect ratio nanostructured extrusion coating roller

- continuously applying a melt of said thermoplastic material between the said moving carrier foil and the said rotating high aspect ratio nanostructured extrusion roller, whereby said thermoplastic melt is solidified upon contact with said high aspect ratio nanostructured extrusion coating roller maintained at a temperature below the solidification temperature of the said thermoplastic melt thereby forming a solid high aspect ratio nanostructured thermoplastic coating on said carrier foil.

The invention furthermore relates to a method for producing a high aspect ratio micro or nanostructured thermoplastic polymer foil comprising at least one high aspect ratio nanostructured surface area, said method comprising at least the following steps:

- providing an initial extrusion roller for an industrial polymer extrusion casting process using a thermoplastic material

- applying a high aspect ratio nanostructured surface on the said extrusion roller thereby forming a high aspect ratio nanostructured extrusion coating roller

- maintaining the temperature of the said high aspect ratio nanostructured extrusion roller below the solidification temperature of the said thermoplastic material

- continuously applying a melt of said thermoplastic material between the said counter roller and the said rotating high aspect ratio nanostructured extrusion roller, whereby said thermoplastic melt is solidified upon contact with said high aspect ratio nanostructured extrusion roller maintained at a temperature below the solidification temperature of the said thermoplastic melt thereby forming a solid high aspect ratio nanostructured thermoplastic foil.

The invention furthermore relates to a method where the aspect ratio of the said nano or microstructure is above 2, more preferably above 1.5, even more preferably above 1.25, and most preferable more than 1.

The invention furthermore relates to a method, where high aspect ratio nanostructures are produced on both sides of the cast foil by using both a high aspect ratio nanostructured extrusion roller and a high aspect ratio nanostructured counter roller.

The invention furthermore relates to a method where the said high aspect ratio nanostructured surface is applied by mounting high aspect ratio nanostructured shims on the said initial extrusion coating roller.

The invention furthermore relates to a method where the high aspect ratio nanostructured surface is applied by coating the said initial extrusion coating roller with a material which is subsequently high aspect ratio nanostructured.

The invention furthermore relates to a method where the said material is a ductile ceramic material precursor which is nanostructured by embossing and where said ductile ceramic material precursor is subsequently cured to form a solid high aspect ratio nanostructured ceramic material.

The invention furthermore relates to a method where the high aspect ratio nanostructured area of the said foil is spatially continuous over a length higher than the circumference of the said high aspect ratio nanostructured extrusion roller

The invention furthermore relates to a method where the seam lines between individual high aspect ratio nanostructured areas have a width of preferably less than 50 μm, more preferably less than 20 μm, more preferably less than 10 μm, even more preferably less than 5 μm and most preferably less than 2 μm.

The invention furthermore relates to a method where the said high aspect ratio nanostructuring of the said thermoplastic coating or foil provides a functionality of increased contact to water angle of at least 30 degrees relative to an otherwise identical, but non-structured thermoplastic coating.

The invention furthermore relates to a method where the foil is subsequently metalized in order to form isolated metal domains on top of the high aspect ratio nanostructures with a lateral size and thickness below 1000 nm. [Need to be inserted in the description]

The invention furthermore relates to a method where the said velocity of the carrier foil and the rotational velocity of the said micro or nanostructured is higher than 10 m/min, preferably higher than 15 m/min, more preferably higher than 25 m/min, even more preferably higher than 50 m/min and most preferably higher than 200 m/min.

The invention furthermore relates to a method where the said thermoplastic polymer is a semi crystalline polymer. Semi-crystalline polymers can under special circumstances act like super cooled liquid. These circumstances are present in the given process, as there is a very high cooling rate, and at the same time an applied pressure, which ensures that the polymer can replicate the shaping surface of the cooling roller before the melt solidifies, which happens when the amount of material which has crystallized has reached a certain level. This also indicates that semi crystalline polymers with slower crystallization rates will perform better in the process.

The invention furthermore relates to a method where the said thermoplastic polymer melt is kept in protected atmosphere in order to maintain the chemical properties of the polymeric material.

The invention furthermore relates to a foil with a high aspect ratio nanostructured thermoplastic coating.

A micro or nanostructured foil is herein defined as an article, e.g., a packaging material, a decorative surface, a toy, a container or part of a container or a part of a medical device or a functional part of a medical device where the micro or nanostructure is intended to be able to change the surface properties of the material, non-limiting examples given; changing the hydrophilicity, molecular binding properties, sensing properties, biological properties or facilitating biological process, the optical, reflective or diffractive properties, its tactile properties or holographic properties.

By carrier foil is meant a thin substrate which is flexible and may be processed using roll-to-roll technologies. Non-limiting examples of foils are polymeric foils, cardboard foils or metal foils or foils comprised of more than one of these types, e.g. a metal-polymeric foil.

By micro or nanostructured thermoplastic polymer coating is meant a thin layer of a thermoplastic material that is applied to the carrier foil during the extrusion process, where the side not facing the carrier foil have a controlled micro or nanometer sized topography.

by a micro or nanostructured surface is meant a part of a surface containing controlled topographical micro or nanostructures.

By extrusion coating is meant the process of coating a foil in a continuous roll-to-roll process, as described in the literature, see e.g. Gregory, B. H., "Extrusion Coating", Trafford, 2007, ISBN 978-1-4120-4072-3

By extrusion coating roller is meant the cooling roller contacting the melt in the extrusion coating process, thereby solidifying the melt, thereby transforming the melt into a solid.

By extrusion roller is meant the cooling roller contacting the melt in the extrusion casting process, thereby solidifying the melt, thereby transforming the melt into a solid.

By a micro or nanostructured extrusion coating roller is meant an extrusion coating roller containing controlled micro or nanostructures on at least part of the outer surface which are in contact with the thermoplastic melt during the extrusion coating process.

By a micro or nanostructured extrusion roller is meant an extrusion roller containing controlled micro or nanostructures on at least part of the outer surface which are in contact with the thermoplastic melt during the extrusion casting process.

By controlled micro or nanostructures are meant deterministic structures, fabricated with the intent of making structures with a given topography, length scale or other functional property. Typical methods for making controlled micro or nanostructures are lithographic methods, such as, but not limited to electron beam lithography, laser writing, deep ultraviolet stepping lithography, optical lithography, nano imprint lithography, self assembling lithography, embossing, colloid lithography, reactive ion etching, wet etching, metalization or other methods well known in the literature, see e.g. "Microlithography Fundamentals in Semiconductor Devices and Fabrication Technology" by Nonogaki et al, 1998 or "Microlithography: Science and Technology" by James R. Sheats and Bruce W.

Smith, 1998 or "Principles Of Lithography, 3rd edition" by Harry J. Levinson, 2011.

By spatially continuous is meant an area which does not have any by eye visible seam lines.

By seam lines is meant a line defect between two areas due to imperfect alignment of the said areas relative to each other.

By solidification temperature is meant the temperature at which a thermoplastic material is transformed from a liquid state to a solid state. For a description of thermoplastics and their behavior around the solidification temperature, see e.g. Tim Osswald and Juan P. Hernandez-Ortiz, Polymer Processing - Modeling and simulation, Munich [u.a.] : Hanser, 2006. If no well-defined solidification temperature exist for the material, the Vicat softening point may be used instead, see e.g. ASTM D1525 - 09 Standard Test Method for Vicat Softening Temperature of Plastics.

By counter pressure roller is meant the roller exerting pressure on the carrier foil, the thermoplastic melt and the extrusion coating roller in the extrusion process.

By rotational velocity is meant the velocity of the surface of a roller, corresponding to the velocity of a foil in contact with the said roller under no-slip conditions.

By a melt is meant a thermoplastic material above its solidification temperature.

By a solid thermoplastic is meant a thermoplastic material below its solidification temperature.

By shims is meant inserts capable of being mounted on the extrusion coating roller, typically comprising micro or nanostructures in the surface. These inserts typically consists of nickel or silicon.

By functionality is meant a change in the material properties relative to a non-structured material. Examples of functionalities that may be induced by micro or nanostructuring are such as but not limited to one of the following; increased or decreased contact angle relative to a liquid, self cleaning properties, diffractive properties, improved welding properties, friction lowering or increasing properties, decreased reflective properties, food repellent properties, holographic properties, iridescent colors, structural colors, anti-fouling or anti-bacterial properties, identificational or information containing properties, biological functional properties, decorative or tactile properties.

By identificational is meant a recognizable topography, allowing an observer to conclude if the sample on which the identificational structure is placed is a genuine or a counterfeit product.

By liquid or ductile ceramic precursor material or liquid or ductile ceramic material precursor solution is meant a liquid or ductile material or solution of material that upon curing is capable of forming a solid, non-ductile ceramic material. As a way of example and not by way of limitation the said ceramic material precursors could be hydrogen silsesquioxane (HSQ) or methyl silsesquioxane (MSQ), capable of forming SiO_2 upon thermal curing at 600°C for 1 hour.

By liquid or ductile is meant a material capable of being permanently, non-elastically deformed upon mechanical deformation, which comprises both low-viscosity liquids, such as water and organic solvents and high-viscosity and ductile substances capable of being plastically deformed, such as HSQ or MSQ.

By solid is meant a material not able to be plastically deformed at the conditions present in the polymer shaping process without fracturing the material or breaking covalent bonds in the material structure, non-limiting examples being SiO_2, glass, Si_3N_4, SiC, Al_2O_3, TiAlN, TiO_2, Ti_3N_2, B_2O_3, B_4C or BN.

By ceramic material is meant both crystalline and amorphous materials consisting of metals or metalloid covalently bound to non-metal and non-metalloid atoms. As a way of example and not by way of limitation the said ceramic material could contain the following materials or mixtures thereof: SiO_2, glass, Si_3N_4, SiC, Al_2O_3, TiAlN, TiO_2, Ti_3N_2, B_2O_3, B_4C or BN.

By coating is meant the process of applying a layer of the liquid or ductile ceramic precursor or precursor solution to the shaping surface of the said mold or mold insert. As a way of example and not by way of limitation the said coating method could comprise spin coating, spray coating or coating by submersion of the mold or mold insert into the said liquid or ductile ceramic material precursor or precursor solution.

By casting is meant the process of solidifying a melt into a solid foil by moving the melt between two rotating rollers whose temperature is maintained below the solidification temperature of the melt, see e.g. "Plastics Extrusion Technology, 2nd edition" by Hensen, 1997.

By an embossing process is meant bringing a primary nanostructure into mechanical contact with the layer of liquid or ductile ceramic material precursor or precursor solution, whereby the inverse form of the primary nanostructure is formed in the layer of liquid or ductile ceramic material precursor or precursor solution. The structuring process may take place at an elevated temperature (hot embossing) in order to non-elastically or permanently deform the layer of liquid or ductile ceramic material precursor or precursor solution. The embossing process may incorporate the curing process, in such a way that the liquid or ductile ceramic material precursor or precursor solution is cured while the primary nanostructure is in contact with the liquid or ductile ceramic material precursor or precursor solution, a non-limiting example being the irradiation curing in step-and-flash NIL.

By curing is meant the process of transforming the liquid or ductile ceramic material precursor or liquid or ductile ceramic material precursor solution into the resulting solid ceramic material. This is typically done by covalent cross-linking of smaller molecular entities into a mesh structure, forming a solid ceramic substance. As a way of example and not by way of limitation the said curing method could be e.g. thermal curing where the ceramic precursor material is heated to a temperature where the cross linking takes place spontaneously, or the curing method could be a plasma curing where a plasma interacts chemically with the ceramic precursor material, thereby cross linking the ceramic precursor material, or the curing method could be an irradiation curing, where ionizing irradiation (e.g. UV exposure or electron irradiation) forms radicals in the ceramic material precursor or precursor solvent, causing the precursor to crosslink.

By thermoplastic materials are meant polymeric materials capable of being molten and solidified by changing the temperature to be above or below the solidification temperature of the material, respectively.. Non-limiting examples of thermoplastic polymer that may be used are acrylonitrile butadiene styrene (ABS), acrylic, celluloid, cellulose acetate, Ethylene-Vinyl Acetate (EVA), Ethylene vinyl alcohol (EVAL), Fluoroplastics, gelatin, Liquid Crystal Polymer (LCP), cyclic oleofin copolymer (COC), polyacetal, polyacrylate, polyacrylonitrile, polyamide, polyamide-imide (PAI), polyaryletherketone, polybutadiene, polybutylene,

polybutylene therephthalate, polycaprolactone (PCL), polychlorotrifluoroethylene (PCTFE), polyethylene terephthalate (PET), polycyclohexylene dimethylene terephthalate (PCT), polycarbonate (PC), polyhydroxyalkanoates (PHAs), polyketone (PK), polyester, polyethylene (PE), polyetheretherketone (PEEK), polyetherimide (PEI), polyethersulfone (PES), Polyethylenechlorinates (PEC), polyimide (PI), polylactic acid (PLA), Polymethylpentene (PMP), polyphenylene oxide (PPO), polyphenylene sulfide (PPS), polyphthalamide (PPA), polypropylene (PP), polystyrene (PS), polysulfone (PSU), polyurethane (PU), polyvinyl acetate (PVA), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC) and styrene-acrylonitrile (SAN), a polymer matrix substance for a medical drug, or mixes or copolymers thereof.

In some embodiments the micro or nanostructure comprises controlled micro or nanostructures made by lithographic or holographic means with a characteristic minimum feature size of less than 1 µm.

All of the features described may be used in combination so far as they are not incompatible therewith.

BRIEF DESCRIPTION OF THE FIGURES

The method and apparatus according to the invention will now be described in more detail with regard to the accompanying figures. The figures show one way of implementing the present invention and is not to be construed as being limiting to other possible embodiments falling within the scope of the attached claim set.

Figure 1 shows one embodiment of the technique. A carrier foil (1) is passed between the micro or nanostructured roller (2) and a counter roller (3). A thermoplastic melt is deposited between the micro or nanostructured roller (2) and the carrier foil (1). The micro or nanostructured roller is kept at a temperature below the solidification temperature of thermoplastic melt. The micro or nanostructured roller and the counter roller rotates as indicated by the arrows, thereby moving the carrier foil while laminating the thermoplastic melt to the carrier foil. Upon contact between the thermoplastic melt (4) and the micro or nanostructured roller (2), a simultaneous cooling and shaping of the thermoplastic melt occurs, thereby forming a micro or nanostructured and solid thermoplastic coating which is laminated to the carrier foil, thereby forming a carrier foil comprising a micro or nanostructured thermoplastic coating (5).

Figure 2 shows another embodiment of the technique. A thermoplastic melt is (1) is passed between the micro or nanostructured extrusion roller (2) and a counter roller (3). The micro or nanostructured roller is kept at a temperature below the solidification temperature of thermoplastic melt. The micro or nanostructured roller and the counter roller rotates as indicated by the arrows, thereby moving the thermoplastic melt. Upon contact between the thermoplastic melt (1) and the micro or nanostructured roller (2), a simultaneous cooling and shaping of the thermoplastic melt occurs, thereby forming a micro or nanostructured and solid thermoplastic foil (4).

Figure 3 shows a flow-chart of a method for making the micro or nanostructured foil. First an initial extrusion coating roller for an industrial polymer extrusion coating process using a thermoplastic material is provided (11), then a micro or nanostructured surface on the said extrusion coating roller is applied (12) thereby forming a micro or nanostructured extrusion coating roller (13) which is maintained at a the temperature below the solidification temperature of the said thermoplastic material. A carrier foil is placed between the rotating micro or nanostructured extrusion coating roller and a rotating counter pressure roller, thereby being moved at a given velocity corresponding to the rotational velocity of the rotating micro or nanostructured extrusion coating roller (14). By continuously applying a melt of said thermoplastic material between the said moving carrier foil and the said rotating micro or nanostructured extrusion roller, the said thermoplastic melt is solidified upon contact with said micro or nanostructured extrusion coating roller maintained at a temperature below the solidification temperature of the said thermoplastic melt thereby forming a solid micro or nanostructured thermoplastic coating on said carrier foil (15).

DETAILED DESCRIPTION OF AN EMBODIMENT

In a first example a ø300 mm, 600 mm wide extrusion roller is mounted with 300 µm thin nickel shims with a diffraction grating topography. A polyethylene melt is extrusion coated onto a PET carrier foil at a velocity of 30 m/min, resulting in the production of a foil covered with diffraction gratings defined in the polyethylene coating which is laminated to the PET carrier foil.

In a second example a ø300 mm, 600 mm wide extrusion roller is coated with a 2 µm layer of HSQ, which is structured by step-and-repeat embossing of a self cleaning nanostructure. The HSQ coating is thermally cured, and the nanostructured roller is used for the extrusion coating process. A stretchable laminate foil with a hotmelt backing is used as carrier foil and a polypropylene thermoplastic melt is applied to the carrier foil at 60 m/min. Thereby 0.6 m2/s of self cleaning foil is produced. The produced foil is laminated to windows in order to make them self cleaning.

In a third example a ø1000 mm, 2500 mm wide extrusion roller is coated with a 2 µm layer of HSQ, which is structured by step-and-repeat embossing of a friction lowering nanostructure. The HSQ coating is thermally cured, and the nanostructured roller is used for the extrusion coating process. A stretchable laminate foil with a hotmelt backing is used as carrier foil and a polypropylene thermoplastic melt is applied to the carrier foil at 60 m/min. Thereby 0.6 m2/s of friction lowering foil is produced. The foil is laminated to cover a ship hull, thereby reducing the friction of the ship, and hence reducing CO2 emissions or increasing the top speed.

In a fourth example ø1000 mm, 2500 mm wide extrusion roller is coated with a 2 µm layer of HSQ, which is structured by step-and-repeat embossing of a yoghurt repellent microstructure. The HSQ coating is thermally cured, and the nanostructured roller is used for the extrusion coating process. A cardboard foil is used as carrier foil and a polypropylene thermoplastic melt is applied to the carrier foil at 200 m/min. Thereby 5 m2/s of food repellent cardboard foil is produced, which is used for yoghurt packaging, ensuring that the yoghurt packaging may be completely emptied, thereby reducing food waste.

In a fifth example a Poly-acrylo-nitrile (PAN) melt is blown extruded at 240 C with cooling roller and counter roller maintained at 70C. The cooling roller comprises decorative structures and has a width of 1.5 m. A 20 µm thin PAN-foil comprising decorative structures is produced at a rate of 0.5 m/s, giving a productivity of 0.75 m2/s of decorative foil used for plastic bags.

In sixth example a 30 µm thick polystyrene (PS) foil is extrusion cast with nanostructured rollers on both sides, resulting in a PS foil with structures on both sides. The rollers comprise cell active structures, resulting in a PS foil comprising structures which has a biological activity. The PS foil is corona treated in line, and cut out in small, hexagonal pieces with a dimension of 30 µm* 100 µm*100 µm. The hexagonal pieces are then used as micro beads in adherent cell proliferation reactors with the main purpose of inducing a more natural cell behavior and the secondary purpose of vastly increasing the available surface area for the cells.

Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to the presented examples. The scope of the present invention is set out by the accompanying claim set. In the context of the claims, the terms "comprising" or "comprises" do not exclude other possible elements or steps. Also, the mentioning of references such as "a" or "an" etc. should not be construed as excluding a plurality. The use of reference signs in the claims with respect to elements indicated in the figures shall also not be construed as limiting the scope of the invention. Furthermore, individual features mentioned in different claims, may possibly be advantageously combined, and the mentioning of these features in different claims does not exclude that a combination of features is not possible and advantageous.

All patents and non-patent references cited in the present application are also hereby incorporated by reference in their entirety.

CLAIMS

1. A method for producing a nanostructured thermoplastic polymer coating on a carrier foil comprising at least one high aspect ratio nanostructured surface area, said method comprising at least the following steps:

- providing an initial extrusion coating roller for an industrial polymer extrusion coating process using a thermoplastic material

- applying a high aspect ratio nanostructured surface on the said extrusion coating roller thereby forming a high aspect ratio nanostructured extrusion coating roller

- maintaining the temperature of the said high aspect ratio nanostructured extrusion coating roller below the solidification temperature of the said thermoplastic material

- moving a carrier foil between the rotating high aspect ratio nanostructured extrusion coating roller and a rotating counter pressure roller at a given velocity corresponding to the rotational velocity of the rotating high aspect ratio nanostructured extrusion coating roller

- continuously applying a melt of said thermoplastic material between the said moving carrier foil and the said rotating high aspect ratio nanostructured extrusion roller, whereby said thermoplastic melt is solidified upon contact with said high aspect ratio nanostructured extrusion coating roller maintained at a temperature below the solidification temperature of the said thermoplastic melt thereby forming a solid high aspect ratio nanostructured thermoplastic coating on said carrier foil.

2. A method for producing a high aspect ratio micro or nanostructured thermoplastic polymer foil comprising at least one high aspect ratio nanostructured surface area, said method comprising at least the following steps:

- providing an initial extrusion roller for an industrial polymer extrusion casting process using a thermoplastic material

- applying a high aspect ratio nanostructured surface on the said extrusion roller thereby forming a high aspect ratio nanostructured extrusion coating roller

- maintaining the temperature of the said high aspect ratio nanostructured extrusion roller below the solidification temperature of the said thermoplastic material

- continuously applying a melt of said thermoplastic material between the said counter roller and the said rotating high aspect ratio nanostructured extrusion roller, whereby said thermoplastic melt is solidified upon contact with said high aspect ratio nanostructured extrusion roller maintained at a temperature below the solidification temperature of the said thermoplastic melt thereby forming a solid high aspect ratio nanostructured thermoplastic foil.

3. A method according to claim 1 or 2, where the aspect ratio of the said nano or microstructure is above 2, more preferably above 1.5, even more preferably above 1.25, and most preferable more than 1.

4. A method according to any previous claim, where high aspect ratio nanostructures are produced on both sides of the cast foil by using both a high aspect ratio nanostructured extrusion roller and a high aspect ratio nanostructured counter roller.

5. A method according to any previous claim where the said high aspect ratio nanostructured surface is applied by mounting high aspect ratio nanostructured shims on the said initial extrusion coating roller.

6. A method according to any previous claim where the high aspect ratio nanostructured surface is applied by coating the said initial extrusion coating roller with a material which is subsequently high aspect ratio nanostructured.

7. A method according to claim 6 where the said material is a ductile ceramic material precursor which is nanostructured by embossing and where said ductile ceramic material precursor is subsequently cured to form a solid high aspect ratio nanostructured ceramic material.

8. A method according to any of the previous claims where the high aspect ratio nanostructured area of the said foil is spatially continuous over a length higher than the circumference of the said high aspect ratio nanostructured extrusion roller

9. A method according to any of the previous claim where the seam lines between individual high aspect ratio nanostructured areas have a width of preferably less

than 50 μm, more preferably less than 20 μm, more preferably less than 10 μm, even more preferably less than 5 μm and most preferably less than 2 μm.

10. A method according to any previous claims where the said high aspect ratio nanostructuring of the said thermoplastic coating or foil provides a functionality of increased contact to water angle of at least 30 degrees relative to an otherwise identical, but non-structured thermoplastic coating.

11. A method according to any previous claims, where the foil is subsequently metalized in order to form isolated metal domains on top of the high aspect ratio nanostructures with a lateral size and thickness below 1000 nm.

12. A method according to any previous claims where the said velocity of the carrier foil and the rotational velocity of the said micro or nanostructured is higher than 10 m/min, preferably higher than 15 m/min, more preferably higher than 25 m/min, even more preferably higher than 50 m/min and most preferably higher than 200 m/min.

13. A method according to any of the previous claims where the said thermoplastic polymer is a semi crystalline polymer.

14. A method according to any previous claims, where the said thermoplastic polymer melt is kept in protected atmosphere in order to maintain the chemical properties of the polymeric material.

15. A thermoplastic foil according to claim 2 or a foil with a high aspect ratio nanostructured thermoplastic coating according to claim 1 made by any of the previous claims.

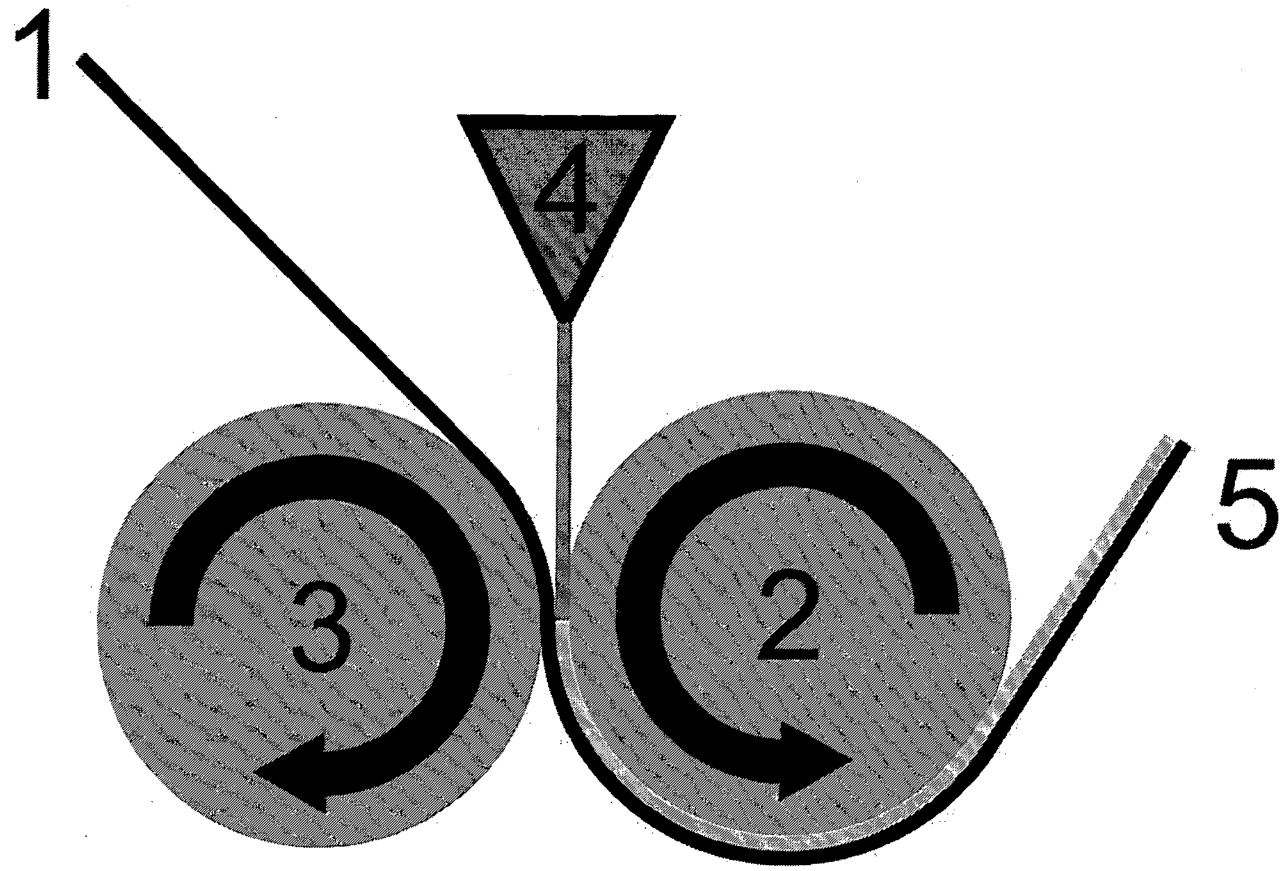

Figure 1

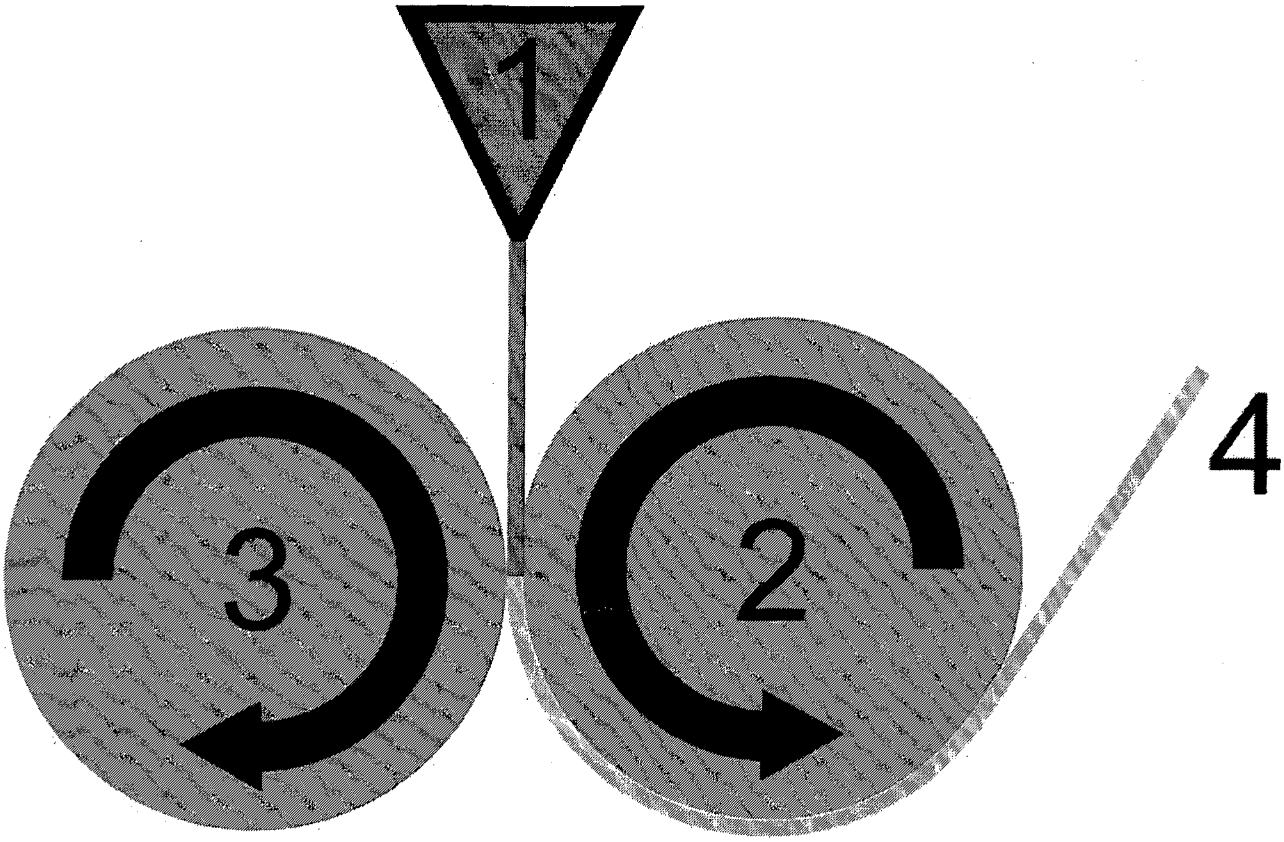

Figure 2

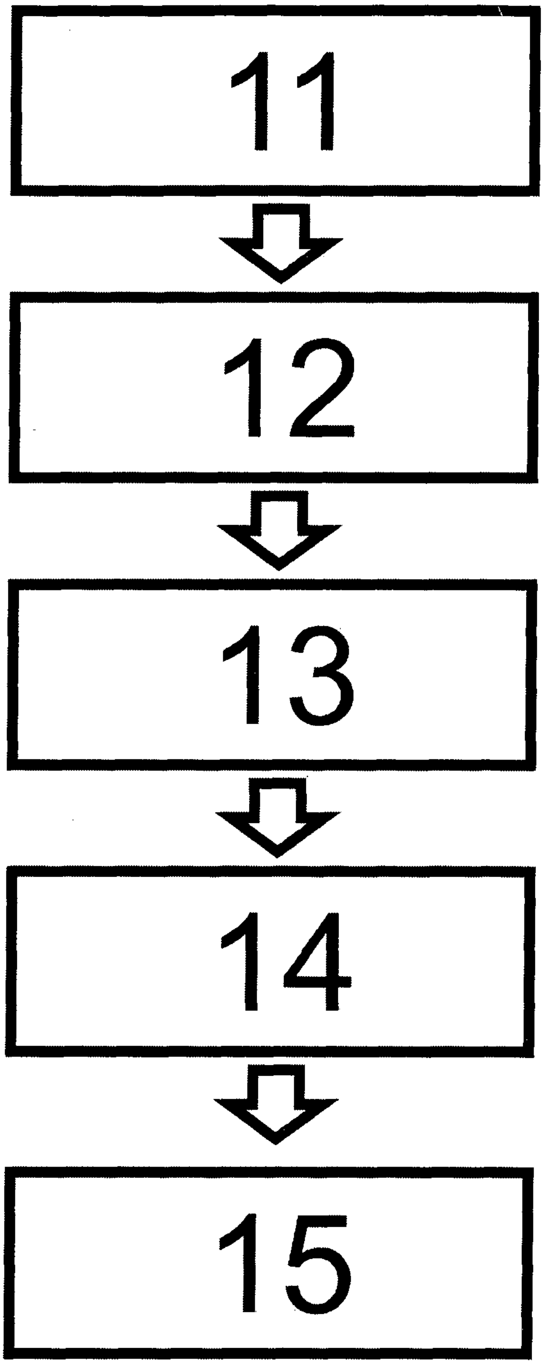

Figure 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/DK2015/000012

A. CLASSIFICATION OF SUBJECT MATTER
B29C 59/04 (2006.01); B82Y 40/00 (2011.01)
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)
CPC: B29C, B32B, B82Y
IPC: B29C, B82Y

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

DK, NO, SE, FI: Classes as above.

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPODOC; WPI; FULL TEXT: ENGLISH, GERMAN, FRENCH

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2007/126607 A1 (ROHM AND HAAS DENMARK FINANCE A/S (DK)) 08/11/2007 See whole document, in particular page 8, lines 20-26; page 10, lines 13-14; page 15, line 28 – page 16, line 19; page 20, lines 7 – 28; page 21, line 5 – page 22, line 5 and Figure 2.	15 1, 3-14
Y	WO 2012/000500 A1 (INMOLD BIOSYSTEMS A/S (DK)) 05/01/2012 See whole document, in particular abstract; page 16, lines 28-34; page 17, lines 20-21; page 22, lines 1-11; page 32, lines 26-30; page 41, lines 14 – 29; Figure 3 and claim 1.	1-14
X Y	US 2007/0013103 A1 (ZHANG, H. et al.) 18/01/2007 See paragraphs [0003]-[0006]; [0023] – [0028]; [0037] – [0040]; [0049] and [0052]; examples; figures 1, 2 and 4; and claims 1. 6 and 13-16.	15 2-14
X A	US 2009/0087506 A1 (HASEGAWA, M. et al.) 02/04/2009 See whole document, in particular abstract; paragraphs [0001]-[0002]; [0087] and [0097] and figures 10A and 11.	15 1-14
X A	EP 2657004 A1 (THE JAPAN STEEL WORKS, LTD. (JP)) 30/10/2013 See paragraphs [0018]-[0020].	15 1-14

☒ 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	Date of mailing of the international search report
22/07/2015	30/07/2015

Name and mailing address of the ISA	Authorized officer
Nordic Patent Institute Helgeshøj Allé 81 DK - 2630 Taastrup, Denmark. Facsimile No. + 45 43 50 80 08	Hans Christian Schiøtz Rudbeck Telephone No. +45 43 50 81 25

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1700680 A1 (EPFL ECOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE (CH)) 13/09/2006 See whole document.	1-15
A	US 2007/0126145 A1 (COYLE, D. J. et al.) 07/06/2007 See whole document.	1-15
A	US 2011/0318535 A1 (JUNG, H.-T. et al.) 29/12/2011 See whole document, in particular abstract; examples; paragraph [0069] and figure 8a.	1-15
	.	

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.:
   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:

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:

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.:

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.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/DK2015/000012

Patent document cited in search report / Publication date	Patent family member(s) / Publication date
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/DK2015/000012

Patent document cited in search report / Publication date	Patent family member(s) / Publication date
	KR 101249981B B1 2013.04.05 WO 2012002717 A2 2012.01.05 WO 2012002717 A3 2012.05.03 US 2015060392 A1 2015.03.05