

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(10) International Publication Number

WO 2016/048335 A1

(43) International Publication Date
31 March 2016 (31.03.2016)

(51) International Patent Classification:
C09K 5/14 (2006.01) *F28F 21/06* (2006.01)
F28F 3/02 (2006.01) *F28F 1/10* (2006.01)

(21) International Application Number:
PCT/US2014/057576

(22) International Filing Date:
26 September 2014 (26.09.2014)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicants: **W.L. GORE & ASSOCIATES GMBH** [DE/DE]; Hermann-Oberth-Strasse 22, 85640 Putzbrunn (DE). **W.L.GORE & ASSOCIATES, INC.** [US/US]; 555 Paper Mill Road, Newark, DE 19711 (US).

(72) Inventors: **ZAGGL, Alexander**; Oberwertach 1a, 83620 Feldkirchen-Westerham (DE). **ZOUDLIK, Holger**; Sulzbergstr. 26, 83059 Kolbermoor (DE). **WENDLANDT, Michael**; Kaulbachstr. 5, 85521 Ottobrunn (DE). **HALL, Michael, Adam**; 113 Lynch Farm Drive, Newark, DE 19713-2812 (US).

(74) Agents: **MILLER, Amy, L.** et al.; W.L. Gore & Associates, Inc., 551 Paper Mill Road, P.O. Box 9206, Newark, DE 19714-9206 (US).

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

Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

— of inventorship (Rule 4.17(iv))

Published:

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

(54) Title: PROCESS FOR THE PRODUCTION OF A THERMALLY CONDUCTIVE ARTICLE

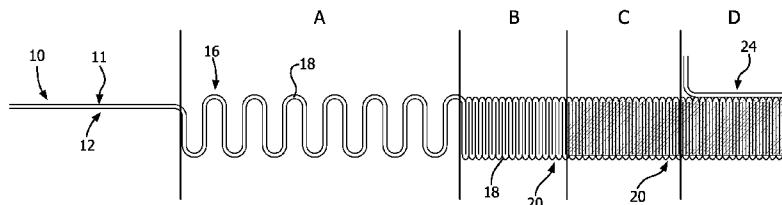


FIG. 1a

(57) Abstract: The present invention relates to a process for the production of a thermally conductive article comprising pleating a thermally anisotropic sheet having a thermal conductivity in plain which is higher than the thermal conductivity perpendicular to the plain, and compacting the pleated structure, to an article obtainable by said process, to the use of said thermally conductive article for production of a device, and to such a device.

Process for the Production of a Thermally Conductive Article

FIELD

[0001] The present invention relates to a process for the production of a thermally conductive article, to a thermally conductive article obtainable by said process, to the use of said article production of a device for conduction of heat and to such a device comprising said article.

BACKGROUND

[0002] Polymers such as polytetrafluoroethylene (PTFE) are known to have a low intrinsic thermal conductivity which for dense, isotropic PTFE is less than 0.35 W/mK within a wide range of temperatures from -140°C to at least 232°C, see e.g. Price, D. M. & Jarratt, M. (2002), "Thermal conductivity of PTFE and PTFE composites", *Thermochimica Acta* 392-393, p. 231-236 or Blumm, J.; Lindemann, A.; Meyer, M. & Strasser, C. (2010), "Characterization of PTFE Using Advanced Thermal Analysis Techniques", *International Journal of Thermophysics* 31, 1919-1927.

[0003] It is known that the thermal conductivity of expanded porous PTFE is generally even lower due to the presence of air, typically only one tenth to about one half of the value for the dense material as a function of the porosity. These materials have therefore found application as thermal insulators (see e.g. US 3,953,566, column 5, line 64 to column 6, line 2).

[0004] For applications as e.g. for the heat transfer from integrated circuits ("IC") it is desired to make use of the advantageous properties of fluoropolymers, but, at the same time, thermal conductivity is required. It is known to make fluoropolymers such as PTFE thermally conductive by the incorporation of thermally conductive particles, for example metal particles, oxides or nitrides, and PCM or elastomers. Such thermally conductive PTFE composites are disclosed e.g. in US 5,945,217 and US 5,738,936.

[0005] However, the use of such filled fluoropolymers has several drawbacks; in particular, there is usually a loss of the outstanding properties of PTFE like stability against harsh chemical environments or a change of dielectric properties.

[0006] It is furthermore known for example from EP 2 551 324 that the intrinsic thermal conductivity of fluoropolymers such as PTFE can be enhanced by a specific orienting process so that sheets of the polymer are obtained which have highly increased thermal conductivity in at least one or even two directions within the plain of the sheet. However, the thermal conductivity perpendicular to the plain of the sheet remains small or even slightly decreases due to the orientation, so that the oriented sheets have a highly anisotropic thermal conductivity.

[0007] It is therefore one of the objects of the present invention to provide a process which allows to increase the thermal conductivity of thermally anisotropic sheets, such as fluoropolymer sheets, in the direction perpendicular to the sheet, so that new and improved thermally conductive articles and devices can be produced.

SUMMARY

[0008] The present invention is based on the finding that the thermal conductivity of a sheet in the direction perpendicular to the sheet can be highly increased by pleating the sheet and compacting the formed pleated structure.

[0009] The present invention therefore provides a process for the production of a thermally conductive article comprising pleating a thermally anisotropic sheet which has a thermal conductivity in plain which is higher than the thermal conductivity perpendicular to the plain, and compacting the pleated sheet.

[00010] It has surprisingly been found that by pleating a sheet and compacting said pleated sheet the thermal conductivity of the pleated sheet perpendicular to the pleats is highly increased compared to the thermal

conductivity of a simple stack of the same sheets in the direction perpendicular to the stack.

[00011] It is thus possible to provide sheets with a highly increased thermal conductivity in the direction perpendicular to the plain of the sheet.

[00012] Furthermore, it is possible to use the pleated structures to design new thermally conductive devices. For example, cooling devices such as cooling ribbons which create additional forced convective heat loss and increased surface area may be provided.

[00013] The term “sheet” is intended to denote all articles with an extension in two dimension being large compared to the extension in the other remaining dimension, e.g. articles usually denoted as sheets, films, membranes or tapes. A sheet therefore has two opposing surfaces, which have a high surface area compared to the two opposing edges of the sheet (in case of an “endless” sheet). In one embodiment, the sheet comprises at least one layer. In another embodiment, the sheet comprises several layers made of one sheet material or made of different sheet materials.

[00014] “Thermally anisotropic” means that the sheets show a different intrinsic thermal conductivity in at least two directions, i.e. that they show a comparatively high intrinsic thermal conductivity in one direction and a comparatively low intrinsic thermal conductivity in another direction. In the thermally anisotropic sheets used in the process of the present invention, the thermal conductivity in plain is higher than the thermal conductivity perpendicular to the plain.

[00015] A pleat is created and defined by three parallel bends of the sheet (a first bend, a middle bend and a last bend), and each pleat has two bends in common with the adjacent pleat(s).

[00016] The pleats thus formed have a certain height, which is defined to be the distance between the middle bend and the closer succeeding bend (either the first or the last bend), measured from the top of each bend.

[00017] Compacting is done so that the surfaces of the sheet which faces each other due to the formation of the pleats are at least partially brought in contact with each other.

[00018] Compacting may be done by exerting a pressure on the pleats in the direction perpendicular to the pleats.

[00019] In one embodiment, the compacted pleated structure, partly or fully, is stabilized. This means that the pleats, partially or fully, are fixed in their relative position to each other.

[00020] In this manner, the pleated structure formed is conserved in the form as obtained (or nearly as obtained) after compacting.

[00021] In one example, stabilization of the pleated structure is effected by bonding a film to one or more of the surfaces (formed by the bends of the pleats) or edges (formed by the edges of the sheet) of the pleated structure. Bonding of said film may be effected e.g. by thermo bonding, i.e. by applying heat and pressure.

[00022] In another example, a film is bonded to one, i.e. upper or lower, or both surfaces of the pleated structure.

[00023] In a further embodiment of the process of the invention, the thermally anisotropic sheet is treated with a thermal interphase wax.

[00024] Treatment of the sheet with a thermal interphase wax further increases the thermal conductivity of the pleated sheet in the direction perpendicular to the pleats.

[00025] As thermal interface wax a commercially available phase change wax can be used, like for example Crayotherm® KU-CR having a thermal conductivity of 0.47W/mK (commercially available by KUNZE Folien GmbH, Germany).

[00026] In the process of the invention, a thermally anisotropic sheet is pleated so that pleats with a certain height as defined above are formed.

[00027] In one example, the pleat height in relation to the sheet thickness is from 1000:1 to 2:1, preferably from 500:1 to 3:1, and most preferably from 100:1 to 5:1.

[00028] Furthermore, in one embodiment the sheet is pleated so that in the resulting pleated structure pleats with different heights exist. The pleat height to be used in the above relation to the film thickness is then the average pleat height.

[00029] The sheet thickness of the unpleated sheet is preferably from 1 to 500 micrometer, more preferably from 2 to 250 micrometer and most preferably from 5 to 100 micrometer.

[00030] In one example, the height of the pleats is from 10 to 10000 micrometer; more preferably is from 20 to 5000 micrometer and most preferably is from 40 to 2500 micrometer.

[00031] Pleating of the sheet is preferably performed perpendicular to the direction of maximum thermal conductivity.

[00032] This means that, for example, if an “endless” sheet is used, the sheet has its maximum thermal conductivity in machine direction and is pleated perpendicular to that direction.

[00033] Pleating of the sheet may be performed in such a manner that the sheet is passed through two counter-rotating toothed wheels, denoted as “pleating rolls”. The teeth of these rotating wheels are designed so that no disruption of the sheet occurs, in particular, the teeth should not be too sharp-edged. For example, the teeth may have a sinusoidal form.

[00034] The height of the teeth determines the height of the pleats formed upon passing through the pleating rolls.

[00035] By compressing the pleats, the thermal conductivity of the pleated structure in the direction perpendicular to the pleats can be further enhanced.

[00036] In one embodiment, the thermally anisotropic sheet comprises, or consists of, a thermally anisotropic polymer layer.

[00037] In a further embodiment, the thermally anisotropic polymer layer comprises, or consists, of a polyolefin, such as polyethylene, or a fluoropolymer.

[00038] The fluoropolymer comprises, or consists of, polytetrafluoroethylene (PTFE), a modified PTFE, a fluorothermoplastic, a fluoroelastomer or any combination thereof.

[00039] The fluoropolymer may be partially fluorinated or fully fluorinated, i.e. perfluorinated.

In one embodiment, the fluoropolymer comprises, or consists of, polytetrafluoroethylene (PTFE), a modified PTFE, a fluorothermoplastic or a fluoroelastomer or any combination of these materials. The term "modified PTFE" as used herein is intended to denote a type of tetrafluoroethylene copolymer in which in addition to tetrafluoroethylene monomer units further perfluorinated, fluorinated or non-fluorinated co-monomer units are present, for example in a range of from 0.005 to 15 mol%.

[00040] In a further embodiment, the substrate fluoropolymer comprises, or consists of, polytetrafluoroethylene (PTFE), a modified PTFE, a fluorothermoplastic or a fluoroelastomer or any combination of these materials.

[00041] In still a further embodiment, the fluoropolymer comprises, or consists of, PTFE and/or a modified PTFE, and in still a further embodiment, the fluoropolymer comprises, or consists of, PTFE.

[00042] In a particularly embodiment, sheets are used in the process of the present invention as disclosed in EP 2 551 324.

[00043] In case a polymeric sheet is used in the process of the present invention, the sheet or at least the polymeric layer(s) of the sheet preferably consist of the pure polymer, i.e. no further compound or filler has been added to the polymer. In this embodiment, undesired water adsorbance due to the

presence of such additives is avoided. This is especially important for the application in electrical components.

[00044] In an embodiment, the intrinsic thermal conductivity of the sheet is 0.5 W/mK or more, in a further embodiment it is 0.7 W/mK or more, in still a further embodiment it is 1 W/mK or more, in a still further embodiment it is 5 W/mK or more, and in still a further embodiment it is 8 W/mK or more, in the direction of maximum intrinsic thermal conductivity.

[00045] All indications of thermal conductivities and diffusivities as well as any ratios thereof as contained herein relate to a measurement temperature of 40 °C, unless otherwise indicated.

[00046] Usually, the intrinsic thermal conductivity in the direction of maximum intrinsic thermal conductivity does not exceed 40 W/mK.

[00047] Of course, intrinsic thermal conductivities as high as possible are desired, however, for certain applications a lower conductivity may be acceptable, for example, where the amounts of heat to be transferred is smaller.

[00048] The thermally anisotropic sheet of the process of the present invention has different intrinsic thermal conductivities in at least two directions, with the anisotropy ratio of the intrinsic thermal conductivity being defined as the ratio of the intrinsic thermal conductivity in the direction of maximum intrinsic thermal conductivity divided by the intrinsic thermal conductivity in the direction of minimum intrinsic thermal conductivity.

[00049] Usually, the sheet has its minimum intrinsic thermal conductivity in the direction perpendicular to the plain, and its maximum intrinsic thermal conductivity in the direction of the plain.

[00050] In the process of the invention, sheets may be used which have differing intrinsic thermal conductivity in different directions within the plain. For example, such sheets are obtained by a mono-axial orientation of fluoropolymer sheets, see EP 2 551 324.

[00051] In one embodiment, the sheet has its direction of maximum intrinsic thermal conductivity perpendicular to the orientation of the pleats, for example, if an "endless sheet" is used preferably the direction of maximum intrinsic thermal conductivity will be in the machine ("endless") direction.

[00052] In one embodiment, the sheet has an anisotropy ratio of the intrinsic thermal conductivity of more than 5, in another embodiment of 10 or more, in still a further embodiment of 15 or more, in still a further embodiment of 20 or more, in still a further embodiment of 25 or more, in still a further embodiment of 30 or more, and in still a further embodiment of 40 or more.

[00053] In practice, the ratio will usually not exceed 100.

[00054] In the embodiment of the present invention where a thermally anisotropic sheet comprising or consisting of a fluoropolymer is used, the sheet may be obtained by orienting a fluoropolymeric sheet in one direction parallel to the plane of the sheet (mono-axial orientation) or in two directions perpendicular to each other parallel to the plane of the sheet (bi-axial orientation).

[00055] The intrinsic thermal conductivity will be increased in the direction(s) of orientation, so that the sheet will show an increased intrinsic thermal conductivity along one direction within the plane (mono-axial orientation), or along all directions within the plane (bi-axial orientation), as described in EP 2 551 324.

[00056] The fluoropolymer of the sheet may be a dense material, i.e. a non-porous material, or may be porous.

[00057] The term "porous" as used herein refers to a material which has voids throughout the internal structure which may form an interconnected continuous air path from one surface to the other.

[00058] The anisotropic fluoropolymer may also be microporous. This means that the voids are very small and are usually referred to as "microscopic".

[00059] A typical pore size of the voids in a microporous fluoropolymer is in the range of 0.01 to 15 micrometer as determined in the mean flow pore size measurement.

[00060] A microporous fluoropolymer, for example, is expanded PTFE (ePTFE, EPTFE).

[00061] The microstructure of a porous fluoropolymer can include nodes and fibrils, only fibrils, only fibril strands or bundles, or stretched nodes interconnected by fibrils.

[00062] In one embodiment of the process of the invention, the thermally anisotropic sheet is composed of more than one layer, and, for example comprises a layer of a thermally isotropic conductive material, such as a metal film.

[00063] The sheet used in the process may accordingly be a multilayer composite sheet, for example comprising an upper and lower layer of FEP, sandwiching a layer of a thermally anisotropic material such as a fluoropolymer, and an adjacent layer of a thermally isotropic material such as a metal.

[00064] The present invention further relates to an article obtainable by the process of the present invention in any of the above described embodiments.

[00065] The present invention further relates to a thermally conductive article comprising a sheet with thickness is from 1 to 500 μm and wherein the article has a thermal conductivity perpendicular to the plain of 1 W/mK or higher wherein preferred embodiments of said article are those as described for the process of the present invention in any of the above described embodiments.

[00066] The present invention further relates to a device for the conduction of heat from a heat source to a heat sink comprising an article formed by the process of the present invention in any of the above described embodiments, and to the use of such an article for the production of a device.

[00067] The terms “heat source” and “heat sink” are intended to denote any item, which gives off heat and receives heat, respectively.

[00068] The device of the invention in addition to the article obtainable by the process of the invention may comprise further components.

[00069] In one embodiment, such further components are fluoropolymers. Thus, the device is stable against harsh chemical environments, high temperatures, or UV-light, has a high dielectric strength, electrical insulating properties, flexibility, repellency to water and other liquids, good dielectric properties, shows a good ageing behavior and a stable conductivity over a broad temperature range.

[00070] Such a device may be in any form or shape known for such articles in the art; in particular, the article may be a laminate, a thermal interface composite, an electrically insulating heat spreader or a heat pipe.

BRIEF DESCRIPTION OF THE DRAWINGS

[00071] The accompanying drawings are included to provide a further understanding of the disclosure and are incorporated in and constitute a part of this specification, illustrate embodiments, and together with the description serve to explain the principles of the disclosure.

[00072] FIG. 1 are schematic depictions of an embodiment of the process of the invention; and

[00073] FIG. 2 is a schematic depiction of two embodiments of the sheet before the pleating step in the process of the present invention; and

[00074] FIG. 3 shows counter-rotating pleating rolls (FIG. 3a) and an enlarged view of the tooth design of the pleating rolls (FIG. 3b) for an embodiment of the pleating step in the process of the present invention; and

[00075] FIG. 4 is a schematic view of one embodiment of the step of compacting the pleated structure in the process of the present invention; and

[00076] FIG. 5a is a picture of a thermally conductive article in the form of a cooling ribbon obtainable by the process according to the invention; and

[00077] FIG. 5b is an enlarged view of the pleated structure of the cooling ribbon in Fig. 5a; and

[00078] FIG. 6 is a picture of a thermally conductive article in the form of a partially pleated structure obtainable by a process according to the invention; and

[00079] FIG. 7 are SEM views of a pleated PTFE film (thickness: 10 micrometer) with a pleat height of 450 micrometer formed according to Example 1; and

[00080] FIG. 8 are SEM views of a pleated PTFE film (thickness: 40 micrometer) with a pleat height of 450 micrometer formed according to Example 2; and

[00081] FIG. 9 is a SEM view of a stack of a PTFE film with a thickness of 40 micrometer, with a total stack height of 450 micrometer, produced as described in Example 3; and

[00082] FIG. 10 are SEM views of a pleated polyethylene film formed according to Example 4.

DETAILED DESCRIPTION

[00083] Persons skilled in the art will readily appreciate that various aspects of the present disclosure can be realized by any number of methods and apparatus configured to perform the intended functions. It should also be noted that the accompanying drawing figures referred to herein are not necessarily drawn to scale, but may be exaggerated to illustrate various aspects of the present disclosure, and in that regard, the drawing figures should not be construed as limiting.

[00084] A schematic illustration of one embodiment of the process of the present invention is shown in Fig. 1. In Fig. 1a an “endless” sheet 10 is shown in a view perpendicular to the plain of the sheet. The sheet 10 comprises a first surface 11 and a second surface 12 and two opposing edges 13. The untreated sheet 10 is subjected to a first pleating step (section A in Fig. 1) in which bends are created perpendicular to the machine direction of the sheet so that pleats 18 are formed. This step is followed by a second compacting step (section B in Fig. 1), in which the formed pleats 18 are brought into contact with each other. This results in a pleated and compacted structure 20. In a following optional bonding step the structure 20 may be fixed, e.g. as shown in Fig. 1 in section C by bonding the surfaces of the pleats 18 to each other. The compacting and bonding of the pleated structure can be carried out in one step.

[00085] In order to stabilize the pleated and compacted structure 20 in one embodiment a stabilizing film 24 can be attached to one or more of the surfaces of the structure 20. In section D in Fig. 1 a stabilization film 24 is bonded to the upper surface 19 of the structure 20.

[00086] Fig. 1b is a perspective view of those steps as shown in Fig. 1a.

[00087] The sheet 10 can be made of at least one single layer of sheet material. In another embodiment, the sheet 10 comprises several layers of sheet material.

[00088] The use of a sheet using several layers is another form to stabilize the pleated and compacted structure 20. Pleats formed by a multilayer sheet are self-standing and show own stability.

[00089] Fig. 2 shows embodiments of sheet 10.

[00090] In Fig 2a the sheet 10 comprises several layers 14 of the same material arranged in a stack of one layer on top of the other, e.g. several layers of an thermally anisotropic expanded PTFE.

[00091] In Fig 2b sheet 10 comprises one layer 14 of thermally anisotropic expanded PTFE attached to a metallic film 15, for example made of

copper, aluminum or silver. The metallic film 15 can be attached to layer 14 by using a thin adhesive layer of FEP or by vaporizing. The composite can further comprise at least one layer of FEP 16, forming either the upper or lower surface or both surfaces 11, 12.

[00092] In Fig. 3, a preferred embodiment for the device used for the pleating of the sheet is shown. Fig. 3a shows the device comprising two counter-rotating pleating rolls 30 with teeth 35 through which the unpleated sheet is passed. The distance between the rolls 30 is selected so that the sheet is not disrupted or adversely affected in any way. Fig. 3b shows an enlarged view of the area A of Fig. 2a. This Figure shows an embodiment of the tooth design of the pleating rolls. The tooth high in this example is about 450 micrometer and determines the high of the pleats formed upon passing through the pleating rolls. The end of the tooth is rounded to prevent a disruption of the sheet.

[00093] Fig. 4 shows a schematic depiction of a possible embodiment for the compacting of the pleated structure. In Fig. 4a the pleated structure 16 is inserted between two plates, e.g. glass plates. In one example the pleats 18 are arranged substantially vertically between a top plate 42 and a bottom plate 44. The distance between the plates 42, 44 is selected so that it corresponds closely to the height of the (highest) pleats of the pleated structure 16. As depicted in Fig. 4b and 4c, steel blades 46 with a thickness of approximately the distance between the plates 42, 44 are inserted at the ends of the pleated structure 16 and a pressure is exerted on at least one of the steel blades, so that the pleats 18 are compacted and the surface of the formed pleats is brought in contact with each other. In one example, the blades have a thickness of about 400 micrometer.

[00094] Fig. 5a and Fig. 5b show an example of a thermally conductive article obtainable by the process according to this invention.

[00095] In that embodiment the pleated and compacted structure 20 comprises a sheet 10 made of multiple layers of a thermally anisotropic material. The pleats 18 are only bonded on its second surface 12, the first and

outer surface 11 of the pleats is un-bonded and therefore available for a heat transfer to the outside. Such a structure of "cooling ribbons" creates additional forced convective heat loss and increased surface area.

[00096] The pleated and compacted structure 20 is arranged around objects like for example around the outer surface of a metallic thermally conductive stick 32. Heat in the stick can move in the pleats 18 of the structure 20 and be rendered to the surrounding environment via the first surface 11 of the sheet 10. Such an arrangement forms a cooling ribbon device for heat conducting articles.

[00097] Fig. 6 shows another example for a thermally conductive article in the form of a partially pleated structure obtainable by a process according to the invention. In this example a sheet made of multiple layers of a thermally anisotropic material has been used. The pleating and compacting step has been carried out only for a part of the sheet. As indicated by the arrows in Fig. 6, the main transport of heat in the non-pleated section is parallel to the main axis and in the folded area the main direction of heat transport is rotated by 90°.

[00098] The thermal conductivity was measured according to ISO 22007-2 using a Hot Disk TPS 2500S thermal constants analyser at 40 °C.

EXAMPLES

[00099] EXAMPLE 1

[000100] A thermally anisotropic expanded PTFE film with a thickness of 10 µm was produced according the following procedure.

[000101] Following the procedures disclosed in U.S. Pat. Nos. 3,953,566, 3,962,153, and 4,064,214 a tape was prepared in the following manner: A fine powder PTFE resin was mixed with mineral spirit (22.6 wt% Isopar K™) to form a paste and extruded through a die to form a wet tape of 0.980 mm thickness. Subsequently, the wet tape was rolled down, stretched at a ratio of 1 to 0.75 and

then dried at 185° C to remove the mineral spirit. The dry tape had a final thickness of 0.415 mm. The tape was stretched over hot plates at 350°C to 370°C, at a total stretch ratio of 78:1. After stretching, tape was not subjected to any further treatment at elevated temperature.

[000102] The tape has a thermal conductivity in machine direction of 7,82 W/mK, a thermal conductivity in transverse direction of 1.12 W/mK and a thermal conductivity in the direction perpendicular to the plain of 0.05 W/mK.

[000103] The tape is subjected to the process of the present invention starting with the first pleating step in using 2 counter rotating gear wheels with a tooth height of 450 µm and a pleated structure of said tape with a corresponding pleat height of around 450 µm is obtained.

[000104] The pleated structure is inserted between two plates, e.g. glass plates, for the second compressing step. The pleats are arranged substantially vertically between a top plate and a bottom plate according to the process as shown in Fig. 4. The distance between the plates is selected so that it corresponds closely to the height of the (highest) pleats of the pleated structure. Steel blades with a thickness of approximately the distance between the plates are inserted at the ends of the pleated structure and a pressure is exerted on at least one of the steel blades by hand for about 3 seconds, so that the pleats are compacted and the surface of the formed pleats is brought in contact with each other. The blades have a thickness of about 400 micrometer.

[000105] The process was carried out once without, and once with the application of a thermal interface wax (Crayotherm® KU-CR of KUNZE Folien GmbH).

[000106] The pleated film is shown in an enlarged view in Figs. 7a and 7b. The results as regards the thermal conductivity in the direction perpendicular to the pleats, with and without an additional thermal interphase wax is given in Table 1.

[000107] EXAMPLE 2

[000108] A thermally anisotropic expanded PTFE film with a thickness of 40 μm was manufactured according to the procedure as described in example 1. In order to manufacture a film with a thickness of 40 μm the dry tape had a final thickness of 0,653mm. Said film is subjected to the pleating and compressing process of the present invention as described in example 1 and a pleated structure of said film with a pleat height of 450 μm is obtained. The process was carried out once without, and once with the application of a thermal interface wax.

[000109] The pleated film is shown in an enlarged view in Figs. 8a and 8b. The results as regards the thermal conductivity in the direction perpendicular to the pleats, with and without an additional thermal interphase wax is given in Table 1.

[000110] EXAMPLE 3 (comparative)

[000111] A thermally anisotropic expanded PTFE film with a thickness of 40 μm was manufactured according to the procedure in example 1. In order to manufacture a film with a thickness of 40 μm the dry tape had a final thickness of 0,653mm. Eight (8) layers of said film were put one on top of the other forming a stack. The stack was slightly compressed and is shown in Fig. 9. The stack was made once without, and once with application of a thermal interface wax.

[000112] The results as regards the thermal conductivity in the direction perpendicular to the film plain are given in Table 1.

[000113] EXAMPLE 4

[000114] A highly oriented UHMW polyethylene film (commercially available by the company ENDUMAX of Teijin Ltd, Japan) with a thickness of 64 μm has been subjected to the following process:

- 1) The film was pleated with two counter rotating saving 2 mm tooth height

- 2) Primer 94 (commercially available by the company 3M Deutschland GmbH, Germany) was applied with a brush on top of the pleat tips and then dried for 3 hours at room temperature to remove the solvent
- 3) The pleated structure was prior to compacting, arranged in a channel construction made of aluminum. The bottom plate of the channel construction has a width of 80mm and the side walls of the channel construction have a height of 2mm. After arranging the pleated structure in the channel construction, a top plate was arranged on top of the construction to close the channel. Two plates, each with a thickness of about 2mm, were put at the respective ends of the pleated structure and pressed against each other with a pressure by hand. From one side additional pressure was applied with a hammer by hand to compact the material even more. Then the material was put in an oven at 80°C for 5 min. After the end of the heating step and a 30 min cooling period the top plate was removed and the compacted pleated structure was taken off the channel construction

[000115] Fig. 10 shows enlarged cross-section views of the pleated and compressed structure.

[000116] The results as regards the thermal conductivity in the direction perpendicular to the film plain are given in Table 1.

[000117] Table 1: Thermal Properties

	Thermal conductivity in z-direction (perpendicular to pleats/plain of sheet(s))
Example 1	
Unpleated PTFE film	0.05 W/mK
Pleated PTFE film without thermal interface wax	4 W/mK
Pleated PTFE film with thermal interface wax	5.5 W/mK
Example 2	
Unpleated PTFE film	0.05 W/mK
Pleated PTFE film without thermal interface wax	2 W/mK
Pleated PTFE film with thermal interface wax	7 W/mK
Example 3 (comparative)	
PTFE film stack without thermal interface wax	0.06 W/mK
PTFE film stack with thermal interface wax	0.06 W/mK
Example 4	
Unpleated PE film	0.093 W/mK
Pleated/compacted/bonded PE film	>10 W/mK

[000118] The invention of this application has been described above both generically and with regard to specific embodiments. It will be apparent to those skilled in the art that various modifications and variations can be made in the embodiments without departing from the scope of the disclosure. Thus, it is intended that the embodiments cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

WHAT IS CLAIMED IS:

1. Process for the production of a thermally conductive article comprising pleating a thermally anisotropic sheet having a thermal conductivity in plain which is higher than the thermal conductivity perpendicular to the plain, and compacting the pleated structure.
2. Process according to claim 1, wherein the pleated structure is stabilized.
3. Process according to claim 2, wherein stabilization of the pleated structure is effected by bonding a film to one or more of the surfaces of the pleated structure.
4. Process according to claim 3, comprising bonding a film to the upper and/or the lower surface of the pleated structure.
5. Process according to any of the preceding claims, wherein the sheet is treated with a thermal interphase wax.
6. Process according to any of the preceding claims, wherein the pleat height in relation to the sheet thickness is from 1000:1 to 2:1, preferably from 500:1 to 3:1, and most preferably from 100:1 to 5:1.
7. Process according to any of the preceding claims, wherein the sheet is pleated so that in the resulting pleated structure pleats with different heights exist.
8. Process according to any of the preceding claims, wherein the thermally anisotropic sheet thickness is from 1 to 500 μm , preferably from 2 to 250 μm and more preferably from 5 to 100 μm .
9. Process according to any of the preceding claims wherein pleating of the sheet is performed perpendicular to the direction of maximum thermal conductivity.

10. Process according the preceding claims wherein the sheet further comprises a layer of a thermally isotropic conductive material.
11. Process according to any of the preceding claims, wherein the thermally anisotropic sheet comprises a thermally anisotropic polymer layer.
12. Process according to claim 11, wherein the polymer layer comprises or consists of a polyolefin or a fluoropolymer.
13. Process according to claim 12, wherein the polyolefin is a polyethylene.
14. Process according to claim 12, wherein the fluoropolymer is polytetrafluoroethylene (PTFE), a modified PTFE, a fluorothermoplastic, a fluoroelastomer or any combination thereof.
15. Process according to any of the preceding claims, wherein the intrinsic thermal conductivity of the sheet is 0.5 W/mK or more in the direction of maximum intrinsic thermal conductivity.
16. Thermally conductive article obtainable by a process according to any of claims 1 to 16.
17. Thermally conductive article comprising a sheet with thickness is from 1 to 500 μm and wherein the article has a thermal conductivity perpendicular to the plain of 1 W/mK or higher.
18. Use of a thermally conductive article according to claim 16 or 17 for production of a device.
19. Device comprising a thermally conductive article of claim 16 or 17.

1/16

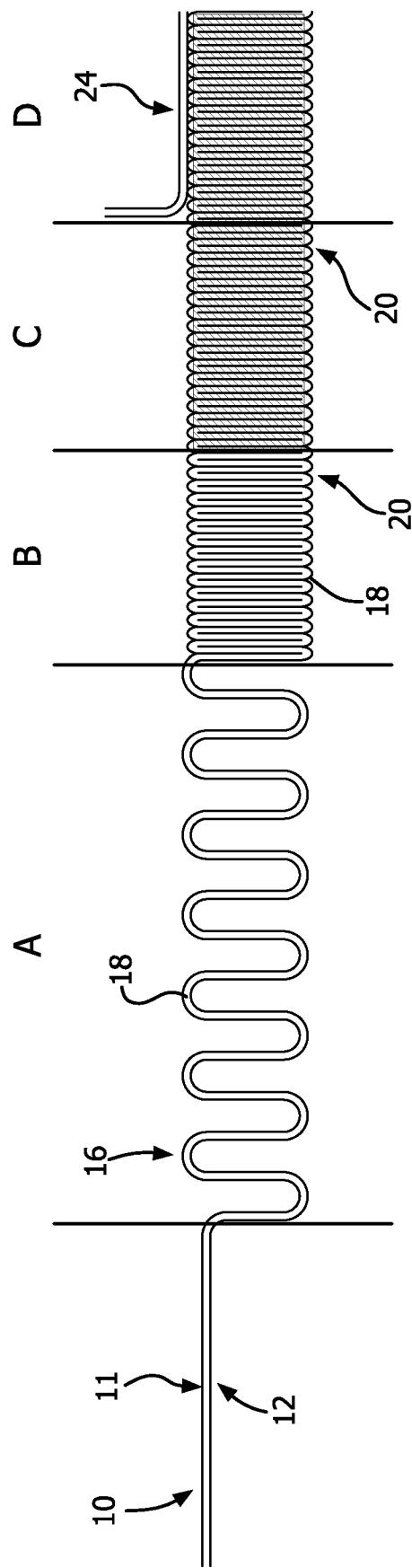


FIG. 1a

2/16

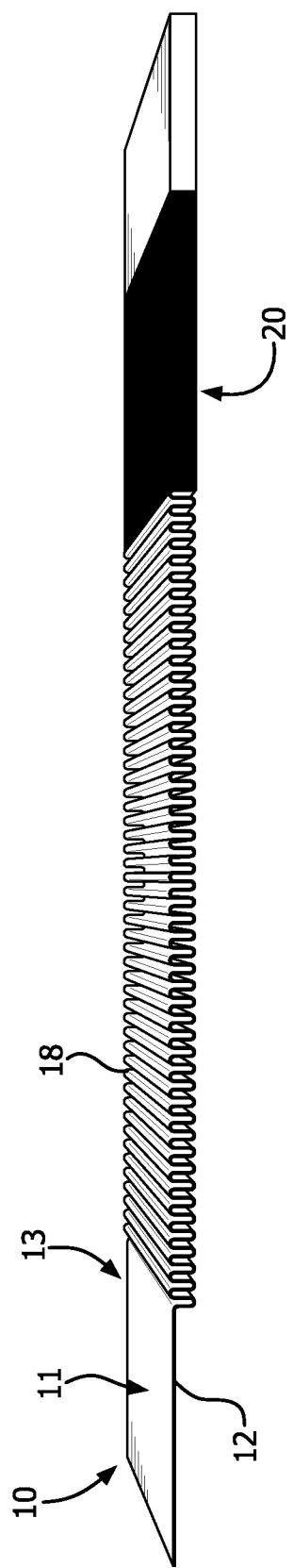
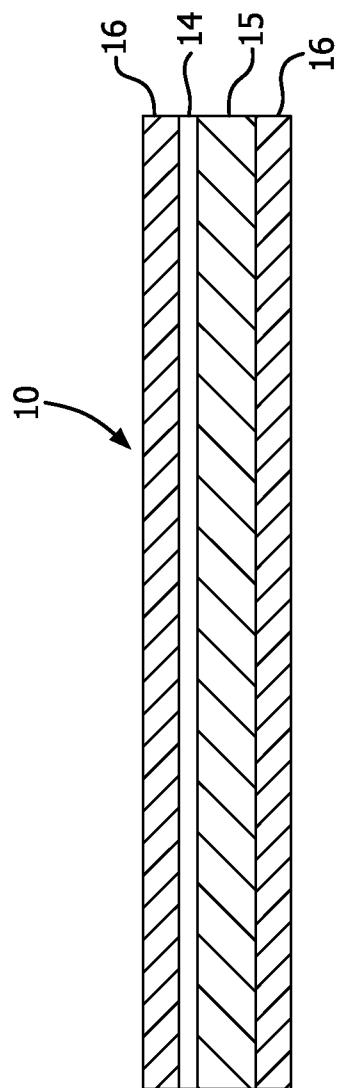
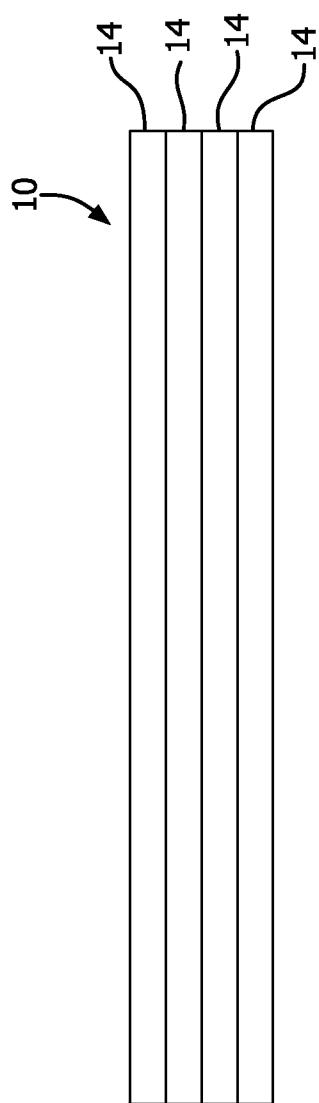


FIG. 1b

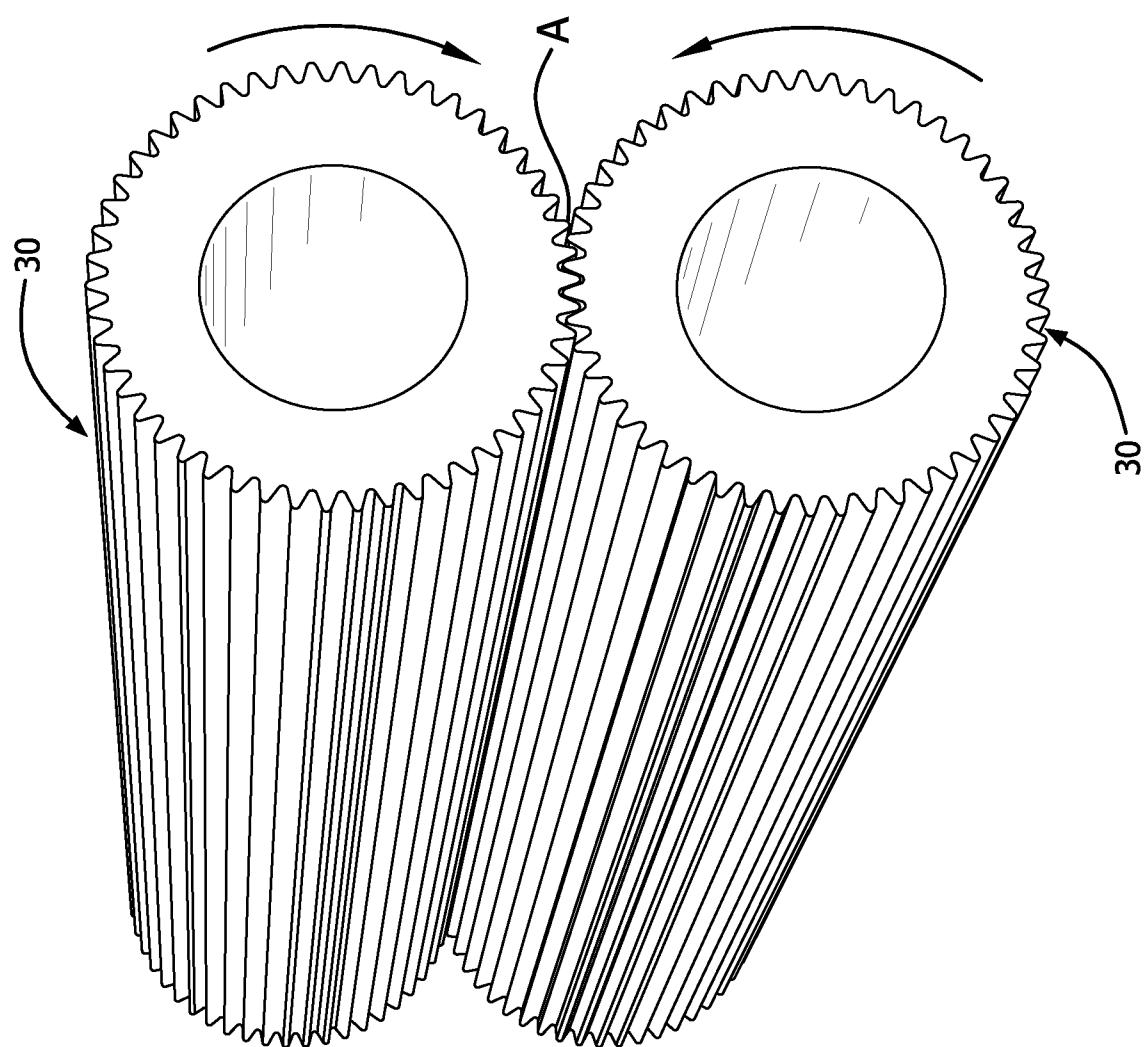
SUBSTITUTE SHEET (RULE 26)

3/16



4/16

FIG. 3a



5/16

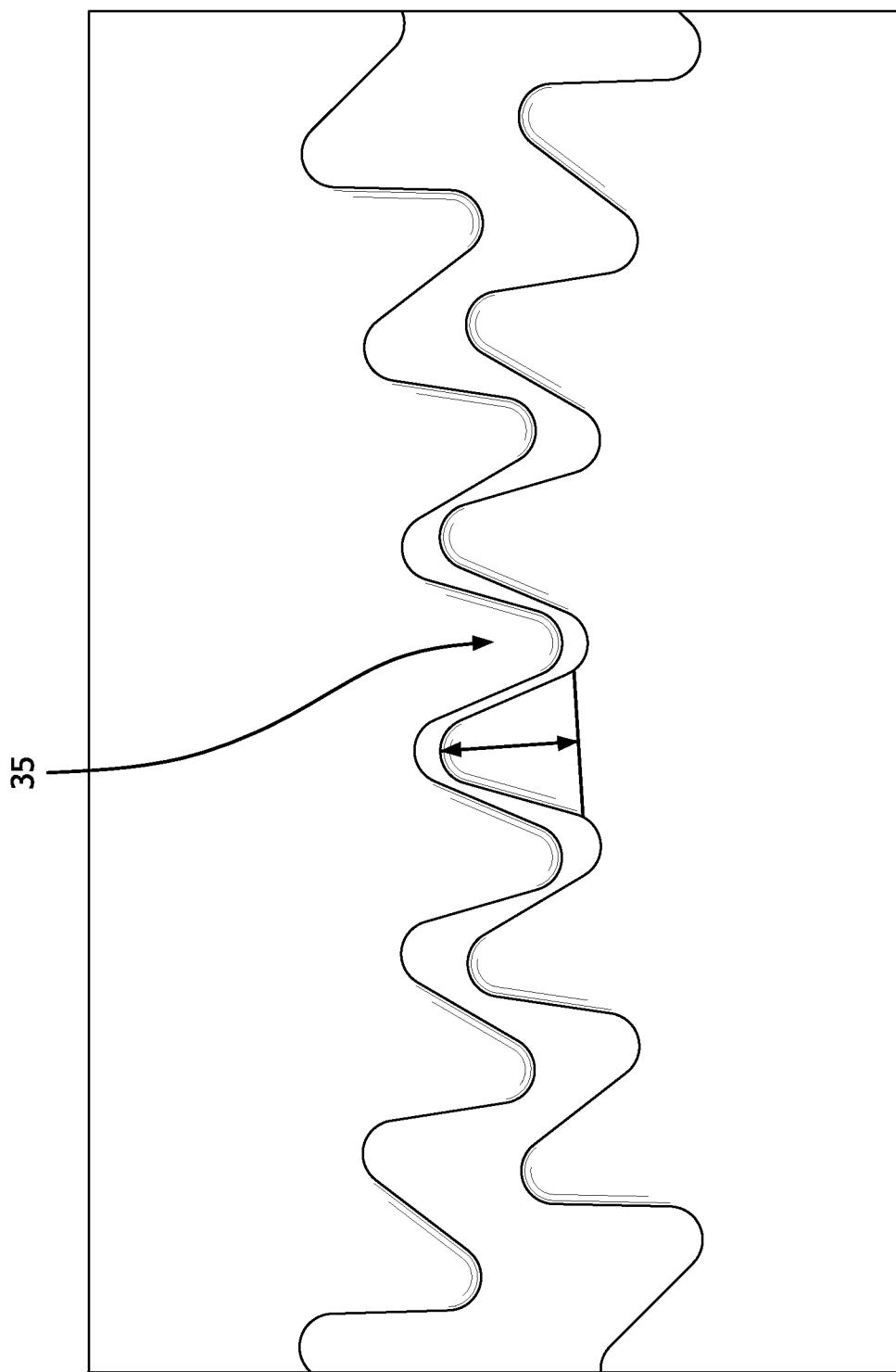


FIG. 3b

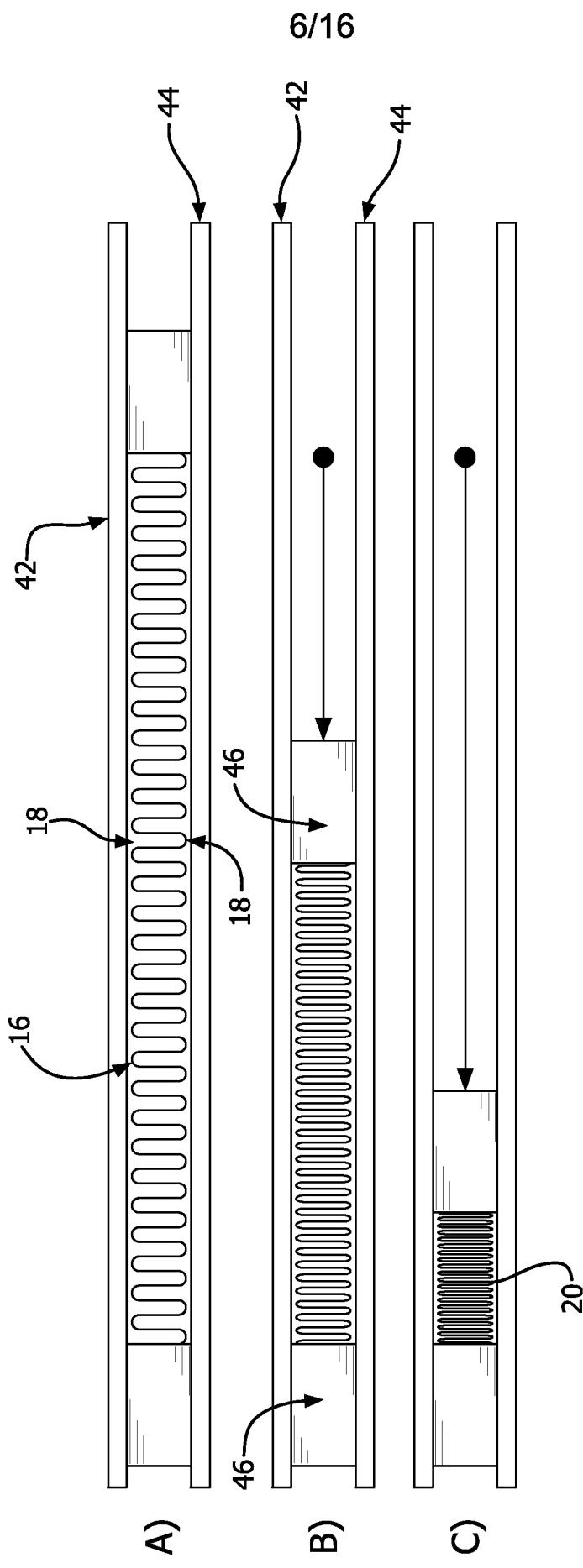
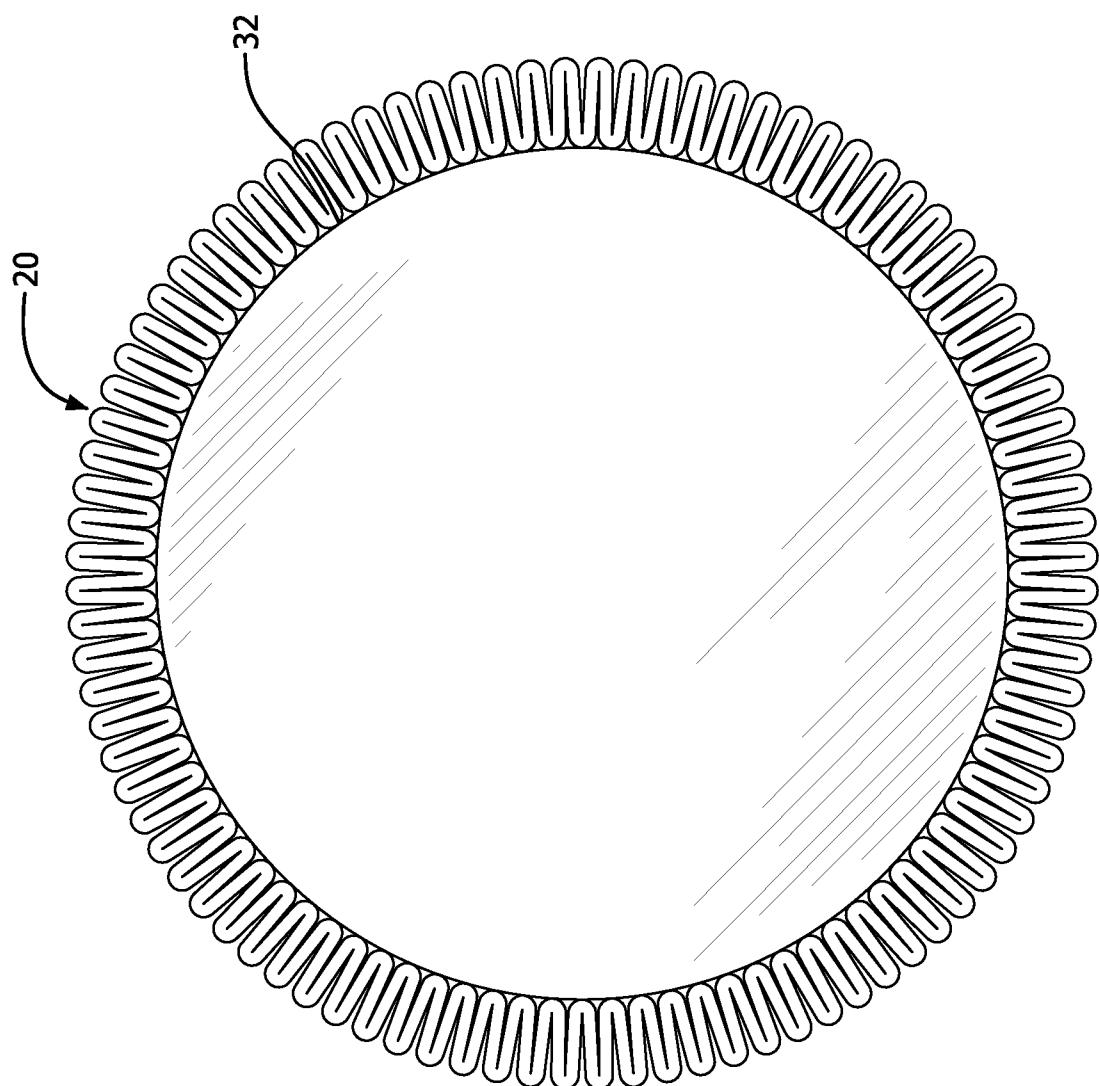


FIG. 4

SUBSTITUTE SHEET (RULE 26)

7/16

FIG. 5a



8/16

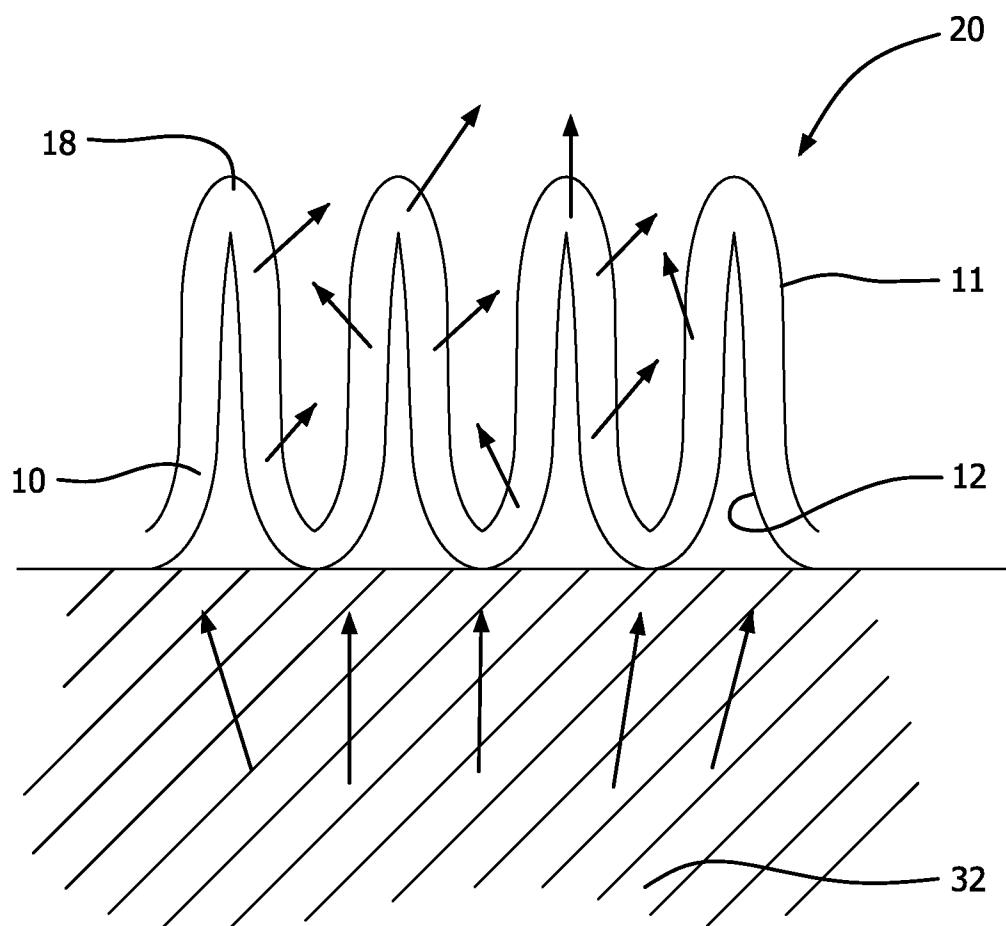
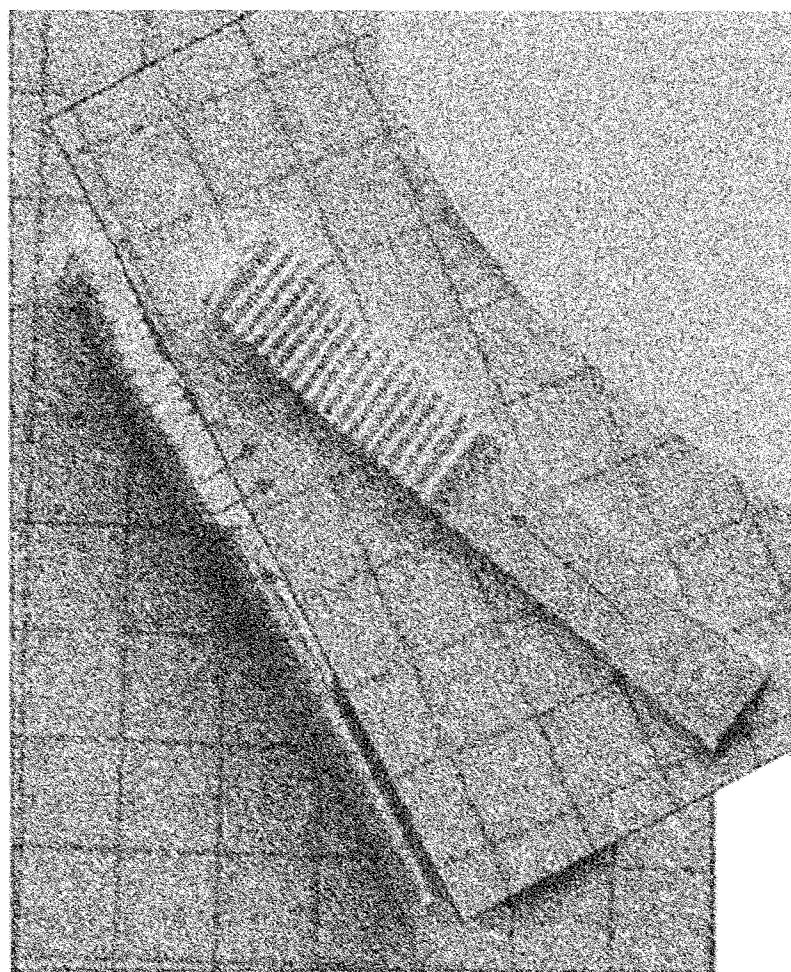


FIG. 5b

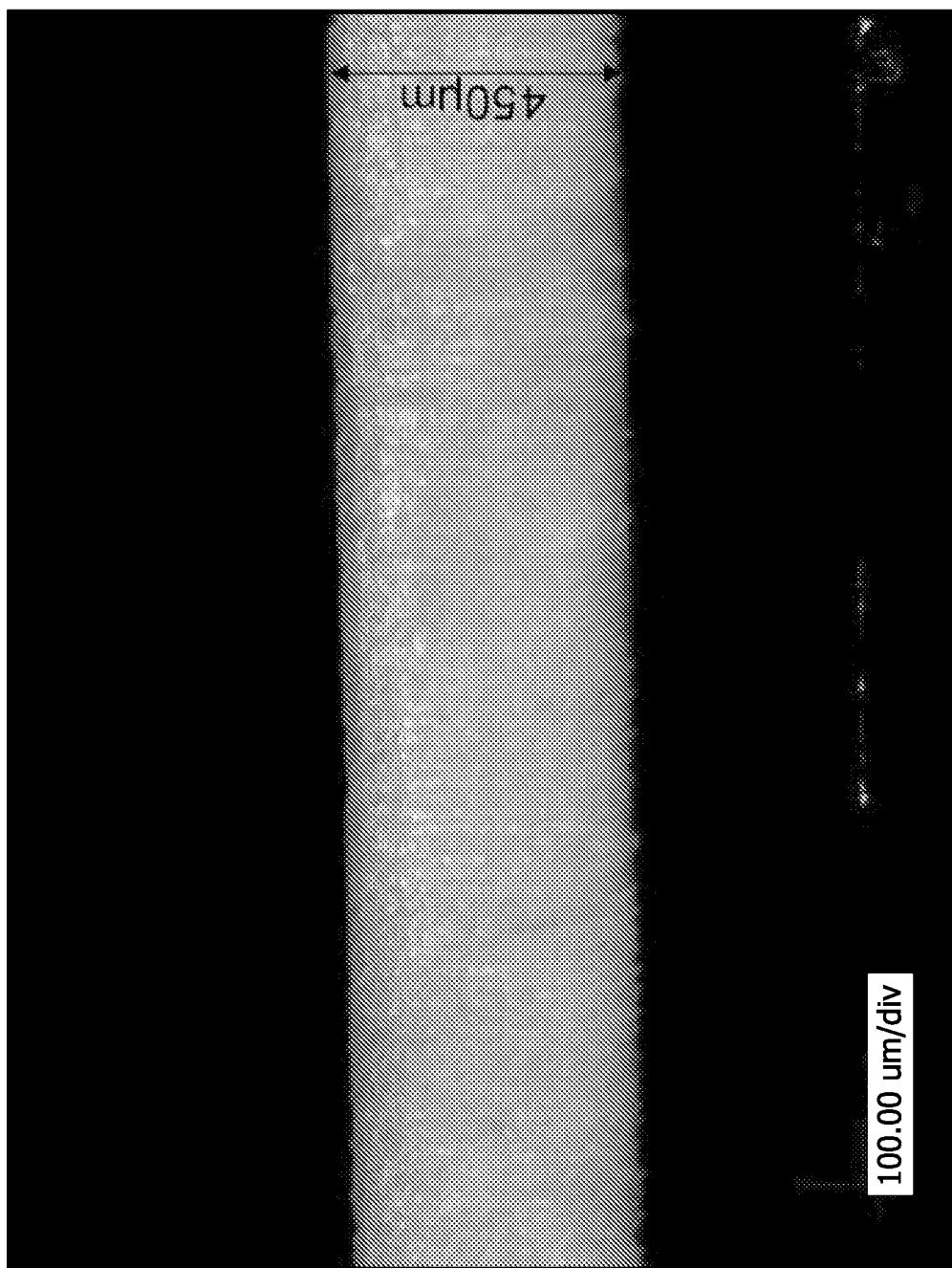
9/16

Fig. 6



10/16

FIG. 7a



SUBSTITUTE SHEET (RULE 26)

11/16

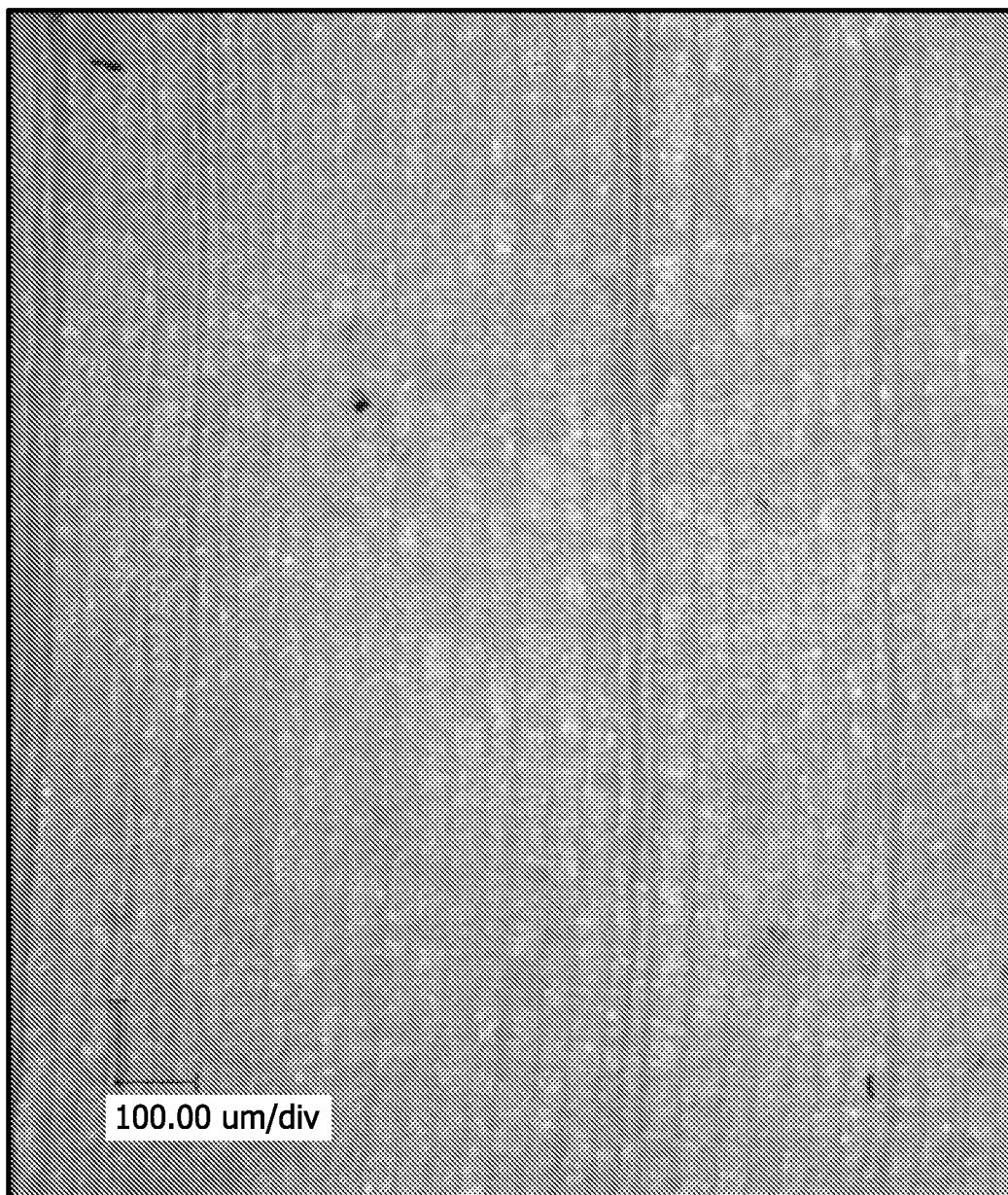
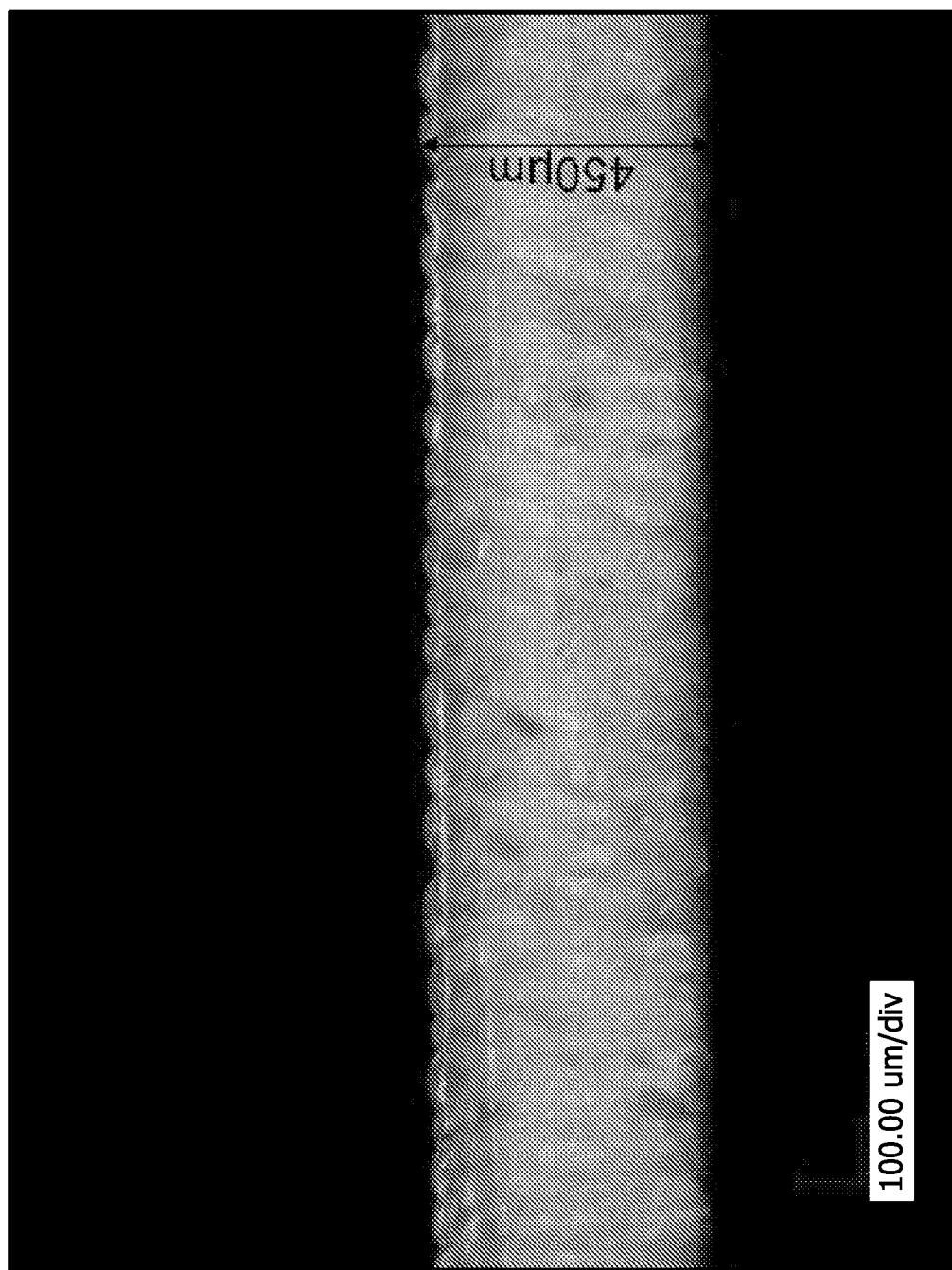


FIG. 7b

12/16

FIG. 8a



SUBSTITUTE SHEET (RULE 26)

13/16

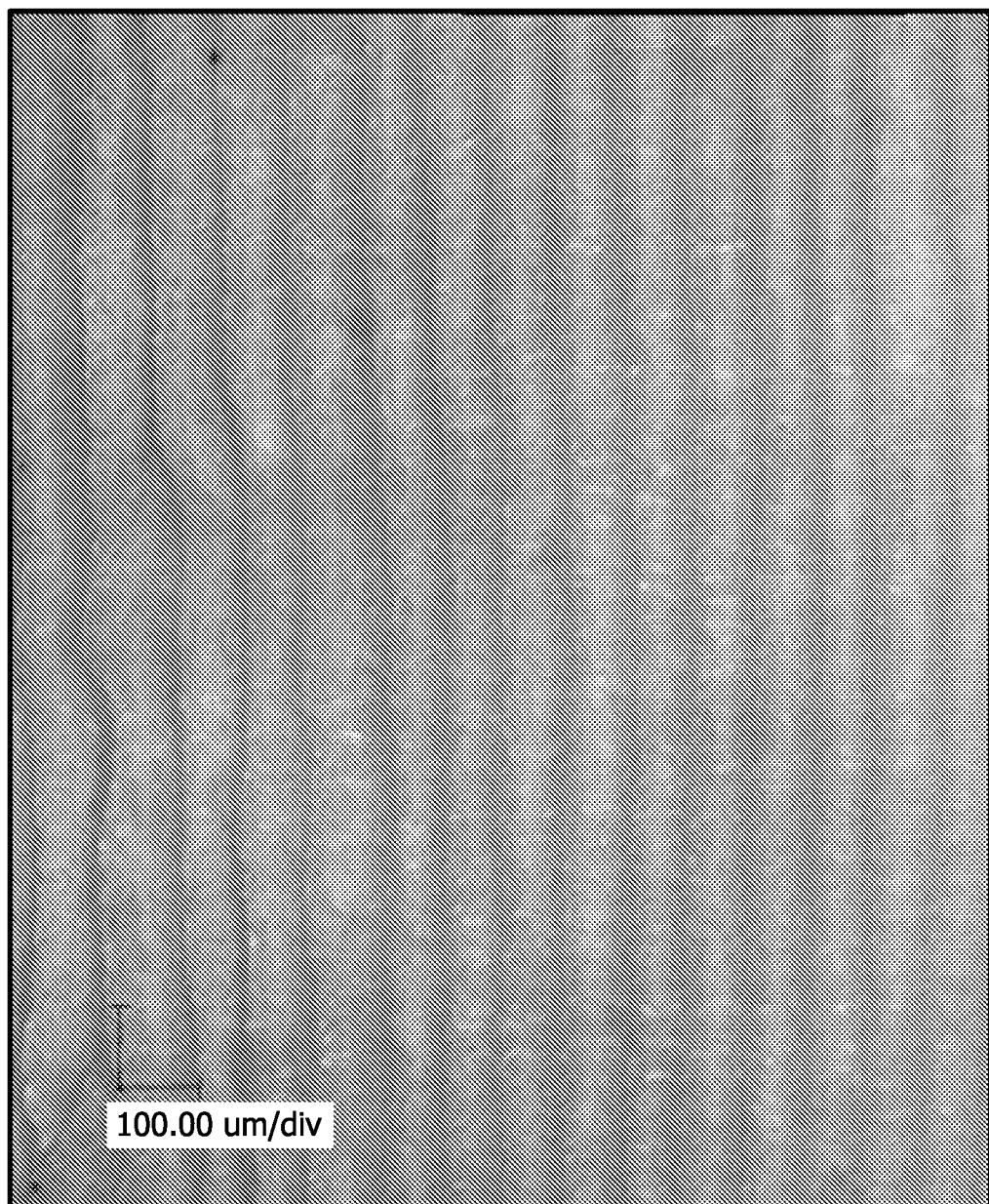
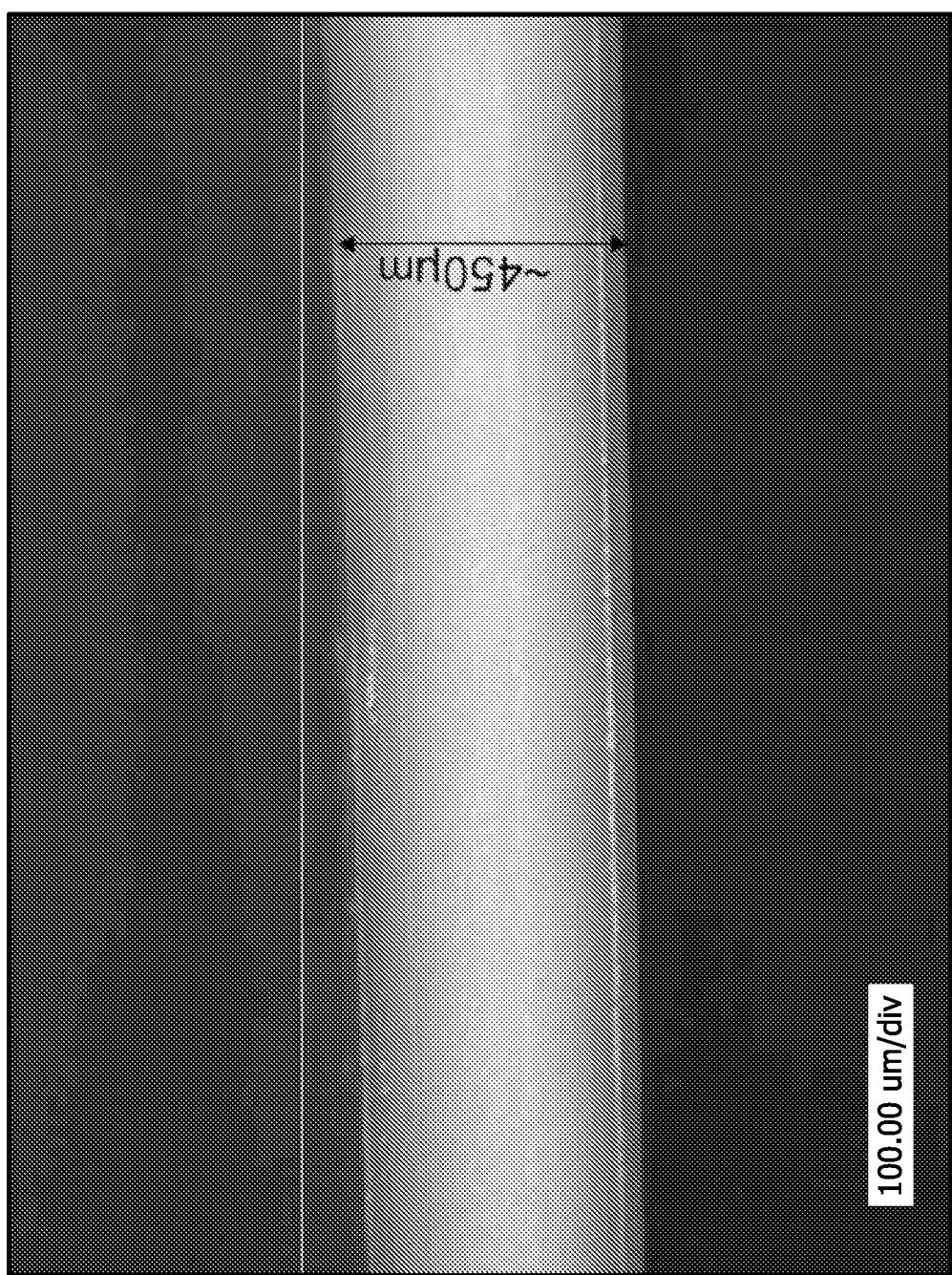


FIG. 8b

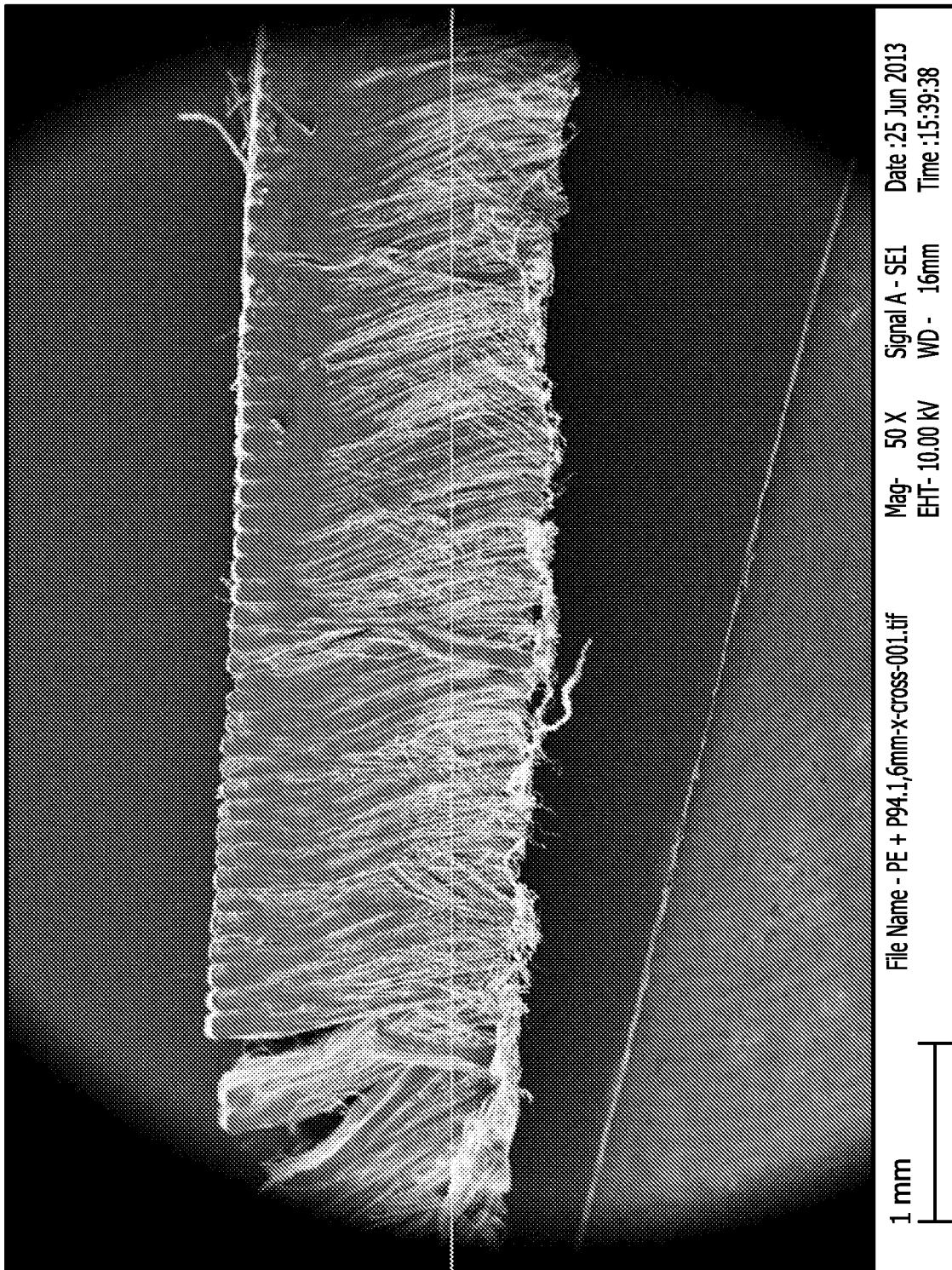
14/16

FIG. 9



15/16

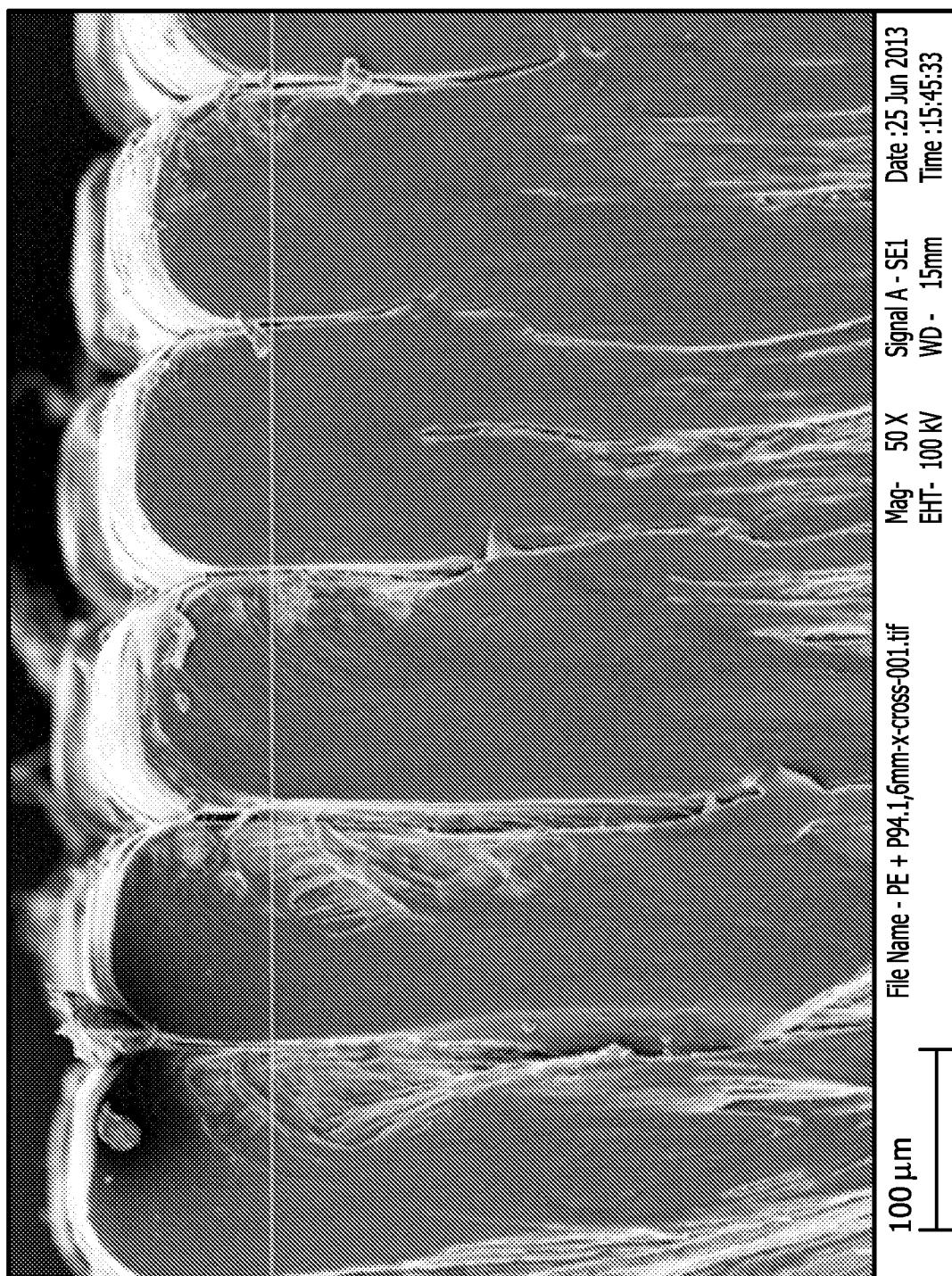
FIG. 10a



SUBSTITUTE SHEET (RULE 26)

16/16

FIG. 10b



INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/057576

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K5/14 F28F3/02 F28F21/06 F28F1/10
ADD.

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)
C09K F28F

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)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98/22770 A1 (MICROMETAL FIBERS INC [US]) 28 May 1998 (1998-05-28) page 1, line 1 - page 3, line 22 page 5, line 2 - page 7, line 4 page 9, line 7 - page 10, line 12 -----	1-19
X	US 2011/135884 A1 (LETTOW JOHN S [US] ET AL) 9 June 2011 (2011-06-09) paragraphs [0011] - [0012], [0056], [0098], [0106], [0112]; figure 3 -----	1-19
X	US 2004/033364 A1 (SPIRIDIGLIOZZI JOHN [US] ET AL) 19 February 2004 (2004-02-19) paragraphs [0002], [0006], [0013], [0043], [0073] ----- -/-	1-4,6-19



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
20 May 2015	28/05/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Martinez Marcos, V

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/057576

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 478 372 A (STARK STEPHEN K [US]) 26 December 1995 (1995-12-26) column 2, lines 3-29; figures 3,4 -----	1,2,6-19
X	WRIGHT J L ET AL: "Radiant and free convective heat transfer through a pleated (V-corrugated) plastic film", SOLAR ENERGY, PERGAMON PRESS. OXFORD, GB, vol. 43, no. 6, 1 January 1989 (1989-01-01), pages 379-384, XP023629205, ISSN: 0038-092X, DOI: 10.1016/0038-092X(89)90110-2 [retrieved on 1989-01-01] Introduction -----	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/057576

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9822770	A1 28-05-1998	AU WO	5261998 A 9822770 A1	10-06-1998 28-05-1998
US 2011135884	A1 09-06-2011		NONE	
US 2004033364	A1 19-02-2004	EP US WO	1663067 A1 2004033364 A1 2005018502 A1	07-06-2006 19-02-2004 03-03-2005
US 5478372	A 26-12-1995	AU AU EP JP US WO	682127 B2 3550895 A 0808207 A1 H10513119 A 5478372 A 9624427 A1	18-09-1997 27-08-1996 26-11-1997 15-12-1998 26-12-1995 15-08-1996