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Fiber reinforced composite material, comprising plies of fiber prepreg with conductive carbon nanotubes or nanofibers interlayers

Technical field of the invention

5 The present invention belongs to the technical field of non-metallic composite materials based on organic or inorganic fiber prepreg sheets. More precisely, it relates to composite materials comprising interlayers of vertically aligned carbon nanotubes or nanofibers, which are provided with means for electrically connecting these interlayers to an external circuit.

10 Said fiber composite materials can be used to make composite materials with electrically conductive interlayers. Such composite materials are multifunctional in the sense that besides their usual function of providing specific mechanical properties (such as strength, impact resistance) to a workpiece, they bring in at least one further function, such as electrical conductivity. Composite materials with electrical conductivity have numerous applications for heating (such as in de-icing and anti-icing devices), auto-curing, thermal control, protection
15 against lightning, *in situ* monitoring of the internal state of a composite material, and can be used for instance in cars, energies devices and in aircraft or aerospace construction.

State of the art

20 Multifunctional composite materials have many potential applications, but their properties do not meet technical requirements where high reliability is required in harsh environments, such as for aerospace, racing sports or outdoor conditions. These composites all comprise one or more conductive additives (such as particles, nanoparticles, graphene, polymeric nanoparticles), said additives being either coated onto the fibers (coated fibers) or dispersed directly in the matrix (mixed resin). Their limitations come mainly from the fact that electrical
25 conductivity cannot reach a sufficiently high level because of the low dispersion limit above which agglomeration of the additives will occur.

Another approach is to insert interlayers of conductive material in between fiber plies. Most interlayers which have been used in prior art do not have sufficient conductivity in both the X-Y plane and at the same time but independently along the Z-axis to meet technical
30 requirements of specific applications such as de-icing and anti-lightning devices. Most of those electrically conductive interlayers are manufactured by electrospinning of polymeric fibers that are made conductive by appropriate additives. Some of them are also made of carbon nanotubes such as CNT mats that are only conductive in the X-Y plane and have no significant conduction in the Z-plane.

35 In many cases, the thickness of such electrically conductive interlayers is also limited because of the risk of reduction in mechanical behaviour of the overall structure of the composite, or because it has never been tested.

However, there is great need for electrically conductive composite materials which can be electrically connected to an external circuit. Such composite materials can be used for heating
40 surfaces. As an example, the formation of ice layers on aircraft structures is undesirable

because it increases the total weight of the aircraft and modifies its aerodynamic behaviour: it may decrease lift and destroy airfoil effectiveness and the desired airflow around the aircraft or structural component. Even a small accumulation of ice on an airframe can greatly alter flight performance; under extreme conditions it may have catastrophic effects on the safe operation of the aircraft. Ice layers can form while the aircraft is grounded or flying. Ice layers may form on all exposed surfaces, such as fuselage, wings, propellers, empennages, engine nacelles, engine inlets, rotors. Ice layers on leading edges are particularly harmful for aerodynamic stability. The accumulation of ice on or within the engine inlet can impede proper airflow into a jet engine greatly reducing engine efficiency or if the ice breaks free cause damage to the engine.

De-icing is usually carried out by spraying specific aircraft de-icing fluids (such as a water – glycol mixtures which may contain functional additives such as thickeners) onto the relevant surfaces prior to take off, or by blasting hot air onto the relevant surfaces. Both procedures are time consuming and labour consuming. Moreover, it does not address the issue of ice layers that may form while the aircraft is flying, even if the liquids used for de-icing may be selected such that they block, to some extent and for a certain period of time, the formation of fresh ice after take-off.

Removal of ice layers and ice formation prevention of inflight icing can be achieved by various de-icing and anti-icing systems which can be classified into the following six categories.

Chemical protection is achieved by distributing a liquid onto the surface that is to be protected, usually by a system of holes or channels within the structure. The de-icing fluid or anti-icing fluid is held in a tank and is fed through a system of tubes, pipes and pumps to the surfaces that require de-icing or anti-icing protection. Besides weight and complexity, the de-icing fluids can have a negative environmental impact and cause maintenance issues due to the nature of the fluid.

Pneumatic boots use air to inflate and break ice free from the surface. This system is usually used on rotors, propeller blades and leading edges of the wing, vertical and horizontal stabilizers. Pneumatic boots are an older technology that dates to the late 1920's and were improved in the 1950's. Pneumatic boots are heavy and do require care in maintenance and operation. In operation it is possible to activate the system too early especially if the ice is a thin layer, this will result in the ice not breaking free from the surface.

Bleed Air systems use heated air which is drawn off the engine and is diverted through pipes and mixing valves to the areas that are to be de-iced (see US 5,114,100). The heated air is then dispersed through a nozzle or hole system in the pipe to heat up the surface (see EP 0 376 371 A2). The use of bleed air decreases engine efficiency. Also, the use of bleed air can be dangerous for polymeric composite structures due to overheating; it may be necessary to mix cold air with the hot engine air. Bleed air systems tend to be heavy, complex, inefficient and expensive to build.

Electromechanical systems (see GB 505,433, US 3,779,488 and US 4,678,144) use thumpers that are attached to the surface that will require de-icing protection. The device is electrically actuated and as it is activated it moves and deforms the surface periodically, thus breaking the adhesion of the ice to the surface and effectively shedding the ice formation. Resistive heating relies on heating wires that are embedded into an insulation jacket that is then bonded or

molded into the structure that is to be deiced. The insulation jacket can be an elastomeric boot or an insulation material such as fiberglass. The current resistive heating systems can be heavy, complex, with the need for overlapping systems to ensure full coverage protection (elimination of cold spots) and inefficient requiring heavy electrical energy draw.

5 In recent years, graphene-based heating elements have been developed. It involves two different areas. The first application is where the graphene sheet is applied to the surface to act as a "slick surface" that does not allow the water to condense on, thus preventing ice formation. The second area is where graphene is used as a heating element to keep the surface warm, similarly to resistive heating applications. The graphene sheets may be bonded
10 directly to a surface or embedded into an insulation layer. Current drawbacks to the use of graphene are cost of the material, a good understanding of how to utilize the material, and that it is an additional process / system on the aircraft.

The present invention focuses on composites allowing resistive heating by passing an electrical current through a conductive material buried in the composite. Such composites are
15 known as such. WO 2010/129 234 A2 (Lockheed Martin Corp.) discloses a method for making CNT-infused fiber materials, each individual fiber being decorated with an arrays of centrifugal carbon nanotubes. These fibers can then be transformed into fabrics. WO 2018/027092 A1 (General Nano LLC) describes a process for randomly coating polymer films or fabrics with carbon nanotubes, using a suspension of dispersed carbon nanotubes and a polymer in a
20 solvent. US 2007/0128960 A1 discloses three-dimensionally reinforced composite laminates made by growing carbon nanotubes onto a surface of a woven fiber cloth, and infiltrating this preform with a resin. US 2017/0019954 A1 (Metis Design Corp) describes various structured CNT-engineered materials that can be used for de-icing or as an antenna.

Another possible construction of the electro-thermal source is provided in the publication
25 "*Carbon Nanotube (CNT) Enhancements for Aerosurface State Awareness*" by Kessler, Dunn, Wicks, Guzman de Villoria and Wardle, presented at IWSHM-2011, available at https://www.researchgate.net/publication/279841119_Carbon_Nanotube_CNT_Enhancements_for_Aerosurface_State_Awareness.

There is room for improving such composites. It must be possible to manufacture flat or curved
30 composite panels, and also to obtain shaped or even flexible parts. The speed of heating and the homogeneity over the panel surface are critical in aircraft applications. This may imply the use of high currents and/or high voltages, to which the composite panels and parts must withstand.

It would also be desirable to be able to use these interlayers for monitoring of the structural
35 composite. Such monitoring should be possible not only close to the surface but also in the bulk of the composite material. Such monitoring would require the measurement of electrical parameters of the interlayers, and to deduce information on the structural state of the material, in order to monitor any damage or failure that may have occurred as early as possible.

40 **Summary of the invention**

The invention relates to the superposition of multiples fibers plies and VACNT interlayers plies, not all the interplies, that can be independently connected to each other in various

configurations, in series or in parallel, static or dynamic operation. This structure can be manufactured in many different embodiments, to create optimized structures for specific applications and technical specifications.

For making multi-ply composites according to the invention, a VACNT layer is deposited onto a layer ("ply") of fibers. The fibers can be previously impregnated or (infiltrated) with a suitable resin. Such a fiber layer that has been impregnated with a suitable resin is commonly called a "pre-preg" in the field of composite materials. These pre-pregs can advantageously be unidirectional prep-pregs, or can be woven or fabric. The resin can in particular be a thermoplastic resin, a thermoset resin or an elastomeric resin. The VACNT layer can be deposited onto one face of the pre-preg ply or on both faces according to certain embodiments of the invention. A unitary sheet of fibers covered with VACNT is called here a "mono ply". Several of such mono plies can be superposed. After curing of the resin, a solid composite panel or a solid composite shaped part is obtained. Said panel or said shaped part can be rigid, semi-rigid or even flexible, depending on the nature of the resin and/or on the number of plies. The mechanical properties of such panels or parts depend mainly on the choice and structure of the fiber layer, on the resin, and on the number of superimposed plies. Mechanical reinforcement of such structures is already well known and validated.

In the framework of the present invention, the deposition of the VACNT layer onto the fiber ply is carried out by known transfer techniques, such as lamination and calendering. It is not practical to grow VACNT layers directly from the gas phase onto pre-preg fiber layers, but direct growth is also possible for raw fabric for instance.

In one embodiment, two or more VACNT layer are used in the composite panel, each sandwiched between two plies. The use of two or more VACNT layers for heating purposes improves the thermal homogeneity of the composite panel devices incorporating said composite panel. The use of two or more VACNT layers also allows to dedicate at least one of these layers to sensing purposes, which allows to monitor for example the structural health of the composite material. The number of VACNT layers between plies can be greater than 2, for example 3, 4, 5, 6, 7, 8 and so on. For de-icing or anti-icing purpose, the specific power at 800 V is preferably at least 3 W/cm², preferably at least 4 W/cm², more preferably at least 4.5 W/cm², still more preferably at least 5 W/cm², and even more preferably at least 6 W/cm².

In one embodiment of the present invention, the VACNT height is the same for all the VACNT layers. In one embodiment the VACNT can be bent so that they are still aligned but not perpendicular to the fiber X-Y plane.

In another embodiment, the VACNT height is not the same in the VACNT layers. In particular, VACNT height may be different for heating layers and for measurement layers (here also called: sensing layers). Advantageously, heating layers have a VACNT height comprised between about 1 µm and about 100 µm, preferably between about 5 µm and about 50 µm, and more preferably between about 15 µm and about 25 µm, while electrically conductive layers dedicated to measurement can have a smaller VACNT height, which is typically between about 1 µm and about 15 µm, preferably between about 1 µm and about 10 µm, and more preferably between about 1 µm and about 5 µm.

The VACNT height can be selected such as to adjust electrical resistance and heat generation of each ply. Each layer may have a different thickness according to the target performance.

This also allows a better compatibility with a broader range of resin. A particularly suitable VACNT height for thermoset resin is 15 μm to 25 μm . For thermoplastic or even elastomeric resins, the VACNT height can be above 25 μm . The density of CNT (i.e., their number per surface area) and/or the spacing of CNT within a VACNT array may also be adjusted.

- 5 Advantageously, the VACNT layers are connected to a metallic conductor. It has been found that establishing a direct electrical contact between the VACNT layer and a metallic conductor ensures a more reliable electrical contact than connecting the metallic conductor to the carbon fibers onto which the VACNT layer has been deposited. More precisely, it allows a better control of the resistivity of each ply, results in a better electrical and thermal homogeneity of
10 the ply, and avoids the formation of hot spots.

Furthermore, connecting the VACNT layer to a metallic conductor allows to deposit the VACNT layers onto insulating fibers. This allows to carry out the invention with a wide range of fibers, as may be appropriate for obtaining parts with specific use properties, such as static mechanical properties, fracture toughness, crack propagation, impact strength. As an
15 example, the invention can be carried out with glass fibers and kevlar fibers.

In another embodiment, which may be combined with each of the other embodiments, each layer is connected separately from the others to a power source and/or a sensing device (here also called monitoring device), and / or can be addressed individually. Each layer can be connected in series or in parallel to each other.

- 20 In another embodiment only part of the interplies is provided with VACNT.

A first object of the invention is a composite panel formed by a stack of pre-preg sheets alternating with layers of vertically aligned carbon nanotubes (VACNT), wherein an electrical connection element is provided on two opposite edges of each VACNT layer.

According to specific aspects of the invention:

- 25 - said electrical connection element is a sheet of metal in contact with a VACNT layer;
- each VACNT layer is sandwiched between two plies of pre-preg sheets;
- at least two VACNT layers are connected in series, and /or at least two VACNT layers are connected in parallel;
- said composite panel is flat or shaped;
- 30 - said prepreg sheets comprise carbon fibers and a thermoset resin or a thermoplastic resin or an elastomeric resin;
- at least one of said VACNT layers has a height comprised between 1 μm and 100 μm ;
- said panel comprises a first set of one or more VACNT layers of a first height, and a second set of one or more VACNT layers of a second height, said first height being comprised between
35 about 1 μm and about 100 μm , and preferably between about 5 μm and about 50 μm , and said second height being comprised between about 1 μm and about 25 μm and preferably between about 1 μm and about 10 μm , and more preferably between about 1 μm and about 5 μm ;

- at least one busbar is provided on each of two opposite edges of said panel, each busbar being connected to at least one of said electrical connection elements.

Another object of the present invention is a composite panel device, comprising a composite panel according to any of the embodiments of the invention, and further comprising electrical connection elements connecting at least two of said VACNT layers in parallel or in series, and at least one electrical apparatus connected such as to form an electrical circuit with said at least two VACNT layers, wherein said electrical apparatus is a power generator.

According to specific aspects of the invention:

- said power generator forms an electrical circuit with said first set of one or more VACNT layers of a first height;

- said composite panel device further comprises a further electrical apparatus which is a measurement device or sensing device;

- said measurement device or sensing device forms an electrical circuit with at said second set of one or more VACNT layers of a second height;

- said first height is comprised between about 1 μm and about 100 μm , and preferably between about 5 μm and about 50 μm , and said second height is comprised between about 1 μm and about 25 μm and preferably between about 1 μm and about 10 μm , and more preferably between about 1 μm and about 5 μm .

Another object of the present invention is a shaped part for mechanical construction, using a shaped composite panel according to any of the embodiments of the present invention.

A further object of the present invention is a de-icing system or anti-icing system for mechanical construction elements such as aircrafts, terrestrial vehicles, stairs, using a composite panel according to any of the embodiments of the present invention, or a shaped part according to the invention.

A further object of the invention is a method for making a composite panel or a shaped part according to any of the embodiments of the present invention, comprising the steps of:

- providing at least a first and a second prepreg sheets, a VACNT array deposited on a substrate, and at least a first and a second metallic connecting elements,

- transferring said VACNT array from said substrate to said first prepreg sheet,

- depositing said first and second metallic connecting elements at two opposite edges onto said VACNT array,

- depositing said second prepreg sheet onto said VACNT array and said metallic connecting elements,

- exerting pressure such as to form a laminated complex comprising a VACNT layer sandwiched between two prepreg sheets.

A further object of the invention is a method for making a composite panel or a shaped part according to any of the embodiments of the present invention, comprising the steps of:

- providing at least a first and a second prepreg sheets, a VACNT array deposited on a substrate, and at least a first and a second metallic connecting elements,
- 5 - transferring said VACNT array from said substrate to said first prepreg sheet and said first and second metallic connecting elements,
- depositing said second prepreg sheet onto said VACNT array and said metallic connecting elements,
- 10 - exerting pressure such as to form a laminated complex comprising a VACNT layer sandwiched between two prepreg sheets.

A further object of the invention is a method for making a composite panel or a shaped part according to any of the embodiments of the present invention, comprising the steps of:

- 15 - providing at least a first and a second prepreg sheets, a VACNT array deposited on a substrate, and at least a first and a second metallic connecting elements,
- depositing said first metallic connecting elements at one edge onto said first prepreg sheet,
- transferring at least said first said VACNT array from said substrate to said first prepreg sheet and said first VACNT array,
- 20 - depositing said second metallic connecting elements at an opposite edge onto said VACNT array,
- depositing said second prepreg sheet onto said VACNT array and said second metallic connecting elements,
- exerting pressure such as to form a laminated complex comprising a VACNT layer sandwiched between two prepreg sheets.

25

Brief description of the figures

Figure 1 schematically shows a transversal cross section of a composite panel according to a first embodiment of the invention.

30 Figure 2 schematically shows a transversal cross section of a composite panel according to a second embodiment of the invention.

Figure 3 schematically shows a transversal cross section of a composite panel according to a third embodiment of the invention.

Figure 4 schematically shows a transversal cross section of a composite panel according to a fourth embodiment of the invention.

Figure 5 schematically shows a transversal cross section of a composite panel according to a fifth embodiment of the invention.

Figure 6 schematically shows a transversal cross section of a composite panel according to a sixth embodiment of the invention.

5 Figure 7 schematically shows perspective view of a shaped part according to the invention.

Figure 8 shows a micrograph obtained by scanning electron microscopy, representing a top view of an array of vertically aligned carbon nanotubes (VACNT) used in the composite panels according to the invention.

10 Figure 9 schematically shows different steps which form part of the method for manufacturing a flat composite panel according to the invention. The step shown here relate to the transfer of a VACNT array from its growth substrate onto a prepreg sheet.

Figure 10 shows a scanning electron microscopic image of a cross section of a ply used for making NawaStitch™ panels. The letter “F” designated the fiber, the letter “R” designated the resin which impregnates the fiber structure, and “VACNT” indicates the location of the VACNT
15 array.

The following reference numbers are used on the figures and in the present specification; they have the same or a similar meaning if increased by one or more hundreds:

1	Composite panel according to the invention
2, 3	Upper face (2) and lower face (3) of 1
20 11,12,13,14,15,16,19	Fiber layers (pre-preg)
21,22,23,24	Interlayers (VACNT)
31,32,33,34	Electrical connection elements
150	Power generator
251,252,253,254; 350; 451,461	Electrical apparatus
25 572,574	Busbar
600	Shaped part
602,603	Upper (internal) face (602) and lower (external) face (603) of 600
650	Electrical apparatus
670,671	Electrical conductor
30 680	Titanium via

Four-digit reference numbers refer to process steps.

Detailed description

35 We will here describe several advantageous embodiments of the invention. Their features may be combined, and the invention is not limited to these embodiments.

The preparation process of VACNT coated pre-preg sheets is schematically shown in Figure 9, in which reference numbers with four characters represent process steps or groups of process steps. In a first step 1010, a metallic substrate, such as steel or aluminium, is provided.

In a first step or sequence of steps 1020, VACNT are deposited from a gas phase onto said substrate. Depending on the deposition method, the provided substrate is coated with a catalyst prior to gas phase deposition, or the catalyst precursor is continuously added to the gas phase during VACNT growth.

5 In a second step or sequence of steps 1030, the VACNT on the coated metallic substrate are then pressed 1030 onto the pre-preg sheet such that the VACNT strongly adhere to the pre-preg sheet; this implies pressure exerted onto the substrate such that the VACNT penetrates the resin. This step or sequence of steps can be carried out at room temperature or at an appropriate temperature above room temperature to allow softening of the resin, which may
10 be a thermoplastic resin or a thermosetting resin or an elastomeric resin.

In a third step or sequence of steps 1040 the metallic substrate is then pulled off, leading to a composite sheet consisting of a pre-preg sheet coated with VACNT 1050. Transfer can be made simultaneously or independently on both side of the same pre-preg ply.

A photography obtained by scanning electron microscopy of a cross section perpendicular to the x-y plane of such a ply is shown on figure 10. The pre-preg sheet comprises carbon fibers impregnated with an appropriate resin. Letter "F" designates a carbon fiber. "VACNT" designates the VACNT interlayer; the carbon nanotubes extend in the z direction. Letter "R" designates the resin in which the carbon fibers are embedded. As described in US
15 2009/0117363 A1, in a typical embodiment, each ply may have a thickness of the order of several hundreds of micrometres, the diameter of the individual fibers being of the order of about 5 μm to about 50 μm . In the framework of the present invention, the surface density and the thickness of said VACNT interlayer need to be adapted to the target value of electrical resistivity. Typical values for the thickness of the VACNT layer (i.e., the length of the nanofibers or nanotubes) are comprised between about 25 μm and about 150 μm , for example.
20

25 Upon lamination (step 1030), said resin may penetrate at least in part into the free space between adjacent nanotubes forming the VACNT array. When the resin is then completely cured, said VACNT interlayer will be intimately bound to the resin component of the adjacent plies. This has been shown to improve adhesion between adjacent plies. In this sense, the composite panel devices according to the invention may also present mechanical properties
30 which are interesting for the designer of mechanical parts. In particular, the presence of a VACNT layer provides z-axis reinforcement of plies. Such panels are known as such, for instance under the trademark NawaStitch™.

In further process steps (not shown on the figures) this pre-preg sheet coated with VACNT can be laminated onto another pre-preg sheet, such that the VACNT are sandwiched between
35 the two pre preg sheets. Prior to this, according to an essential feature of the present invention, a metallic connecting element needs to be added which establishes an electrical connection to the VACNT layer. Said metallic connecting element can typically be a metallic foil, such as a copper foil or an aluminium foil. Such a metallic foil is added at two opposite edges of the composite sheet, between the VACNT layer and the pre-preg, such that it slightly overlaps the
40 VACNT layer.

In this way, composite panels comprising a stack formed by a plurality of pre-preg sheets and at least one layer of VANCT can be manufactured. The lamination of sandwiches comprising pre-preg sheets and a VACNT layer is known as such and will not be explained here in more

detail. The fiber direction of the pre-preg sheets can be chosen such that the resulting composite panel exhibits specific properties. As an example, pre-preg composite comprising several pre-preg sheets can be built up such that each pre-preg sheet that is added to the composite has a fiber direction that is rotated by typical angles of 15° or 30° or 45° or 60° or even 90° with respect to the pre-preg sheet onto which it is laminated.

In the composites according to the invention, the pre-preg sheets can be identical or different, in particular with respect to their thickness, with respect to the nature and/or thickness of the fibers, with respect to the density of the fiber textile, with respect to nature and thickness of the resin. The VACNT layers can be identical or different, in particular with respect to the height of the nanotubes forming the VACNT sheet, and/or with respect to their surface density.

Depending on its thickness, its rigidity and the nature of the resin, the composite panel can be shaped during its manufacture or after its manufacture. Shaping during manufacture can be achieved typically when lamination is carried out as compression molding, in an autoclave or by hand. After its manufacture, the composite panels can be curved or otherwise shaped. Shaping after manufacture will normally require a thermoplastic resin to be selected for the pre-preg sheets; it can be carried out in as compression molding at a temperature that is sufficiently high such that the thermoplastic resin will soften.

This allows to manufacture curved or shaped parts, as required, for example, for leading edges. These curved or shaped parts will usually be rigid. Flexible parts can be manufactured using soft resin and appropriate VACNT layers (i.e., rather thin layers not exceeding about 100 µm VACNT height, and preferably not exceeding 75 µm height).

Figure 1 schematically shows a first embodiment of a composite panel according to the invention. Said composite 1 has an upper face 2 and a lower face 3. Said composite comprises a plurality of fiber layers 11,12,13,14,15,16,19 with interlayers 21,22,23,24 each of which is formed by a VACNT array. Each of said VACNT interlayers is in contact with a pair of electrical connection elements 31a,31b;32a,32b;33a,33b;34a,34b. These electrical connection elements are typically made from metal foil. They are put in place prior to transferring the VACNT arrays onto the fiber layer. Preferred metal foils are copper, aluminium, or appropriate aluminium alloys or appropriate copper alloys.

There may be no VACNT interlayer between certain adjacent fiber layers 14,15.

It should be noted that in this figure, as well as in figures 2, 3, 4, 5, and 6, the fiber layers represent the pre-preg sheets, the resin layers being omitted in these figures. The resin is visible in figure 10 which is a micrograph.

When this composite panel is used for a de-icing device, the upper face 2 will normally be the external face (i.e., the face on which ice may form when the de-icing device is not heating), and the lower face 3 will be the internal face, i.e., the face in contact with a structural element of the aircraft.

Figures 2 schematically shows a first embodiment of a composite panel device 100 according to the invention. All reference numbers corresponding to those of figure 1 are increased by 100. The structure of the different layers forming said composite is the same as in figure 1. This figure shows in addition an external electrical circuit to which the device is connected. This external electrical circuit allows for example to pass a current through each of the VACNT

arrays, said current leading to resistive heating of said VACNT interlayers 121,122,123,124. In this embodiment, there is one single power generator 150 for all of the VACNT interlayers 121,122,123,124, said VACNT interlayers 121,122,123, 124 forming a parallel circuit.

5 The same circuit can be used for sensing (monitoring) purposes, in which case the reference number 150 would not necessarily be a power generator, but an electrical apparatus configured to inject a current, possibly as a pulse, into the composite panel device 100, and configured to measure a response.

10 In an advantageous variant, this sensing (monitoring) function can be used intermittently, that is to say from time to time, and the electrical apparatus 150 can be configured such as to pass a current through the composite panel device 100 sufficient for heating. In this variant, the composite panel device 100 is in fact a multifunction device: it can serve as a heating device and as a sensing or monitoring device, too.

15 Figure 3 schematically shows a second embodiment of a composite panel device 200 according to the invention. All reference numbers corresponding to those of figure 1 are increased by 200. The structure of the different layers forming said composite is the same as in figure 1. This figure shows in addition an electrical circuit for passing a current through the VACNT array. In this embodiment, each of the VACNT interlayers 221,222,223,224 has its own independent electrical apparatus 251,252, 253, 254, which can be an independent power generator or an independent channel of a power generator. "Independent" means here that
20 said electrical apparatus or said channel can be addressed and controlled individually, and in particular independently of the other electrical apparatuses or channels. This can be achieved by using one electrical apparatus per circuit, or by providing appropriate switching or controlling means for each circuit.

25 As in the figure 2, said electrical apparatus can be a power generator and / or a sensing (monitoring) device.

While this embodiment requires a more complex electronic system than the other ones, it allows individual addressing and temperature control of each of the layers of the composite panel 200.

30 Figure 4 shows a third embodiment a composite panel device 300 according to the invention. The structure of the different layers forming said composite is the same as in figure 1. The difference is that all the VACNT interlayers are connected in series to the electrical apparatus 350, which can be a power generator for heating. As explained in relation with figure 2, the same circuit can be used for sensing (monitoring) purposes.

35 Intermediate solutions can be used, too. In particular, there can be one common channel, or one common electrical apparatus (such as a power generator), for a group of two or more VACNT interlayers, which can be adjacent or distant. Figure 5 schematically shows such an embodiment of a composite panel device 400 according to the invention, with a composite comprising a plurality of groups of VACNT interlayers. Within in each group of VACNT interlayers, two interlayers 421,424; 422,423 are connected in series and can be connected to
40 a common electrical apparatus 451,461. This heating device can be carried out in two different variants.

In a first variant, both electrical apparatuses 451,461 are power generators, and can be used and tuned independently from each other.

In a second variant, one of the electrical apparatuses 451,461 is a power generator (or a channel of a power generator) and the other one is a sensing or monitoring device.

- 5 Said sensing or monitoring device is configured to measure at least one electrical parameter of at least one of the VACNT interlayers. In the framework of the present invention, said sensing or monitoring device can be connected to any of the VACNT interlayers, by using an appropriate switching circuit (not shown on the figures).

- 10 Various measurement methods can be used to detect a change in a physical property or characteristics of the composite panel device, using at least one of the conductive VACNT interlayers. In certain embodiments, this physical property or characteristics can be related to the structural health of said composite panel, and can be used to monitor the state of health of a said composite panel.

- 15 As an example, the electrical resistance and / or the impedance can be measured, and its evolution in time can be monitored. This monitoring can be carried out in particular under solicitations, such as vibration. Electrical pulses can be injected, and their response can be monitored by time-of-flight techniques or wave analysis. Local temperature measurement can be carried out by measuring the electrical resistance, and/or by an external IR camera for instance. The acoustic and / or electric coupling of adjacent layers can be measured and / or
20 monitored.

This monitoring can be done at rest, or under solicitation (vibrations for example), and/or while the workpiece is being used. Non destructive testing methods can be implemented using at least one of the conductive VACNT interlayers.

- 25 Some of these measurements can be carried out as static measurement, and/or periodically and/or as dynamic measurements. In some cases, these signals are analysed by the recognition of typical signatures.

In a variant (not shown on the figures), within each group of VACNT interlayers, said interlayers are connected in parallel.

- 30 In the framework of the present invention, NawaStitch™ composites can be used with various numbers of plies. A ply is defined as a complex comprising a fiber layer onto which a VANCT layer is provided (either by direct growth of VACNT onto said fiber layer, or by transfer from an intermediate substrate, which can be the growth substrate, onto said fiber layer). The optimum structure of the composites depends on the electrical operating parameters.

- 35 As suggested by the dots in each of figures 1 to 5, it is possible to add plies to the depicted composite structures, as may be needed, and there need not be a VANCT layer between each pair of stacked plies. As a further example, figure 6 schematically shows an embodiment with six plies; in this example, the four VACNT layers are electrically connected in parallel. On each side of the composite panel, a busbar 572,574 collects the electrical current and leads it to or from the electrical apparatus 550.

- 40 Depending on the voltage under which the composite panel device according to the invention is intended to be operated, it may be advantageous that the composite panel be held inside

an insulating envelope. Said envelope should be flexible, and should be thin, so as not to impede thermal conduction. Kapton films can be used for making this insulating envelope.

The composite panel device according to the invention can be manufactured into shaped parts. Figure 7 shows a shaped part 600 representing, for example, a heating device for use with (or as) a leading edge of an aircraft wing, made from a bent composite panel according to the invention. As mentioned in relation with figure 1, when this bent composite panel is used for a de-icing device, the upper face 602 is the external face (i.e., the face on which ice may form when the de-icing device is not heating), and the lower face 603 is the internal face, i.e., the face in contact with a structural element of the aircraft. The VACNT interlayers are concentrated in the region of thickness close to the upper face 603, as shown on figures 1 to 5.

Each extremity of the composite panel 600 has its busbar 672,674 connected to an electrical conductor 670,671 connecting the panel 600 to the electrical apparatus 650. Titanium vias 680 can be used to fix the busbar onto the panel surface.

In the framework of the present invention, for heating layers, the VACNT height is typically comprised between about 1 μm and about 100 μm , preferably between about 5 μm and about 50 μm , and more preferably between about 15 and about 25 μm . VACNT layers dedicated to measurement can have a smaller height, typically between about 1 μm and about 25 μm , and preferably between about 1 μm and about 10 μm , and more preferably between about 1 μm and about 5 μm .

In one advantageous embodiment the busbar can be a straight bar. In other embodiments the busbar can have another regular shape, or an irregular shape. As an example, the busbar can have an S shape, or a saw tooth shape.

The invention has numerous advantages compared to prior art composites. The addition of VACNT increases the electrical and thermal conductivity in the z-direction. Such panels show a more uniform heat profile. By tailoring the height of the VACNT the electrical conductivity of the panel can be adjusted to a target value. The addition of VACNT reduces the electrical power required to achieve a specific surface temperature. VACNT interlayers do not increase the weight of the structure by more than few percent. In some cases, they improve specific mechanical properties of the composite panel or part.

The method according to the invention avoids VACNT growth directly onto the prepreg, which would not be practical, as VACNT growth requires high temperatures which are not compatible with a resin-impregnated growth substrate. The method according to the invention also avoids VACNT growth directly onto the fibers or onto the fiber tissue, which would also impose certain boundary conditions to the growth process and/or to the choice of fiber material, and which would require to impregnate the growth substrate after VACNT growth with an appropriate resin.

Examples

Example 1: Flat plates

The inventors have manufactured flat composite panels according to the invention, with different numbers of plies containing VACNT layers. The voltage was controlled until the panel maximum temperature was steady at 125 °F. Voltage and current were recorded at steady state. It can be seen that the sheet resistance decreases with the number of plies.

- 5 The properties of these panels are described in table 1.

Ply count	Gage width [cm]	Gage length [cm]	Voltage [V]	Current [A]	Power at 125 °F [W]	Total resistance [Ω]	Sheet resistance [Ω/□]	Specific power at 800 V [W/cm ²]
5	20.3	18.4	106.3	0.20	21.3	532	586	3.22
5	20.3	18.4	103.9	0.23	23.9	452	498	3.79
7	20.5	18.5	76.5	0.33	25.2	232	257	7.28
6	20.5	18.5	82.4	0.26	21.4	317	351	5.32

The panels with 6 and 7 plies had a specific power at 800 V above 4.5 W/cm², which makes them particularly useful for de-icing.

Example 2: U-shaped parts

- 10 U-shaped test pieces from NawaStitch™ composite panels, simulating roughly the shape of a leading edge, have been manufactured. Two electrical contacts were provided according to the invention. Figure 7 schematically shows the shape and structure of these test pieces.

These test pieces according to the invention were cooled in a freezer to about -20 °F (about -28.9 °C), and ice was allowed to build up.

- 15 The thickness of the ice layer was about 0.082 inches (about 2.08 mm); certain areas had a thicker layer, others a thinner layer. The test pieces were removed from the freezer, and an electric current was supplied to the panel at ambient temperature. The test pieces were observed by a FLIR thermography camera.

During this test the panels had the following electrical characteristics:

- 20
- Supplied voltage: 120.5 V
 - Absorbed current: 0.92 A
 - Sheet resistance: 294 Ohms/square
 - Power dissipated: 111 W
 - Specific power: 0.18 W/cm³

- 25 The first noticeable change in ice adherence to the panel was observed after 90 seconds, and the first drops formed. Major ice separation occurred after about two minutes, and half of the ice layer broke off after four minutes. The highest value of surface temperature was determined as 19 °F (-7.2 °C) after two minutes, 82 °F (27.8 °C) after three minutes, 118 °F (47.8 °C) after four minutes, and 174 °F (78.9 °C) after 5.5 minutes.

Figure 8 shows micrographs obtained by Scanning Electric Microscopy (SEM) of a top view of VACNT arrays used for the composite panel according to the invention.

CLAIMS

1. Composite panel (1,100,200,300,400,500) formed by a stack of pre-preg sheets alternating with layers of vertically aligned carbon nanotubes (21,22,23,24; 121,122,123,124; 221,222,223,224; 321,322,323,324; 421,422,423,424; 521,4522,523,523) abridged VACNT, wherein an electrical connection element (31,32,33,34; 131,132,133,134; 231,232,233,234; 331,332,333,334; 431,432,433,434) is provided on two opposite edges of each VACNT layer.
2. Composite panel according to claim 1, wherein said electrical connection element is a sheet of metal in contact with a VACNT layer.
3. Composite panel according to claim 1 or 2, wherein each VACNT layer is sandwiched between two plies of pre-preg sheets.
4. Composite panel according to any of claims 1 to 3, wherein at least two VACNT layers are connected in series.
5. Composite panel according to any of claims 1 to 4, wherein at least two VACNT layers are connected in parallel.
6. Composite panel according to any of claims 1 to 5, wherein said panel is flat or shaped.
7. Composite panel according to any of claims 1 to 6, wherein said prepreg sheets comprise carbon fibers and a thermoset resin or a thermoplastic resin or an elastomeric resin.
8. Composite panel according to any of claims 1 to 7, wherein at least one of said VACNT layers has a height comprised between 1 μm and 100 μm .
9. Composite panel according to any of claims 1 to 8, wherein said panel comprises a first set of one or more VACNT layers of a first height, and a second set of one or more VACNT layers of a second height, said first height being comprised between about 1 μm and about 100 μm , and preferably between about 5 μm and about 50 μm , and said second height being comprised between about 1 μm and about 25 μm and preferably between about 1 μm and about 10 μm , and more preferably between about 1 μm and about 5 μm .
10. Composite panel according to any of claims 1 to 10, wherein at least one busbar (572,574; 672,674) is provided on each of two opposite edges of said panel, each busbar being connected to at least one of said electrical connection elements.
11. Composite panel device, comprising a composite panel according to any of claims 1 to 10, and further comprising electrical connection elements connecting at least two of said VACNT layers in parallel or in series, and at least one electrical apparatus (150; 251,252,253,254; 350; 451,452) connected such as to form an electrical circuit with said at least two VACNT layers, wherein said electrical apparatus is a power generator.
12. Composite panel device according to claim 11, wherein said power generator forms an electrical circuit with said first set of one or more VACNT layers of a first height.
13. Composite panel device according to any of claims 11 or 12, further comprising a further electrical apparatus which is a measurement device or sensing device.

14. Composite panel device according to claim 13, wherein said measurement device or sensing device forms an electrical circuit with at said second set of one or more VACNT layers of a second height.

15. Composite panel device according to claim 14, wherein said first height is comprised between about 1 μm and about 100 μm , and preferably between about 5 μm and about 50 μm , and said second height is comprised between about 1 μm and about 25 μm and preferably between about 1 μm and about 10 μm , and more preferably between about 1 μm and about 5 μm .

16. Shaped part (600) for mechanical construction, using a shaped composite panel according to any of claims 1 to 10.

17. De-icing system or anti-icing system for mechanical construction elements such as aircrafts, terrestrial vehicles, stairs, using a composite panel according to any of claims 1 to 10 or a shaped part according to claim 16.

18. Method for making a composite panel according to any of claim 1 to 10, or a shaped part according to claim 16, comprising the steps of:

- providing at least a first and a second prepreg sheets, a VACNT array deposited on a substrate, and at least a first and a second metallic connecting elements,
- transferring said VACNT array from said substrate to said first prepreg sheet,
- depositing said first and second metallic connecting elements at two opposite edges onto said VACNT array,
- depositing said second prepreg sheet onto said VACNT array and said metallic connecting elements,
- exerting pressure such as to form a laminated complex comprising a VACNT layer sandwiched between two prepreg sheets.

19. Method for making a composite panel according to any of claim 1 to 10, or a shaped part according to claim 16, comprising the steps of:

- providing at least a first and a second prepreg sheets, a VACNT array deposited on a substrate, and at least a first and a second metallic connecting elements,
- transferring said VACNT array from said substrate to said first prepreg sheet and said first and second metallic connecting elements,
- depositing said second prepreg sheet onto said VACNT array and said metallic connecting elements,
- exerting pressure such as to form a laminated complex comprising a VACNT layer sandwiched between two prepreg sheets.

20. Method for making a composite panel according to any of claim 1 to 10, or a shaped part according to claim 16, comprising the steps of:

- providing at least a first and a second prepreg sheets, a VACNT array deposited on a substrate, and at least a first and a second metallic connecting elements,
- depositing said first metallic connecting elements at one edge onto said first prepreg sheet,
- transferring at least said first said VACNT array from said substrate to said first prepreg sheet and said first VACNT array,
- depositing said second metallic connecting elements at an opposite edge onto said VACNT array,
- depositing said second prepreg sheet onto said VACNT array and said second metallic connecting elements,
- exerting pressure such as to form a laminated complex comprising a VACNT layer sandwiched between two prepreg sheets.

Fig. 1

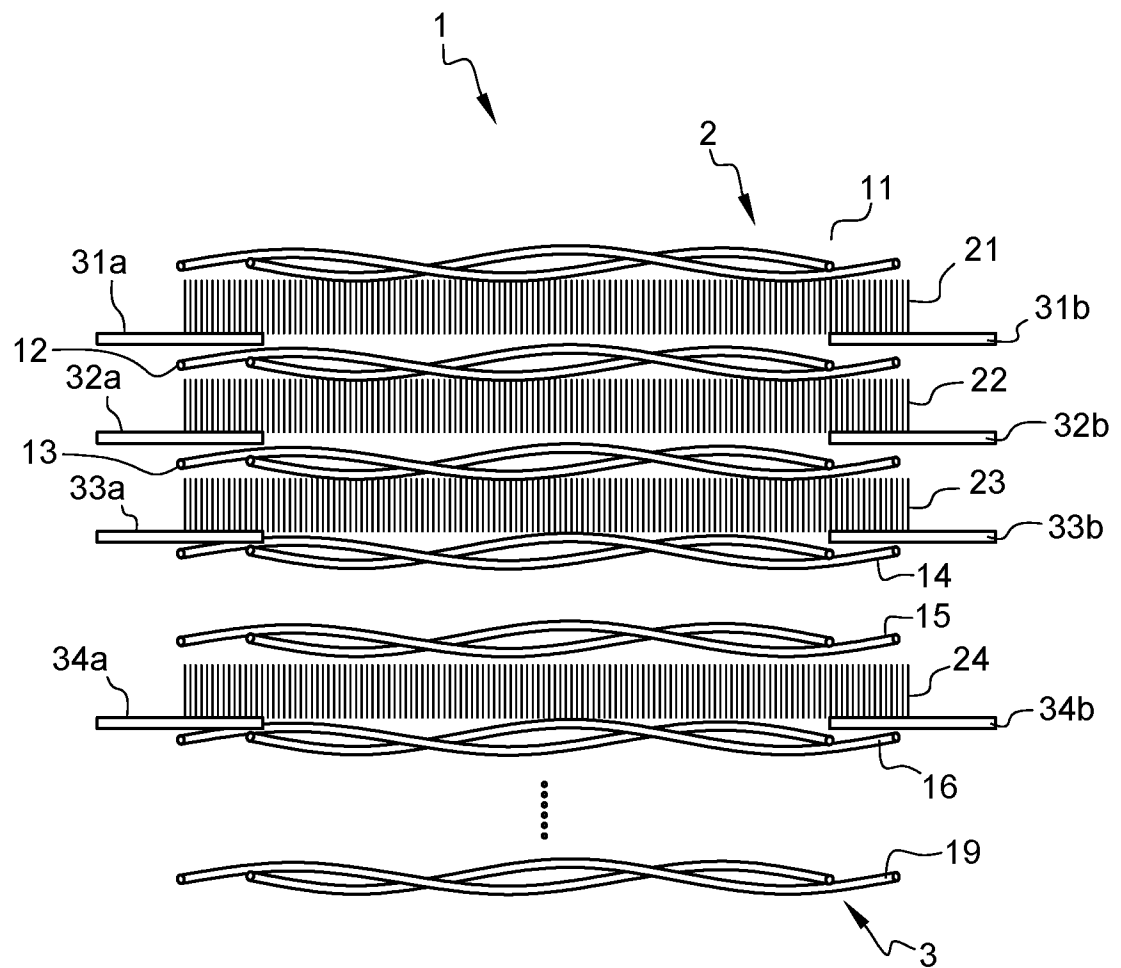


Fig. 2

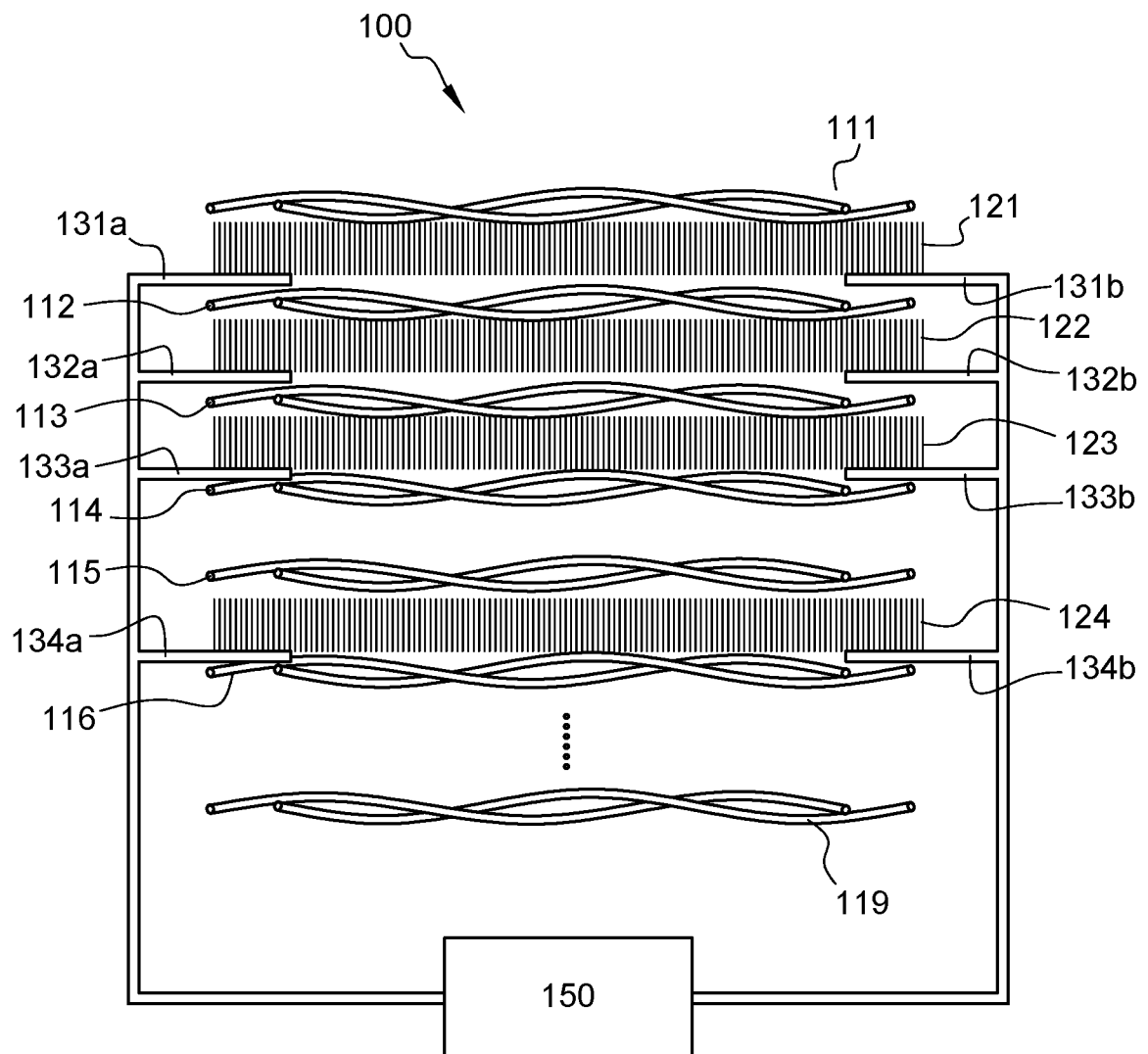


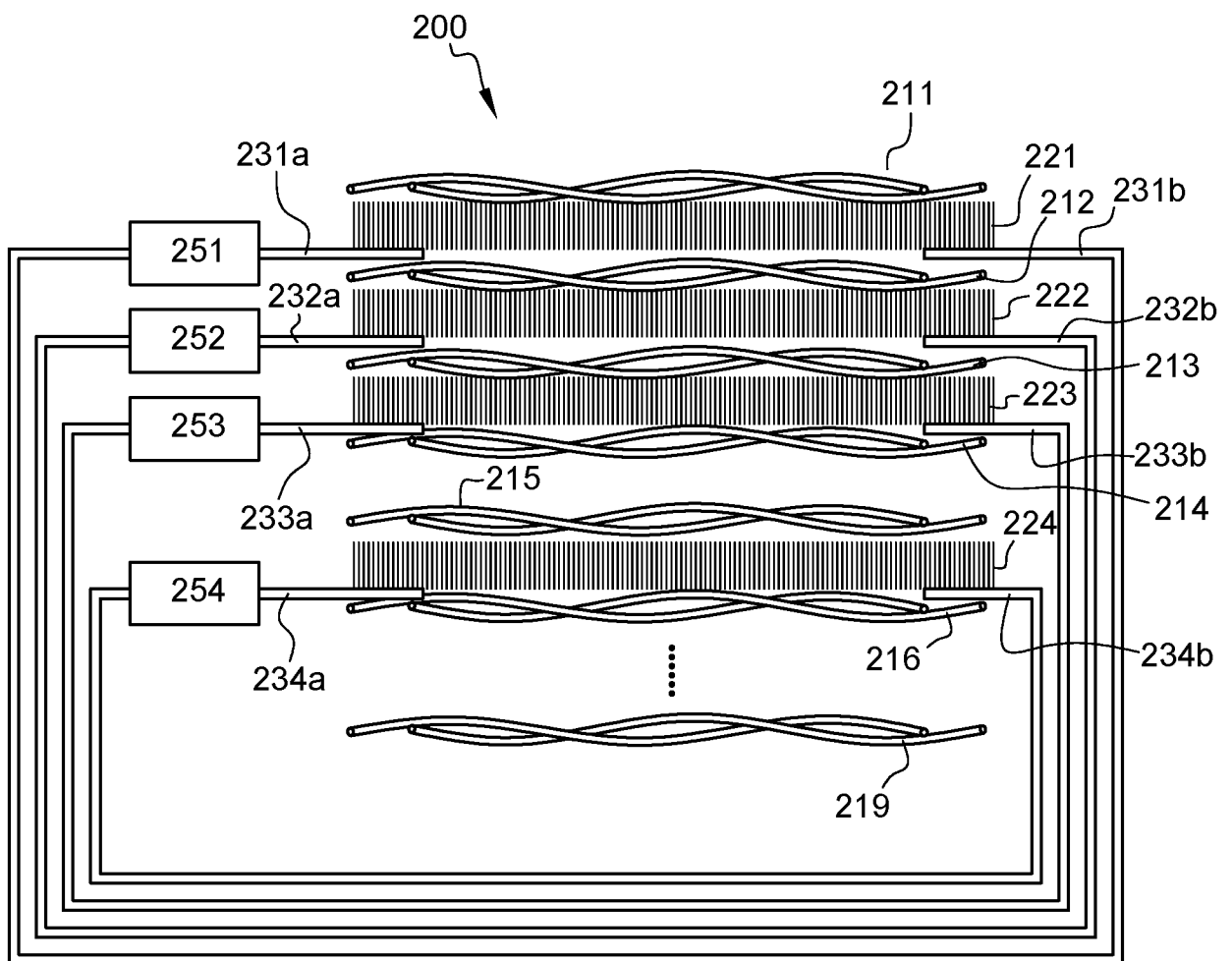
Fig. 3

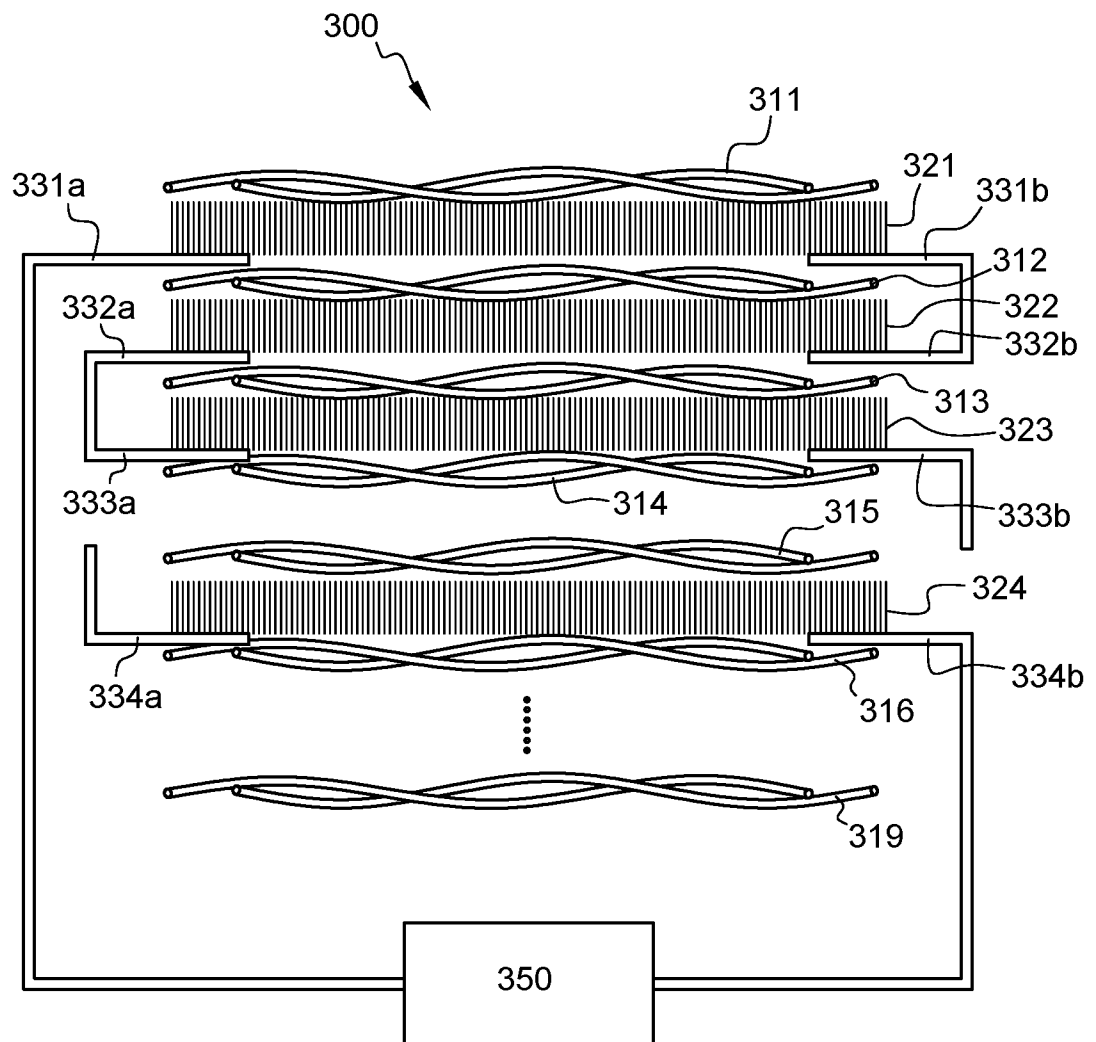
Fig. 4

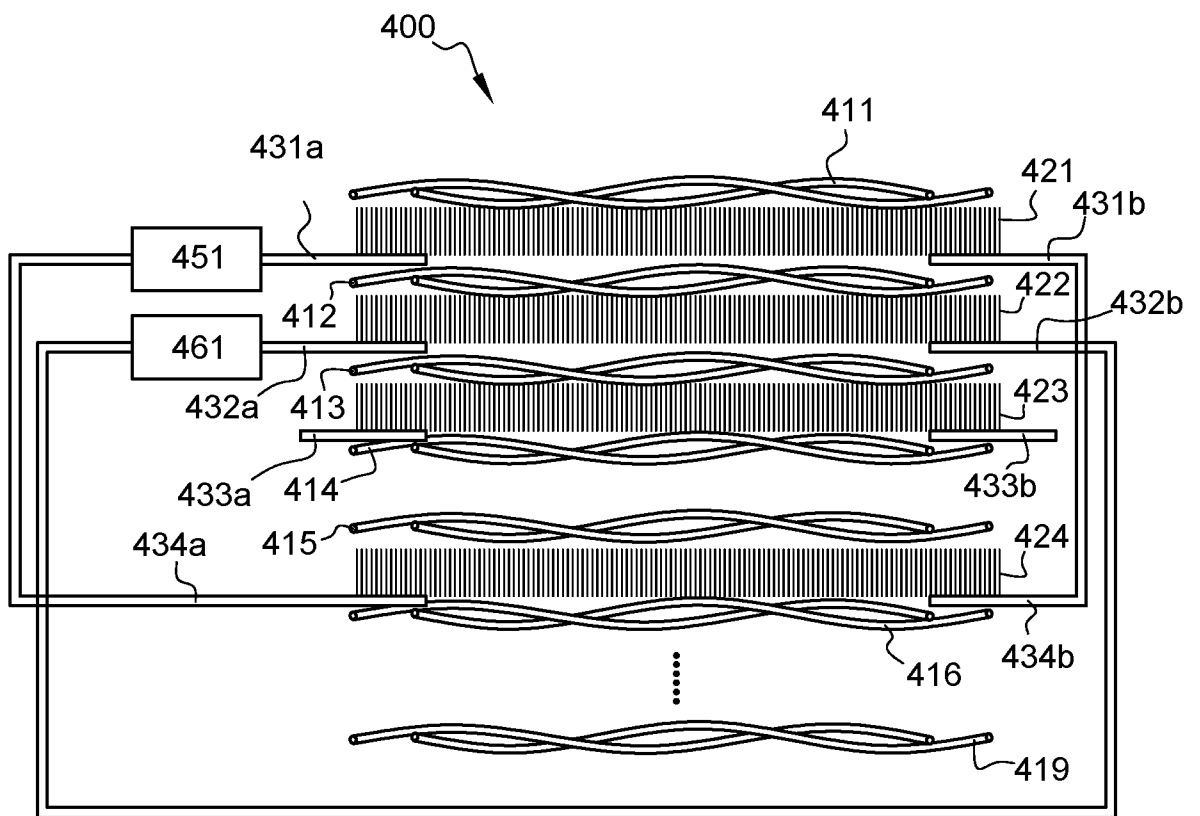
Fig. 5

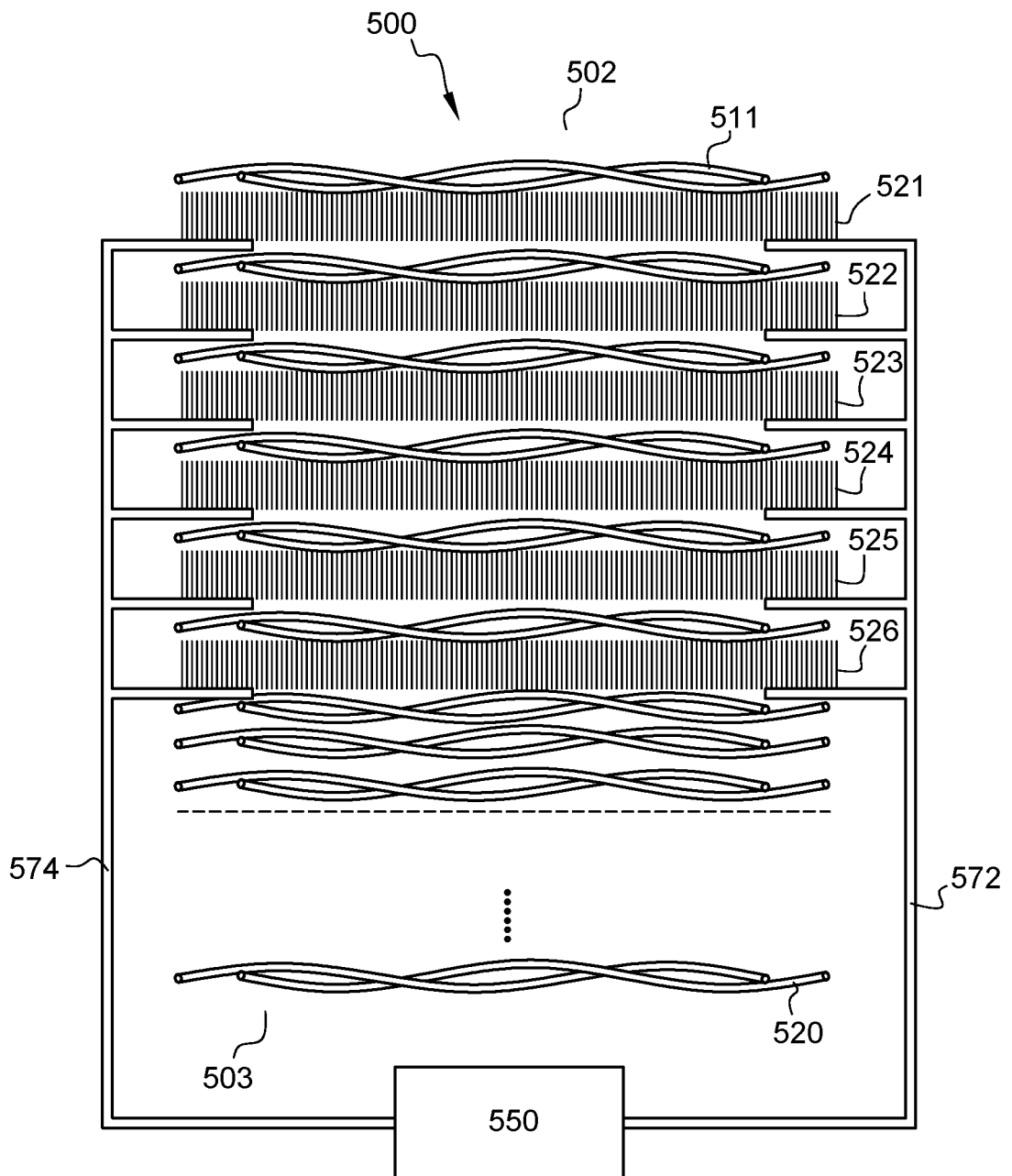
Fig. 6

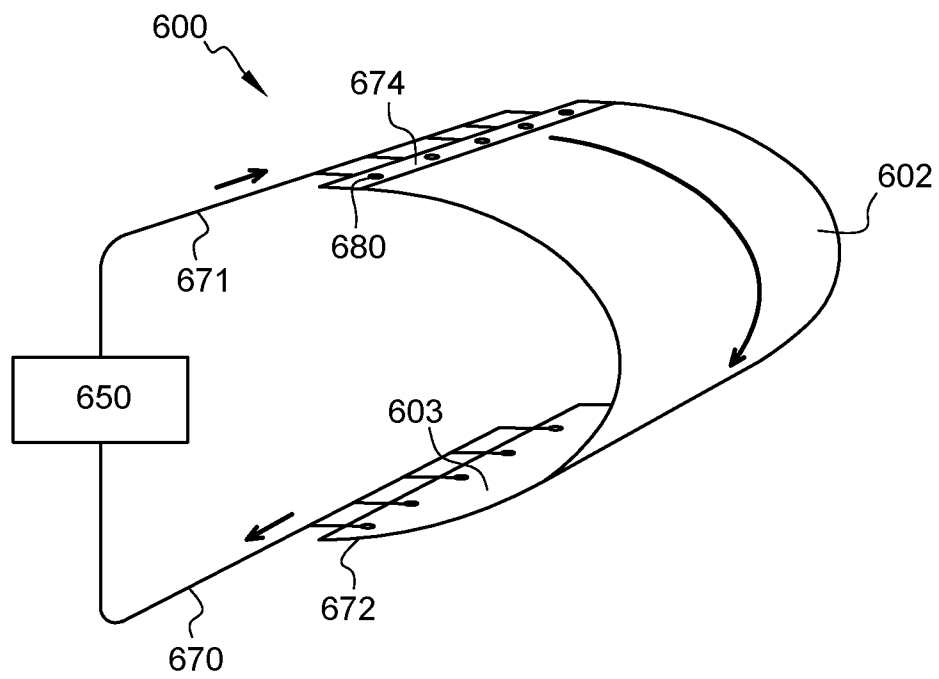
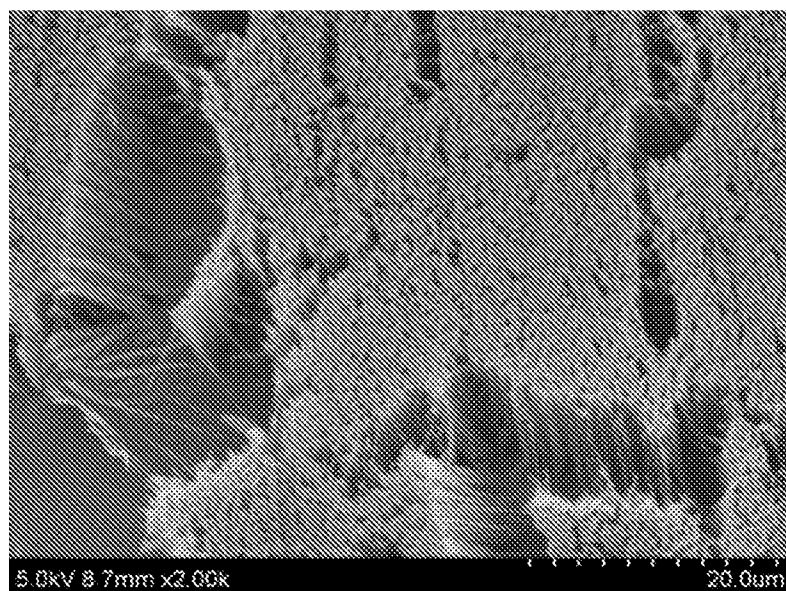
Fig. 7

Fig. 8

a)



b)

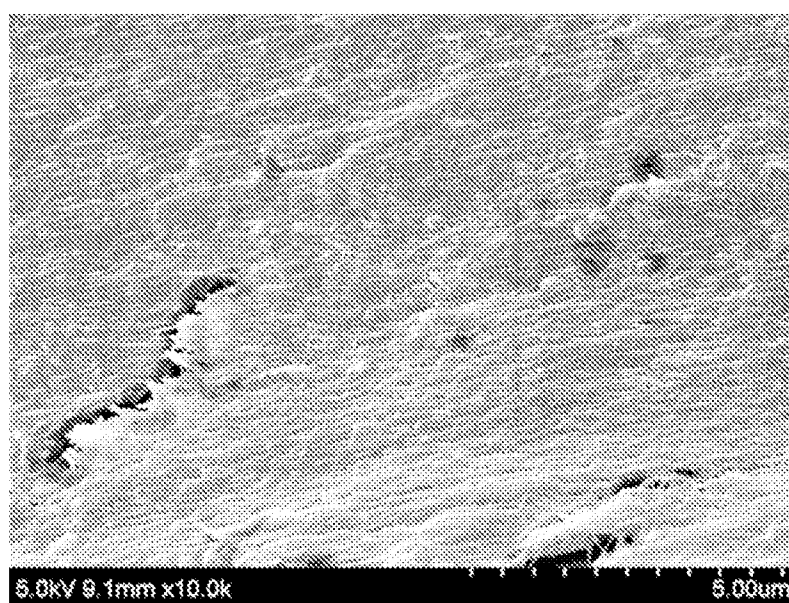
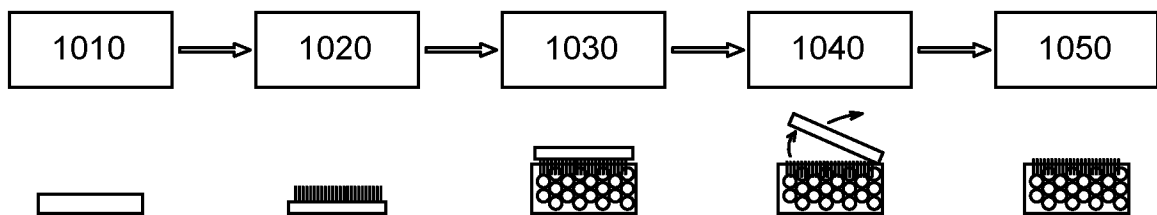
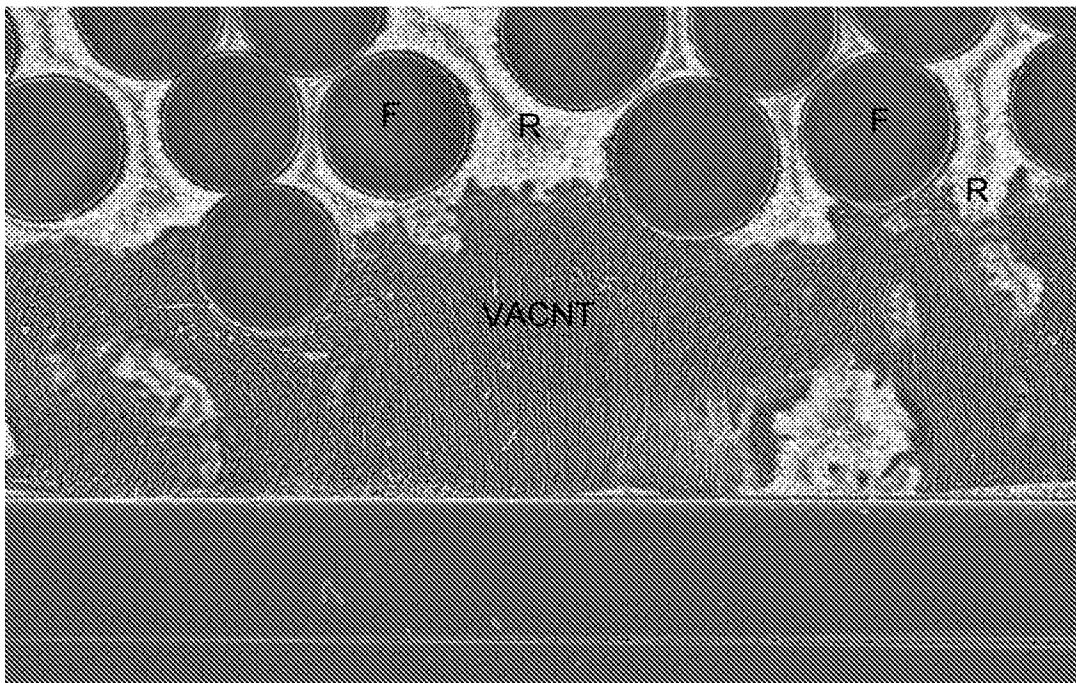


Fig. 9**Fig. 10**

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2024/055531

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	B32B1/00	B32B3/08
		B32B5/02
		B32B5/26
		B82Y30/00
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)		
B32B B82Y		
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)		
EPO - Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2017/129207 A1 (HALLANDER PER [SE] ET AL) 11 May 2017 (2017-05-11) paragraphs [0042], [0068] - [0073], [0078], [0083], [0094], [0102], [0103], [0128], [0160], [0208], [0246], [0247]; figures 2,5,9a paragraphs [0251] - [0253], [0259] - [0261] -----	1 - 20
A	US 2015/290845 A1 (HALLANDER PER [SE] ET AL) 15 October 2015 (2015-10-15) paragraphs [0026], [0038] - [0040], [0053] - [0066], [0077] - [0080], [0083], [0084]; figure 5 -----	1 - 20
A	US 2013/028744 A1 (NORDIN PONTUS [SE] ET AL) 31 January 2013 (2013-01-31) paragraphs [0074] - [0082]; figure 2g -----	1 - 20
☐ Further documents are listed in the continuation of Box C.		
☒ See patent family annex.		
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"&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
3 September 2024		10/09/2024
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 Aspeby, Erika

INTERNATIONAL SEARCH REPORT

Information on patent family members

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