(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 400 645 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
17.07.2024 Bulletin 2024/29

(21) Application number: **23151775.6**

(22) Date of filing: **16.01.2023**

(51) International Patent Classification (IPC):
D06M 11/11 *(2006.01)* ***D06M 11/28*** *(2006.01)*
D06M 11/48 *(2006.01)* ***D06M 11/56*** *(2006.01)*
D06M 13/272 *(2006.01)* ***D06M 13/352*** *(2006.01)*
D06M 13/355 *(2006.01)* ***D06M 23/06*** *(2006.01)*
D06M 23/14 *(2006.01)* ***D06M 23/16*** *(2006.01)*
D06M 11/83 *(2006.01)* ***D06M 11/50*** *(2006.01)*
D06M 15/356 *(2006.01)* ***D06M 13/256*** *(2006.01)*
D06M 15/03 *(2006.01)* ***D06M 101/16*** *(2006.01)*
D06M 101/04 *(2006.01)* ***D06M 101/10*** *(2006.01)*

(52) Cooperative Patent Classification (CPC):
D06M 11/28; D06M 11/48; D06M 11/50; D06M 11/83; D06M 13/256; D06M 15/03; D06M 15/3562; D06M 15/3566; D06M 23/06; D06M 23/14; D06M 23/16; D06M 2101/04; D06M 2101/10; D06M 2101/16

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(71) Applicant: **ETH Zurich**
8092 Zurich (CH)

(72) Inventors:
- **MENON, Carlo**
  Zürich 8001 (CH)
- **CUTHBERT, Tyler**
  8008 Zürich (CH)
- **SHOKUROV, Aleksander**
  8008 Zürich (CH)

(54) METHOD FOR PROVIDING A CONDUCTIVE POLYMER MATERIAL ON FABRIC

(57) According to the present invention there is provided a method for providing a conductive polymer material (9) on a fabric (1), the method comprising the steps of, (a) providing a fabric (1); (b) impregnate the fabric (1) with oxidant (2); (c) exposing the fabric (1) to a monomer vapor (7) so that the monomer vapor (7) reacts with the oxidant (2) impregnated in the fabric (1) to generate a conductive polymer material (9) on the fabric (1). There is further provided a fabric comprising a conductive polymer material formed using the method of the present invention.

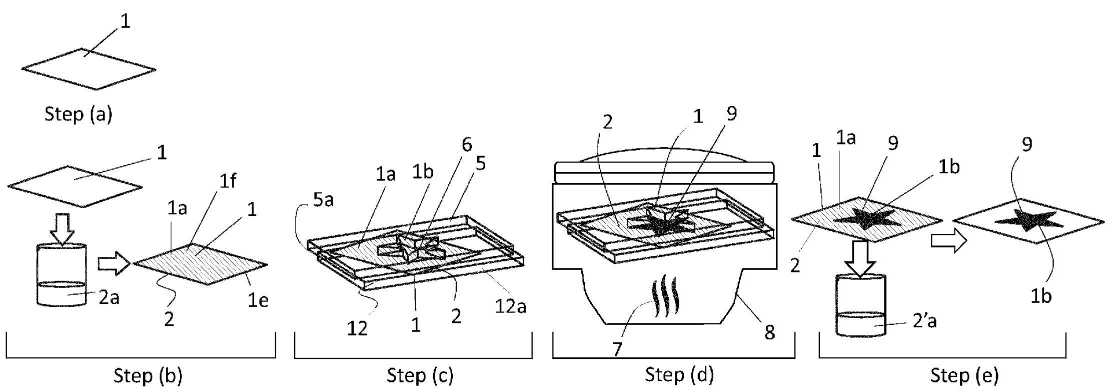

Fig. 1

EP 4 400 645 A1

Description

Field of the invention

[0001] The present invention concerns a method for providing a conductive polymer material on a fabric which involves impregnating the fabric with oxidant and then exposing the fabric to a monomer vapor.

Background

[0002] The application of conductive material to fabrics is becoming increasing important with the advent of electronic wearable garments (such as, for example, e-textiles and smart garments). Such wearable garments are provided with conductive material which, for example, may serve as a flat antenna, concentric windings, capacitors (such as interdigitated capacitors), and/or electrodes to support higher levels of integration to wearable technology devices.

[0003] However, existing methods for providing conductive material onto fabrics are inadequate. Existing methods for applying conductive material to fabrics include screen-printing and inkjet printing of conductive inks (comprising conductive carbon or polymers) on the fabric. These existing methods involve multiple complicated steps, are expensive to set up, waste large amounts of materials, and typically only work well when the conductive material/ink is applied to a flat surface of the fabric. These limitations of existing methods make them unsuitable for mass producing electronic wearable garments (such as, for example, e-textiles and smart garments).

[0004] Furthermore, the existing methods cannot be easily introduced into existing fabric manufacturing processes and are also unsuitable for applying conductive material to existing wearable garments so are not useful to adapt existing wearable garments to make them smart garments.

[0005] Also, some of existing methods used to apply conductive material to fabric do not apply the conductive material in a way to make it robust enough to withstand subsequent bending and stretching without loss of function and performance.

Summary of the invention

[0006] An aim of the present invention to obviate or mitigate at least some of the disadvantages associated with existing methods used to apply conductive material to fabric.

[0007] According to the present invention, this aim is achieved by a method having the steps recited in independent claim 1. The dependent claims recite favourable, optional, features of various embodiments of the inventions.

Brief description of drawings

[0008] Exemplary embodiments of the invention, given by way of example only, will be described in the detailed description, with reference to the following drawings in which:

Figure 1 provides an illustration of the steps involved in a method according to an embodiment of the present invention;

Figure 2 provides an illustration of the steps involved in a method according to the present invention, wherein the fabric is in the form of wearable garment (a sock), and the method involves mounting the sock on a support, and involves using a stencil which has a curved profile corresponding to a profile of a portion of an outer surface the sock;

Figure 3a shows an example of a stencil which can be used when performing the method of the present invention; Figure 3b shows another example of a stencil which can be used when performing the method of the present invention.

Detailed description of drawings

[0009] Figure 1 provides an illustration of the steps involved in method for providing a conductive polymer material 9 on a fabric 1, according to a favourable embodiment of the present invention. In this embodiment the method comprises the steps of, (a) providing a fabric 1 and (b) impregnating the fabric with oxidant 2 using any suitable means.

[0010] The fabric 1 may be woven or unwoven fabric, such as, for example, cotton, nylon, wool, paper, polyester, polyethylene any other suitable material; most preferably the fabric 1 will comprise fibres (i.e. most preferably the fabric will comprise a fibrous material). In an embodiment the fabric 1 is a wearable garment, such as pants, sweater, T-shirt, or the likes, which is to be provided with a conductive polymer material, in a predefined pattern or form (preferably a predefined 2-dimensional pattern or 2-dimensional form). Wearable garments used in the present invention, such as T-shirts, typically comprise cotton fabric; other wearable garments used in the present invention, such as leggings, typically comprise nylon fabric, or spandex fabric. Because the conductive polymer material is electrically conductive, wearable garments which have been provided with a conductive polymer material using the method of the present invention, will have electronic capabilities enabling then to be used to form smart garments.

[0011] The step (b) of impregnating the fabric 1 with oxidant may be performed using any suitable means. Preferably, the step (b) of impregnating the fabric 1 with oxidant comprises submersing the fabric 1 in an oxidant solution 2a. It should be understood that in step (b) the oxidant 2a will penetrate into the fabric 1, so that oxidant 2 which is in the oxidant solution 2a will become impregnated in the fabric 1. So, after step (b) has been performed oxidant 2 will be present both on the surface of the fabric 1 and also within the fabric 1 (i.e. between the fibres of the fabric, below the surface of the fabric).

[0012] Preferably after the fabric 1 has been submersed in the oxidant solution 2a, the fabric 1 is removed from the oxidant solution 2a and then dried. The fabric 1 may be allowed to dry passively, or, the fabric 1 may be actively dried using a dryer means (such as, a heater, a dehumidifier, or a ventilation cabinet, for example). Most preferably, the step of drying the fabric 1 is done in such a way to minimize contact with the fabric 1; contact with the fabric 1 after it has been removed from the oxidant solution 2a could result in removal of some of the impregnated oxidant 2 from the fabric 1 at the point of contact, so minimizing contact with the fabric 1 will ensure that a higher portion of the oxidant 2 will remain impregnated in the fabric 1.

[0013] For example, in one embodiment after the fabric 1 is removed from the oxidant solution 2b the fabric 1 may be positioned on a drying rack; the drying rack is preferably configured to hold (and thus contact) the fabric 1 at opposite ends 1d,1e of the fabric 1 only, so that the portion 1f of the fabric 1 which is between the opposite ends 1d,1e remain untouched by the drying rack. The fabric 1 is preferably dried using a drying rack; the drying rack preferably comprises a frame member which supports a plurality of rods, threads or wires, which are arranged to form a grid. The frame member of the drying rack may comprise any one of metal, plastic, and/or glass. Fabric 1 which is to be dried can be laid on the grid and arranged on the grid in such a way to ensure that the fabric 1 is without folds; alternatively, the fabric 1 which is to be dried can be hung over a rod, thread or wire, of the grid. The drying rack is then positioned in a well-ventilated area to allow solvent of the oxidant solution 2a to evaporate from the fabric 1; in an embodiment the fabric 1 is allowed to air dry on the drying rack for a period of time until dry. Most preferably the drying rack is arranged to hold the fabric taut over a vessel, and oxidant solution 2a drips from the fabric 1 into the vessel where it is collected and may be reused. While the fabric 1 is held on the drying rack the fabric 1 could, optionally, be exposed to an air flow so as to promote drying of the fabric 1. The fabric 1 preferably remains on the drying rack until the solvent of the oxidant solution 2a, which was absorbed into the fabric 1 when the fabric was submerged in the oxidant solution 2a in step (b), has evaporated and the fabric 1 is dry; the fabric 1 will retain the oxidant 2 on its surface and within the fabric (i.e. the oxidant 2 will be present both on the surface of the fabric 1 and also within the fabric 1 (i.e. between the fibres of the fabric, below the surface of the fabric)).

[0014] Alternatively, in another embodiment after the fabric 1 is removed from the oxidant solution 2a the fabric 1 is heated so that the fabric 1 is actively dried; for example after the fabric 1 is removed from the oxidant solution 2a the fabric 1 may be placed in a drying oven and the temperature within the drying oven is adjusted to a suitable temperature which will promote the evaporation of the solvent of the oxidant solution, from the fabric 1, thereby leaving the fabric 1 dry and with the oxidant 2 remaining on the surface of the fabric 1 and within the fabric 1. In another embodiment after the fabric 1 is removed from the oxidant solution 2a the fabric 1 is exposed to an air flow; for example after the fabric 1 is removed from the oxidant solution 2a the fabric 1 may be placed in a ventilation cabinet where the fabric 1 will be exposed to a suitable air flow which will promote the evaporation of the solvent of the oxidant solution 2a, from the fabric 1, thereby leaving the fabric 1 dry and with the oxidant 2 remaining on the surface of the fabric 1 and within the fabric 1.

[0015] In this embodiment, next, a step (c) of applying a stencil 5 (most preferably a rigid stencil) having a cut-out 6, to the fabric 1, is carried out, so that at least some part 1a of the fabric 1 is covered by the stencil 5 and at least some other part 1b of the fabric 1 is exposed through the cut-out 6 of the stencil 5.

[0016] It should be understood that the stencil 5 may take any suitable form and the cut-out 6 may take any suitable form. In the embodiment illustrated in Figure 1 (and Figure 2) the stencil 5 has a 'star-shaped' cut-out 6. In another embodiment the cut-out 6 in the stencil 5 has an interdigitated shape, as shown in Figure 3a. Using a stencil 5 which has cut-out 6 having an interdigitated shape enables the conductive polymer material 9 to be generated in a shape which will ensure that the conductive polymer material 9 will define an interdigital capacitor (having two electrodes and a dielectric separator) and/or one or more interdigitated electrodes on and within the fabric 1.

[0017] In another embodiment the cut-out 6 in the stencil 5 has a zig-zag shape (or saw-tooth shape), as shown in Figure 3b. Using a stencil 5 which has cut-out 6 having a zig-zag shape enables the conductive polymer material 9 to be generated in shape which will ensure that the conductive polymer material 9 will define an electrode with a zig-zag profile, which can be used as a strain sensor. Such a strain sensor can be used to measure the strain within the fabric 1 when the fabric 1 is stretched for example. During use, the electrical resistance of the zig-zag shaped electrode can be measured; when the fabric 1 is stretched the zig-zag shaped electrode will also be stretched together with the fabric 1; stretching of the zig-zag shaped electrode will reduce the electrical resistance of the zig-zag shaped electrode. The electrical resistance of the zig-zag shaped electrode can thus be used as an indicator of the amount of strain within the fabric 1 (caused by stretching the fabric).

[0018] In another embodiment the cut-out 6 in the stencil 5 has a shape of a circular spiral or polygonal spiral, as shown in Figure 3c. Using a stencil 5 which has cut-out 6 having a circular spiral or polygonal spiral shape enables the conductive polymer material to be generated in shape which will ensure that the conductive polymer material will define an inductive coil and/or an antenna, which can be used for wireless communication.

[0019] It should be understood that it is not essential for the stencil 5 fo have a cut-out 6; in an embodiment the stencil 5 has no cut-out 6.

[0020] In the embodiment illustrated in Figure 1, the method further comprises providing a support member 12 (preferably a rigid support member 12) and clamping the fabric 1 between the support member 12 and the stencil 5, so that the stencil 5 is held against fabric 1 with force. For example, the fabric 1 may be positioned between a support member 12 and the stencil 5 and clips, screws, or magnets, can be applied to the support member 12 and stencil 5 which apply a force to the support member 12 and the stencil 5 to cause the support member 12 and the stencil 5 to clamp the fabric 1. Preferably, the perimeter 12a of the support member 12 matches the perimeter 5a of the stencil 5 i.e. the dimensions of the perimeter 12a of the support member 12 match the dimensions of the perimeter 5a of the stencil 5. In the embodiment shown in Figure 1, the support member 12 has a rectangular shape which matches the rectangular shape of the stencil 5.

[0021] In the case fabric 1 which is to be provided with conductive polymer material 9 can be arranged in a planar profile (e.g. a sheet of fabric), then the stencil 5 which is used may have a planar profile. In the embodiment shown in Figure 1 the fabric 1 is a sheet of fabric 1 that can be arranged in a planar profile, and the stencil 5 and also the support member 12 each have a planar profile.

[0022] In case the fabric 1 which is to be provided with conductive polymer material 9 has a non-planar profile (e.g. a sleeve of a wearable garment, which has a cylindrical profile) then the stencil 5 used may have a curved profile corresponding to the profile of the surface of the fabric 1 (or corresponding to the profile of a portion of the surface of the fabric 1). If the fabric 1 which is to be provided with conductive polymer material 9 is in the form of a sock then the stencil 5 used may have a profile corresponding to the profile of a portion of a surface of the sock so as to allow the stencil 5 to fit snugly onto the sock, as illustrated in Figure 2. If the fabric 1 which is to be provided with conductive polymer material is in the form of a glove, then the stencil 5 used may have a profile corresponding to the profile of a portion of a surface of the of the glove, so as to allow the stencil 5 to fit snugly onto that portion of the surface of the glove.

[0023] In the present invention the stencil 5 may comprise any suitable material. For example, the stencil 5 may comprise any one or more of polymethylmethacrylate, and/or polylactic acid, and/or polyethylene, and/or polyether ether ketone, and/or metal (such as sheet metal), and/or stainless steel, and/or aluminium.

[0024] In an embodiment the method further comprises providing a support member 12 (preferably a rigid support member) and then positioning the fabric 1 on the support member 12 (or mounting the fabric 1 on the support member 12). For example, in the case the fabric 1 is in the form of a wearable garment, then the wearable garment is mounted onto the support member 12. The support member 12 has a suitable 3-D profile so that it can receive the wearable garment (most preferably the support member has a curved profile matching the profile of the inside of the wearable garment or, at least, matching the profile of a portion of the inside of the wearable garment). For example, the support member 12 may have a shape corresponding to a portion of the inside of a sock if the wearable garment is a sock; the support member 12 may have a cylindrical shape, corresponding to the inside of a sleeve, if the wearable garment is a sleeve of a sweater; the support member may have a shape resembling a hand, if the wearable garment is a glove. Providing a support member 12 which has a suitable 3-D profile so that it can receive the wearable garment allows for a snug fit of the wearable garment on the support member 12. In this embodiment the stencil 5 will preferably have a suitable 3-D profile so that it can be placed on at least a part of the wearable garment when the wearable garment is mounted on the support member 12. For example, the stencil 5 may have a cylindrical profile or semi-cylindrical profile if the wearable garment a sleeve of a sweater, or a sock, or a glove; in another example, the stencil 5 may have a substantially L-shaped profile with semi-cylindrical cross section, if the wearable garment is a sock. In this embodiment the method will comprise the steps of mounting the wearable garment onto the support member 12 so that the support member 12 contacts an inside surface of the wearable garment; then applying the stencil 5 onto an outer surface of the wearable garment, so that the wearable garment is sandwiched between the support member 12 and the stencil 5, the support member being in contact with the inside surface of the wearable garment and the stencil 5 being in contact with and overlaying at least portion of the outer surface of the wearable garment. This embodiment facilitates providing a conductive polymer material 9 on a surface of a fabric 1 which has a non-planar profile (e.g. surface of sleeve, sock, finger of a glove, which has a substantially cylindrical profile); in particular this embodiment facilitates providing a conductive polymer material 9 on a surface of wearable garments without having to unstitch/dismantle the wearable garments.

[0025] Referring to the embodiment illustrated in Figure 1, with the stencil 5 applied to the fabric 1, a step (d) of exposing the fabric 1 to a monomer vapor 7 so that the monomer vapor 7 reacts with the oxidant 2 impregnated in the fabric 1 to generate a conductive polymer material 9 on the fabric 1 and within the fabric 1, is carried out. In the present invention the conductive polymer material 9 which is generated on the fabric 1 and within the fabric 1, is electrically conductive. The part 1a of the fabric 1 which is covered by the stencil 5 will not be exposed to the monomer vapor 7, while the other part 1b of the fabric 1 is exposed to the monomer vapor 7 through the cut-out 6 of the stencil 5; as a result, the conductive polymer material 9 is generated only on and within the part 1b of the fabric 1 which is exposed to the monomer vapor 7 through the cut-out 6 of the stencil 5. Consequently the 2-dimensional shape of the conductive polymer material 9 which is generated only on and within the part 1b of the fabric 1, will correspond to the 2-dimensional shape of the cut-out 6 in the stencil 5. In the example shown in Figure 1 the 2-dimensional shape of the cut-out 6 is a star-shape, consequently the conductive polymer material 9 which is generated only on and within the part 1b of the fabric 1 is star-shaped (however it should be understood that the cut-out 6 could have any suitable shape).

[0026] It should be noted that when the fabric 1 is exposed to the monomer vapor 7 then the monomer vapor 7 reacts both with the oxidant 2 on the surface of the fabric 1 and also with the oxidant 2 that is within the fabric 1 (i.e. oxidant 2 that is below the surface of the fabric 1, between the fibres of the fabric 1), so that a conductive polymer material 9 is generated both on the surface of the part 1b of the fabric 1 which is exposed to the monomer vapor 7 through the cut-out 6 of the stencil 5, and, also within the fabric 1 (i.e. below the surface of the fabric, between the fibres of the fabric) of the part 1b of the fabric which is exposed to the monomer vapor 7 through the cut-out 6 of the stencil 5. In other words, the generated conductive polymer material 9 will be 3-dimensional, penetrating into the fabric 1 to below the surface of the fabric 1, but will have a 2-dimensional shape which corresponds to the 2-dimensional shape cut-out 6 of the stencil 5.

[0027] It should be understood that the monomer vapor 7 may have any suitable composition. For example, the monomer vapor 7 may be a conductive monomer vapor 7, such as pyrrole, and/or pyrrole's derivatives such as pyrrole's alkyl, and/or alkoxy, and/or hydroxyl, and/or carboxyl derivatives (e.g. 1-methylpyrrole); and/or aniline, including aniline's derivatives such as aniline's alkyl, and/or alkoxy, and/or hydroxyl, and/or carboxyl derivatives (e.g. o-aminophenol); thiophene, including thiophene's derivatives such as thiophene's alkyl, and/or alkoxy, and/or hydroxyl, and/or carboxyl derivatives (e. g. 3,4-ethylenedioxythiophene).

[0028] Preferably the monomer vapor 7 is provided by a precursor to the monomer vapor 7. A precursor to the monomer vapor 7 is a chemical compound in a solid or liquid state which can release the monomer vapor 7. The monomer vapor 7 will preferably provide a partial vapor pressure of at least 5 mmHg of a total vapor pressure of 1 atm. Most preferably the monomer vapor 7 will provide a partial vapor pressure between 5 mmHg-10 mmHg of a total vapor pressure of 1 atm. A partial vapor pressure between 5 mmHg-10 mmHg facilitates the monomer vapor to polymerize the oxidant 2 that is on and within the fabric 1, so as to form the conductive polymer material 9 on and within the fabric 1.

[0029] In an embodiment the precursor to the monomer vapor 7 releases enough monomer vapor 7 when the precursor is at 20°C (or at room temperature) so that the monomer vapor 7 will provide a partial vapor pressure between 5 mmHg-10 mmHg of a total vapor pressure of 1 atm. In another embodiment the precursor needs to be heated to a temperature which is above 20°C (or above room temperature), so that the precursor releases enough monomer vapor 7 sufficient to ensure that the monomer vapor 7 will provide a partial vapor pressure between 5 mmHg-10 mmHg of a total vapor pressure of 1 atm. Increasing the temperature of precursor to the monomer vapor 7 (i.e. heating the precursor) to a temperature which is above 20°C (or above room temperature), will increase the amount of monomer vapor 7 which the precursor provides, which in turn will increase the partial pressure of monomer vapor 7. As described above, the monomer vapor 7 may have any suitable composition (the invention is not limited to requiring the monomer vapor 7 to comprise pyrrole vapor and/or aniline vapor). The temperature to which any precursor to a suitable monomer vapor 7 should be heated to in order to provide a partial vapor pressure between 5 mmHg-10 mmHg, is known in the art.

[0030] For example, the monomer vapor 7 may comprise pyrrole; a precursor to pyrrole vapor (e.g. pyrrole in a liquid or solid state) is provided at 20°C (or at room temperature), and at this temperature the precursor provides a pyrrole vapor (monomer vapor 7) which exhibits a partial vapor pressure of 7 mmHg of a total vapor pressure of 1 atm. In another example, the monomer vapor 7 may comprise aniline; a precursor to aniline vapor (e. g. aniline in a liquid or solid state) is provided; when the precursor to aniline vapor is at 20°C (or room temperature) the aniline vapor released by the precursor provides only a partial vapor pressure of less than 1 mmHg, which is outside of the desired partial vapor pressure range between 5 mmHg-10 mmHg; accordingly the precursor to aniline vapor is preferably heated to a predefined, known, temperature which is above 20°C (above room temperature) so that the aniline vapor provided by the precursor provides a partial vapor pressure of between 5 mmHg-10 mmHg of a total vapor pressure of 1 atm. Most preferably the precursor to aniline vapor is heated to a temperature of 69°C; at a temperature of 69°C the precursor to aniline vapor provides an aniline vapor which exhibits a partial vapor pressure of 10 mmHg of a total vapor pressure of 1 atm.

[0031] In the embodiment shown in Figure 1, step (d) of exposing the fabric 1 to a monomer vapor 7 comprises placing the fabric in a chamber 8 (such as a desiccator); then closing the chamber 8, preferably so that the chamber is air-tight (i.e. the fabric is contain in an air tight chamber 8).

[0032] While the fabric 1 is contained within the closed chamber 8, the monomer vapor 7 is provided inside the chamber 8 so that the part 1b of the fabric 1 which is exposed through the cut-out 6 of the stencil 5 is exposed to the monomer vapor 7. In the preferred embodiment a precursor of the monomer vapor 7 is provided inside the chamber 8, in liquid or solid form, and this precursor provides the monomer vapor 7 within the chamber 8 (i.e. the precursor releases monomer vapor 7 into the chamber 8). In an embodiment the precursor to the monomer vapor 7 releases the monomer vapor 7 when the precursor is at 20°C (or at room temperature); in this embodiment when the temperature inside the chamber 8 is at 20°C (or at room temperature) the precursor to the monomer vapor 7 can simply be placed inside the chamber 8 and will release the monomer vapor 7 into chamber 8 without requiring any heating. In another embodiment the precursor needs to be heated to a temperature which is above 20°C (or above room temperature), before it releases a sufficient amount of the monomer vapor 7; in this embodiment the precursor to the monomer vapor 7 is first placed inside the chamber 8 and the precursor is then heated to a predefined temperature which is above 20°C (or above room temperature) while in the chamber 8, to cause the precursor to release the monomer vapor 7 into the chamber 8.

[0033] In the most preferred embodiment, the monomer vapor 7 provided inside the chamber 8 will provide a partial vapor pressure between 5 mmHg-10 mmHg of a total vapor pressure of 1 atm inside the chamber 8. As described above, the monomer vapor 7 may have any suitable composition (the invention is not limited to requiring the monomer vapor 7 to comprise pyrrole vapor and/or aniline vapor). The temperature to which any precursor to a suitable monomer vapor 7 should be heated to in order to provide a partial vapor pressure between 5 mmHg-10 mmHg, is known in the art.

[0034] For example, the monomer vapor 7 may comprise pyrrole; in this case the inside of the chamber 8 is set to be 20°C (or at room temperature); and a precursor to pyrrole vapor (in a liquid or solid state) is provided inside the chamber 8. At 20°C (or at room temperature) the precursor to pyrrole vapor releases a pyrrole vapor, which defines the monomer vapor 7, which exhibits a partial vapor pressure of 7 mmHg of a total vapor pressure of 1 atm inside the chamber 8. Thus, in this embodiment the precursor does not need to be heated. A partial vapor pressure of 7 mmHg facilitates the pyrrole vapor to polymerize the oxidant 2 that is on and within the fabric 1, so as to form the conductive polymer material 9 on and within the fabric 1. Optionally, in another embodiment, the precursor to pyrrole vapor may be heated to a temperature above 20°C; for example, the precursor to pyrrole vapor may be heated to a temperature between 20°C - 30°C.

[0035] In another example, the monomer vapor 7 may comprise aniline; in this case a precursor to aniline vapor (in a liquid or solid state) is provided inside the chamber 8; the precursor to aniline vapor is preferably heated to a temperature of 69°C; at a temperature of 69°C the precursor to aniline vapor provides an aniline vapor which exhibits a partial vapor pressure of 10 mmHg of a total vapor pressure of 1 atm inside the chamber 8. A partial vapor pressure of 10 mmHg facilitates the aniline vapor to polymerize the oxidant 2 that is on and within the fabric 1, so as to form the conductive polymer material 9 on and within the fabric 1. Optionally, in another embodiment, the precursor to aniline vapor may be heated to a temperature above 69°C; for example, the precursor to aniline vapor may be heated to a temperature between 70°C -180°C.

[0036] In another example, the monomer vapor 7 which in the chamber 8 is 3,4-ethylenedioxythiophene vapor; in this case a precursor to 3,4-ethylenedioxythiophene vapor (in a liquid or solid state) is provided inside the chamber 8; then the precursor to 3,4-ethylenedioxythiophene vapor is heated to a temperature in the range 150°C -300°C to provide a 3,4-ethylenedioxythiophene vapor which has a sufficiently high partial vapor pressure of the total vapor pressure inside the chamber 8, to facilitate the 3,4-ethylenedioxythiophene vapor to polymerize the oxidant 2 that is on and within the fabric 1, so as to form the conductive polymer material 9 on and within the fabric 1.

[0037] When the precursor releases the monomer vapor 7 the part 1b of the fabric 1 which is exposed through the cut-out 6 of the stencil 5 is exposed to the monomer vapor 7 inside the chamber 8. The monomer vapor 7 will polymerize the oxidant 2 that is on and within the part 1b of the fabric 1, so as to form the conductive polymer material 9 on and within the part 1b of the fabric 1. A partial vapor pressure between 5 mmHg-10 mmHg facilitates the monomer vapor to polymerize the oxidant 2.

[0038] In another embodiment, the method comprises providing a vacuum within the chamber 8. Most preferably the method comprises providing a vacuum within the chamber 8 so as to remove all gases and vapours from inside the chamber 8 so that the monomer vapor 7 is the only vapor inside the chamber. The precursor of the monomer vapor 7 is provided inside the chamber 8. Since all gases and vapour were removed from the chamber 8 by the vacuum, the only vapor in the chamber 8 is the monomer vapor 7 which is provided by the precursor of the monomer vapor 7. Consequently, all of the vapor pressure inside the chamber 8 will be provided solely by the monomer vapor 7 since there are no other gases or vapours within the chamber 8 to contribute to the total vapor pressure within the chamber 8. This embodiment can remove the need to heat the precursor to the monomer vapor 7 to achieve a monomer vapor pressure which will facilitate the monomer vapor 7 to polymerize the oxidant 2 that is on and within the fabric 1, so as to form the conductive polymer material 9 on and within the fabric 1. For example, if the precursor to aniline vapor (in a liquid or solid state) is provided inside the chamber 8 which has had all gases and vapour removed by vacuum, then the precursor to aniline vapor will provide aniline vapor which provides a vapor pressure of 10 mmHg inside the chamber, without the need to heat the precursor; a vapor pressure of 10 mmHg facilitates the aniline vapor to polymerize the oxidant 2 that is on and within the fabric 1, so as to form the conductive polymer material 9 on and within the fabric 1.

[0039] In another embodiment, the method comprises decreasing the pressure within the chamber 8 so as to reduce the temperature to which a precursor to the monomer vapor 7 needs to be heated to provide sufficient amount of monomer vapor 7 inside the chamber 8, so that monomer vapor 7 provides a partial vapor pressure between 5 mmHg-10 mmHg of a total vapor pressure of 1 atm inside the chamber 8. Most preferably the method comprises decreasing the pressure within the chamber 8 so that the pressure within the chamber 8 is less than 1atm. In this embodiment the pressure within the chamber 8 is decreased and the precursor is heated to provide sufficient monomer vapor 7; the decreased pressure within the chamber 8 reduces the temperature to which the precursor of the monomer vapor 7 needs to be heated to in order to achieve a monomer vapor pressure which will facilitate the monomer vapor 7 to polymerize the oxidant 2 that is on and within the fabric 1, so as to form the conductive polymer material 9 on and within the fabric 1. In this embodiment the temperature which a precursor to the monomer vapor 7 needs to be heated to depends on the composition of the precursor and also on the pressure inside the chamber 8; typically, the more the pressure inside the chamber 8 is decreased the lower the temperature to which the precursor will need to be heated to in order to provide a suitable amount of monomer vapor 7 within the chamber 8. In this embodiment, the pressure inside the chamber 8 should be decreased to a level, and the precursor of the monomer vapor 7 heated to a temperatures, which is sufficient to cause the precursor to provide a sufficient amount of monomer vapor inside the chamber 8 so that the monomer vapor pressure inside the chamber 8 is sufficient to facilitate the monomer vapor 7 to polymerize the oxidant 2 that is on and within the fabric 1, so as to form the conductive polymer material 9 on and within the fabric 1.

[0040] After the fabric has been exposed to a monomer vapor 7 (more specifically after the part 1b of the fabric 1 has been exposed to the monomer vapor 7 inside the chamber 8), the method preferably, comprises a step (e) of retrieving the oxidant 2 that is impregnated in the part 1a of fabric 1, which was covered by the stencil 5, for reuse. The step (e) of retrieving the oxidant 2 may be done using any suitable means. In the embodiment shown in Figure 1 the step (e) of retrieving the oxidant 2 comprises submersing the fabric 1 in a suitable solvent 2a'; when the fabric is submersed in a suitable solvent 2a' the oxidant 2 that is on and within the part 1a of fabric 1 will dissolve in the solvent 2a', to form an oxidant solution 2a. Suitable solvents 2a' include, but are not limited to, methanol, and/or ethanol, and/or water, and/or any combination of one or more of said aforementioned; most preferably the solvent 2a' comprises methanol. Most preferably the solvent 2a' which is used will depend on the chemical characteristics of the oxidant 2 which is impregnated in the part 1a of fabric 1 (i.e. the solvent 2a' which is used will depend on the chemical characteristic of the oxidant 2 which is to be retrieved from the part 1a of fabric 1); for example methanol, acetone, isopropyl alcohol can be used as solvent to dissolve $FeCl_3$ oxidant; in another example water can be used as a solvent; water is a cheaper and environmentally friendly solvent 2a'. Most preferably the method involves moving (stirring and/agitating), manually and/or using suitable mechanical means, the fabric 1 when it is submersed in the solvent 2a' so as to promote the movement of the oxidant 2 from the part 1a of fabric 1 into the solvent 2a'.

[0041] After the fabric 1 has been submersed in the solvent 2a' so that the oxidant 2 that is on and within the part 1a of fabric 1 has dissolved in the solvent 2a' to form an oxidant solution 2a, the method may further comprise heating said oxidant solution 2a, so that some of the solvent evaporates, to bring the oxidant solution 2a to a predefined oxidant concentration. Evaporating the solvent will increase the oxidant concentration of the oxidant solution 2a.

[0042] In an embodiment, like the embodiment illustrated in Figure 1, in which step (b) of impregnating the fabric 1 with oxidant preferably comprises submersing the fabric 1 in an oxidant solution 2a, the step (e) of retrieving the oxidant 2 comprises submersing the fabric 1 in the same solution 2a as was used in step (b); the oxidant 2 will move out of the part 1a of the fabric 1 and into the oxidant solution 2a thereby increasing the concentration of oxidant in the oxidant solution 2a. After the oxidant has been retrieved back into the oxidant solution 2a (i.e. after step (e) is completed) the resulting oxidant solution 2a forms an oxidant solution 2a which can be reused (e.g. for performing another step (b)). Reusing the oxidant solution 2a will reduce waste. Optionally after the oxidant 2 has been retrieved out of the part 1a of the fabric 1 and back into the oxidant solution 2a (that was used in step (b)) the oxidant solution 2a may then be heated, so that some of the solvent evaporates, to bring the oxidant solution 2a to a predefined oxidant concentration before the oxidant solution 2a is reused; most preferably, the oxidant solution 2a is heated to bring the oxidant solution 2a to the same oxidant concentration as the concentration the oxidant solution 2a initially had, prior to submersing the fabric 1 in the oxidant solution 2a in the step (b). Evaporating the solvent will increase the oxidant concentration of the oxidant solution 2a.

[0043] In an embodiment the conductive polymer material 9 may be doped. Doping the conductive polymer can be done by any suitable means. For example, in one embodiment the method further comprises a step of adding dopant to the oxidant solution 2a before submersing the fabric 1 in the oxidant solution 2a in step (b). Then when step (b) is carried out the fabric 1 is submersed in the doped oxidant solution; the fabric 1 will thus be impregnated with both oxidant 2 and dopant. Subsequently, when step (d) is carried out (wherein the monomer vapor 7 reacts with the oxidant impregnated in the fabric) the dopant will be present in the generated conductive polymer material 9; so step (d) will result in a doped conductive polymer material 9 being generated on and within the fabric 1.

[0044] In another example the method comprises doping the conductive polymer material 9 with a dopant after it has been generated on and within the fabric 1. In other words, after step (d) has been carried out, the method may further comprise a step of doping the conductive polymer material 9 with a dopant. The conductive polymer material 9 may be doped using any suitable means. For example, the method may further comprise providing a solution which comprises the dopant (i.e. providing a dopant solution); then after the conductive polymer material 9 has been generated on and within the fabric 1 (e. g. after step (d) has been carried out), then submersing the conductive polymer material 9 which is on and within the fabric 1 in said dopant solution. When the conductive polymer material 9 is submersed in the dopant solution the dopant which is in the solution will be absorbed into the conductive polymer material 9 to dope conductive polymer material 9.

[0045] It should be understood that the dopant used in any of the embodiments of the present invention may take any suitable form. The dopant is preferably a material that will improve predefined properties of the conductive polymer material 9 which is generated on and within the fabric 1. For example, the dopant may comprise, any one or more of, p-toluene sulfonate, chondroitin sulfate, dodecylbenzenesulfonate, anthraquinone sulfonate, camphorsulfonic acid.

[0046] It should be understood that the use of an stencil 5 is not essential to the present invention i.e. the step (c) of applying a stencil 5 having a cut-out 6, to the fabric 1, is not essential to the present invention (and it follows that any subsequent steps relating to the stencil 5 of the above mentioned embodiments, are also not essential to the present invention). In the above-mentioned embodiment, illustrated in Figure 1, the stencil 5 is used to restrict the parts of the fabric which are provided with conductive polymer material 9 and/or to ensure that the conductive polymer material 9 will have a predefined 2-dimensional form/shape on the fabric 1. However, if for example the whole of the fabric 1 (or the whole of a section of a fabric 1) is to be provided with conductive polymer material 9 then there is no need to use a stencil 5 and thus there is no need to perform a step (c) of applying a stencil 5 having a cut-out 6, to the fabric 1. If, for example, the fabric 1 is to be provided with conductive polymer material 9 in any form/shape then, again in this scenario, there is no need to use a stencil 5 and thus there is no need to perform a step (c) of applying a stencil 5 having a cut-out 6, to the fabric 1.

[0047] In yet another variation of the invention the stencil 5 which is used in step (c) has no cut-out 6. In this embodiment the stencil 5 will be arranged to cover some part of the fabric 1 leaving another part of the fabric exposed. In this embodiment the conductive polymer material 9 will be provided on the exposed part of the fabric 1.

[0048] In yet another embodiment the stencil 5 may comprise a plurality of mechanically independent pieces which can be individually applied to the surface of the fabric 1. In this embodiment the method may further comprise a step of arranging the plurality of pieces in a predefined pattern on the fabric 1. In this embodiment the conductive polymer material 9 will be provided on the part(s) of the fabric 1 which are not covered by any of the plurality of pieces.

[0049] It should be understood that the monomer vapor 7 used in any of the embodiments of the present invention may comprises one or more of, either pyrrole, aniline, thiophene, and/or any derivatives of the aforementioned compounds, such as, for example, pyrrole, including its alkyl, alkoxy, hydroxyl, carboxyl derivatives (e.g. 1-methylpyrrole); aniline, including its alkyl, alkoxy, hydroxyl, carboxyl derivatives (e.g. o-aminophenol); thiophene, including its alkyl, alkoxy, hydroxyl, carboxyl derivatives (e.g. 3,4-ethylenedioxythiophene).

[0050] It should be understood that the oxidant 2 used in any of the embodiments of the present invention may comprise one or more of, ferric chloride, ammonium persulfate, ammonium dichromate, chloroauric acid, potassium permanganate, iron(III) salts of p-toluenesulfonic acid, dodecylbenzenesulfonic acid, 4-morpholinepropanesulfonic acid, 3-pyridinesulfonic acid.

[0051] A further advantage of the method of the present invention is that it can be used to provide a conductive polymer material on a fabric which has a non-planar profile. The method of the present invention can thus be used to provide a conductive polymer material directly on to any part of an existing wearable garment without the need to unstitch/dismantle the garment. For example, the method of the present invention can thus be used to provide a conductive polymer material directly on to a sock, sweater/pullover, sleeve, or glove for example, without having to unstitch/dismantle the sock, sweater/pullover, sleeve, or glove. In another example the method of the present invention can be used to provide a conductive polymer material directly on finger portion of a glove, which has a cylindrical profile, without having to unstitch/dismantle the finger portion of the glove to make a finger portion into a planar profile. As a result the method of the present invention can easily be incorporated into existing wearable textile manufacturing processes because it does not require any adaptation of the existing manufacturing steps, rather the method of the present invention is an add-on which can be used when it is desired to transform the already manufactured wearable textiles into wearable textiles with electronic capability (e.g. to form smart wearable textiles).

[0052] Figure 2 illustrates a method of the present invention used to provide a conductive polymer material 9 on a fabric 1 in the form of a sock 1. The method illustrated in Figure 2 is similar to the method illustrated in Figure 1 and like features are awarded the same reference numbers.

[0053] In the method illustrated in Figure 2, the stencil

5 used has a profile which corresponds to the profile of an outside surface 20 of the sock 1. In this example the stencil 5 used has a substantially L-shaped profile with a substantially semi-cylindrical cross section corresponding to the profile of an outside surface 20 of the sock 1. The support member 12 has a shape corresponding to the profile of an inside surface of the sock 1.

[0054] The step (c) comprise mounting the sock onto the support member 12 so that the support member 12 contacts an inside surface of the sock 1; in this particular example the support member 12 is pushed inside the sock 1 so that the support member 12 contacts an inside surface of the sock 1. The size of the support member 12 is preferably substantially equivalent to the volume inside the sock 1, so that when the support member 12 will fit snugly inside the sock when the support member 12 is pushed inside the sock 1.

[0055] The stencil 5 is then applied to the outer surface 20 of the sock so that the sock is sandwiched between the support member 12 and the stencil 5, the support member 12 being in contact with the inside surface of the sock 1 and the stencil 5 being in contact with and overlaying at least part of the outer surface 20 of the sock 1.

[0056] The methods of the present invention may be used to form a wearable textile capacitor. Preferably, in order to form a wearable textile capacitor, the fabric which is used when performing the steps of any of the above-mentioned embodiments, is a wearable garment; and the stencil 5 which is used a has cut-out 6 having an interdigitated shape.

[0057] The methods of the present invention may be used to form a wearable textile strain sensor. Preferably, in order to form a wearable textile strain sensor, the fabric which is used when performing the steps of any of the above-mentioned embodiments, is a wearable garment; and the stencil 5 which is used a has cut-out 6 having a zig-zag shape (or saw-tooth shape).

[0058] The methods of the present invention may be used to form a wearable antenna and/or induction coil. Preferably, in order to form a wearable antenna and/or induction coil, the fabric which is used when performing the steps of any of the above-mentioned embodiments, is a wearable garment; and the stencil 5 with the cut-out 6 in form of a circular spiral or polygonal spiral. Providing a wearable garment with an antenna will enable wireless communication between the wearable garment and another electronic device (such as a mobile device, like, for example, a smart watch or smart phone, or the likes).

[0059] Various modifications and variations to the described embodiments of the invention will be apparent to those skilled in the art without departing from the scope of the invention as defined in the appended claims. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiment

Claims

1. A method for providing a conductive polymer material (9) on a fabric (1), the method comprising the steps of,

(a) providing a fabric (1);
(b) impregnate the fabric (1) with oxidant (2);
(c) exposing the fabric (1) to a monomer vapor (7) so that the monomer vapor (7) reacts with the oxidant (2) impregnated in the fabric (1) to generate a conductive polymer material (9) on the fabric (1).

2. A method according to claim 1 further comprising a step of applying a stencil to the fabric, so that the conductive polymer material is generated only in the part of the fabric which is not covered by the stencil.

3. A method according to claim 2 wherein the stencil has a cut-out, so that the conductive polymer material is generated on the part of the fabric which is exposed through the cut-out of the stencil, and no conductive polymer material is generated on the part of the fabric which is coved by the stencil.

4. A method according to claim 3 wherein the cut-out is an interdigitated shape or a zig-zag shape.

5. A method according to any one of claims 2-4 wherein the stencil has a curved profile.

6. A method according to any one of claims 2-5 further comprising providing a support member in contact with a first surface of the fabric, and providing the stencil in contact with a second, opposite, surface of the fabric, so that the fabric is located between the support member and stencil.

7. A method according to any one of the preceding claims wherein step (b) comprises submersing the fabric in an oxidant solution.

8. A method according to claim 7 wherein the oxidant solution further comprises a dopant.

9. A method according to claim 7 or 8 further comprising the step of drying the fabric after it has been removed from the oxidant solution.

10. A method according to any one of the preceding claims comprising a step of retrieving oxidant which has not reacted with the monomer vapor, for reuse.

11. A method according to claim 10, wherein step (b) comprises submersing the fabric in an oxidant solution, and wherein the step of retrieving the oxidant comprises submersing the fabric in the same solution which was used in step (b).

12. A method according to claim 11, after the fabric has been submersed in the same solution which was used in step (b), removing the fabric from said solution, and then evaporating some of the solvent of the solution so as to bring the oxidant solution to a predefined oxidant concentration.

13. A method according to any one of the preceding claims further comprising the step of submersing the conductive polymer material which was generated on the fabric in a dopant solution.

14. A method according to any one of the preceding claims wherein the fabric is a wearable garment.

15. A fabric comprising a conductive polymer material which has been formed using a method according to any one of claims 1-14.

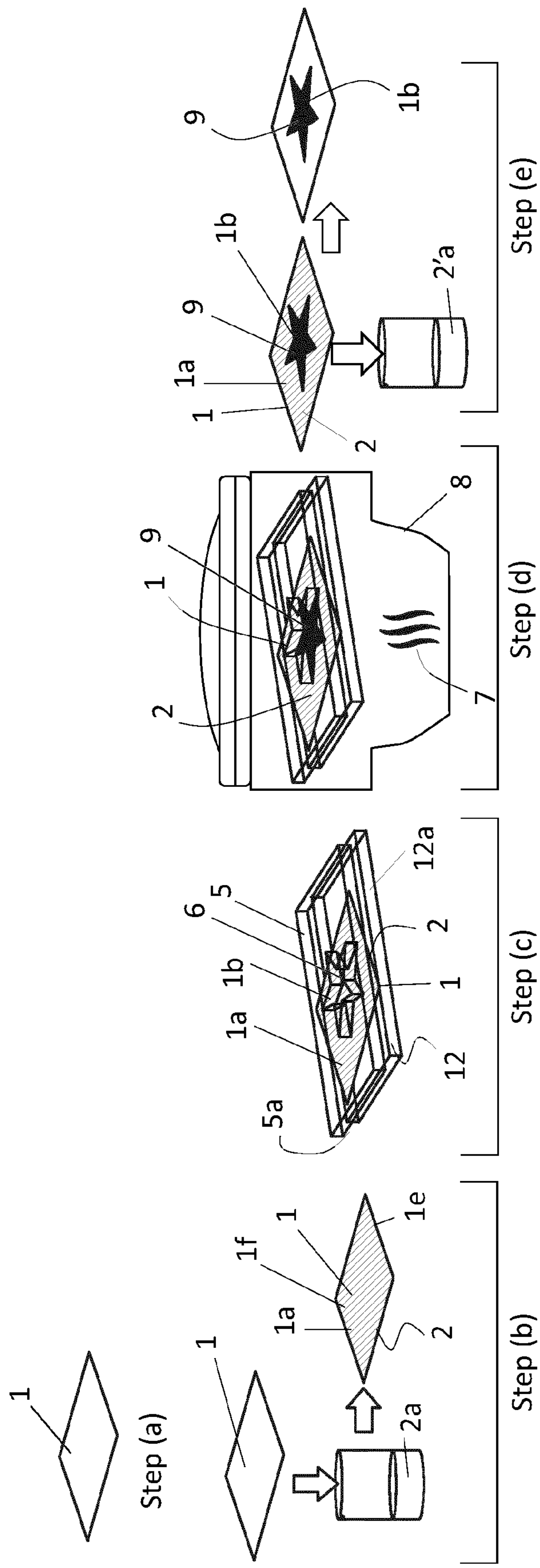
1
Step (a)
1
2a
1a
1f
1
1e
2
Step (b)
5a
1a
1b
6
5
12
1
2
12a
Step (c)
2
1
9
7
8
Step (d)
1
1a
9
1b
2
2'a
9
1b
Step (e)

Fig. 1

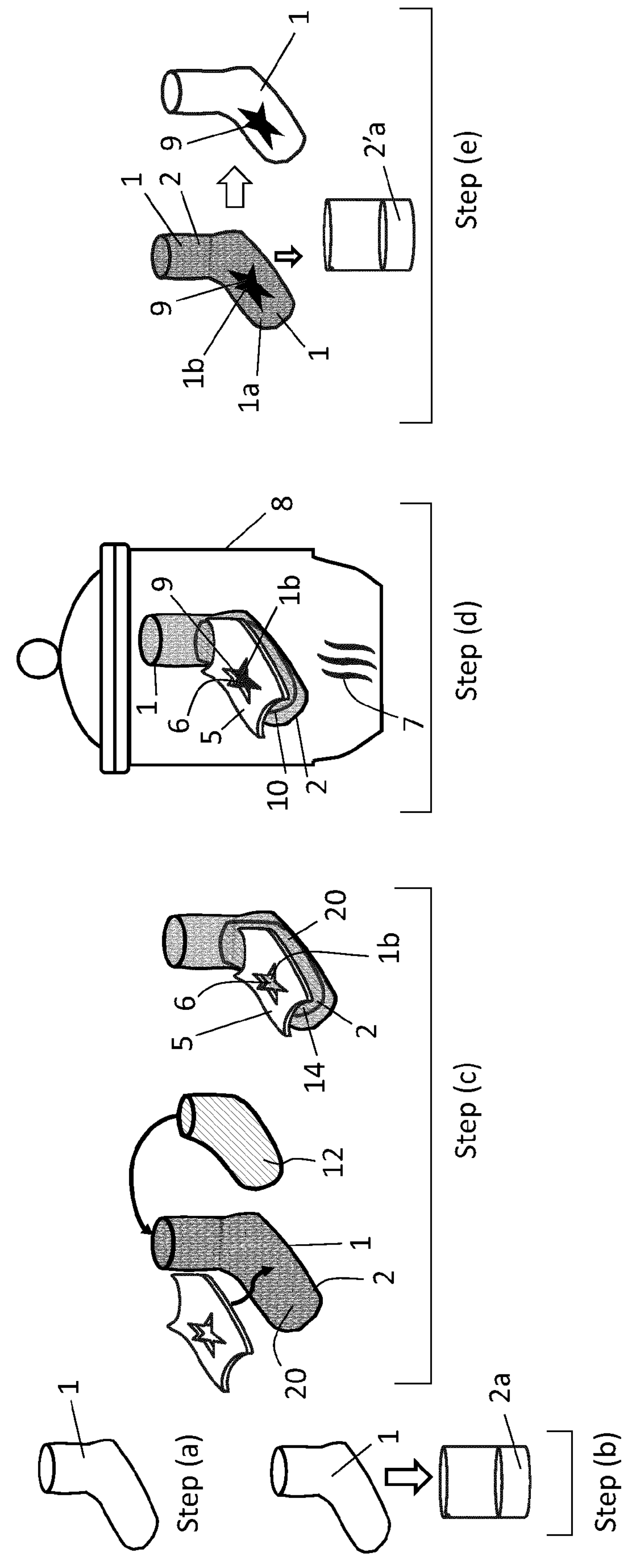

Fig. 2

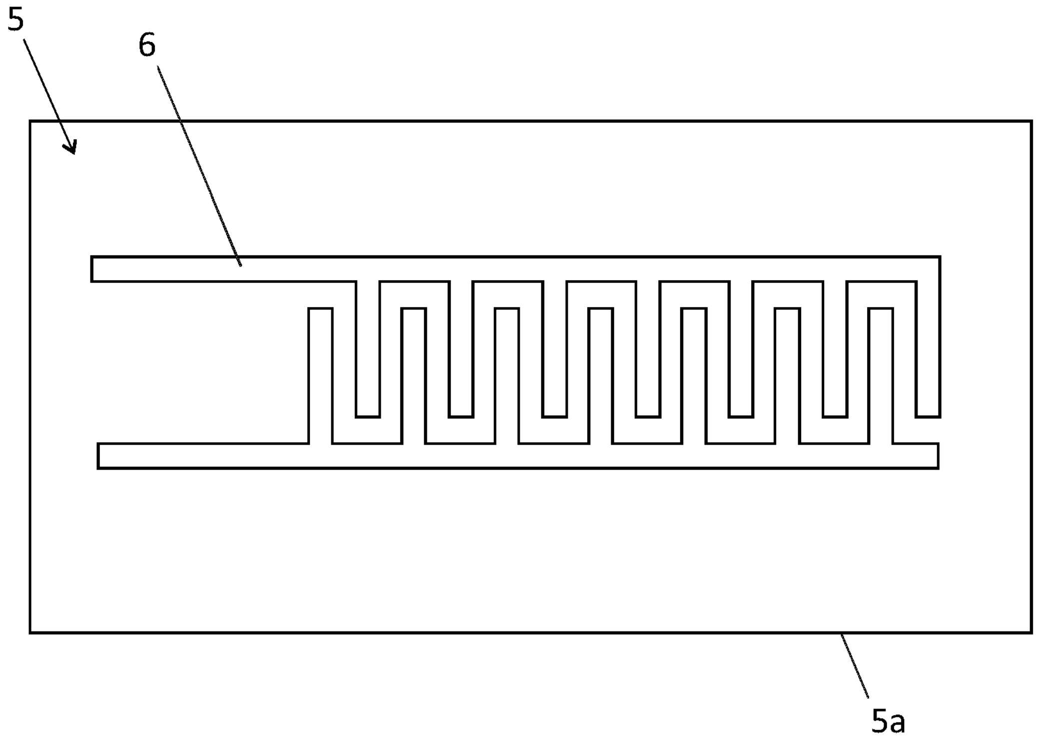

Fig. 3a

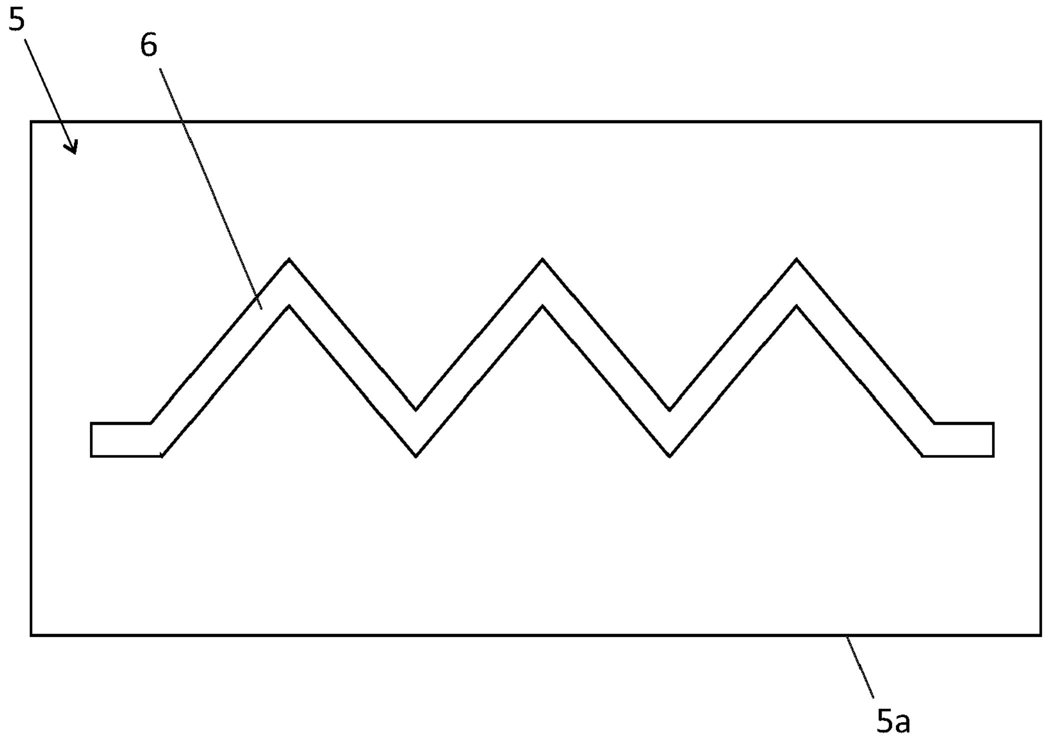

Fig. 3b

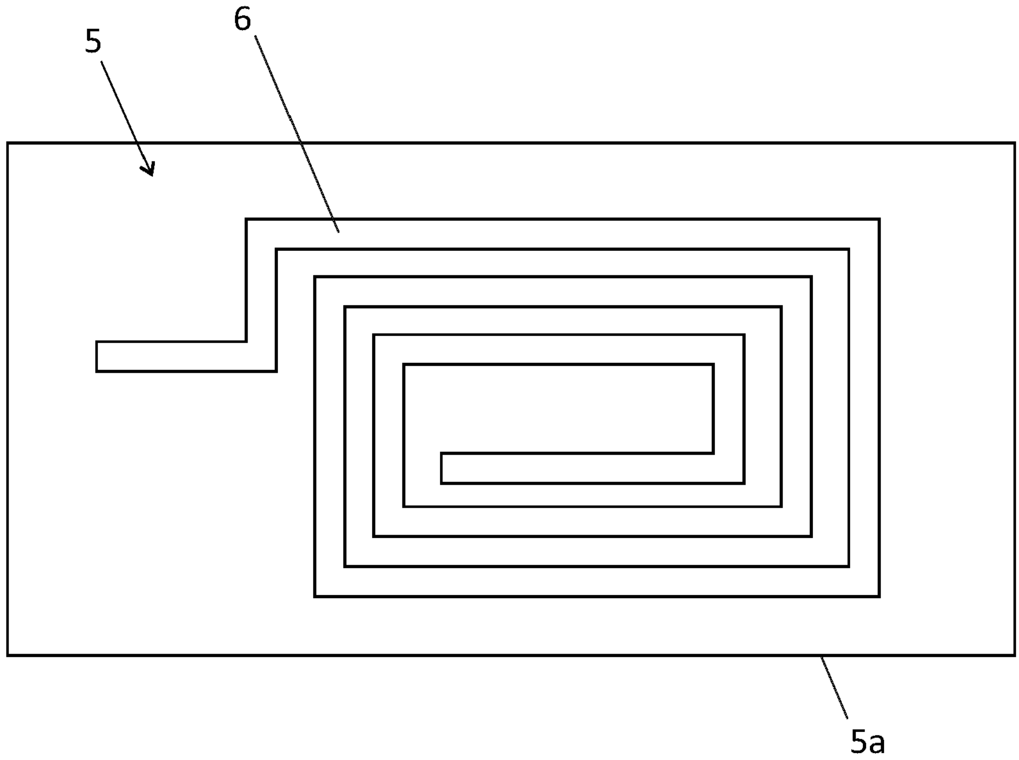

Fig. 3c

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 23 15 1775

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X Y	US 11 378 471 B2 (KOREA INST IND TECH [KR]) 5 July 2022 (2022-07-05) * paragraph [[0011]] - paragraph [[0059]]; claims 1, 8, 14, 15 *	1,8,14, 15 2-6,13	INV. D06M11/11 D06M11/28 D06M11/48 D06M11/56 D06M13/272 D06M13/352 D06M13/355 D06M23/06 D06M23/14 D06M23/16 D06M11/83 D06M11/50 D06M15/356 D06M13/256 D06M15/03 D06M101/16 D06M101/04
X	US 2013/199822 A1 (FAN QINGUO [US] ET AL) 8 August 2013 (2013-08-08) * column 6, line 53 - column 6, line 65; claims 1, 7, 15; figures 1,2 *	1,7,15	
X	CUTHBERT TYLER J. ET AL: "HACS: Helical Auxetic Yarn Capacitive Strain Sensors with Sensitivity Beyond the Theoretical Limit", ADVANCED MATERIALS, [Online] vol. 35, no. 10, 6 January 2023 (2023-01-06), page 2209321, XP093047783, DE ISSN: 0935-9648, DOI: 10.1002/adma.202209321 Retrieved from the Internet: URL:https://onlinelibrary.wiley.com/doi/full-xml/10.1002/adma.202209321> [retrieved on 2023-06-05] * See Experimental section *	1,7,9-12	**TECHNICAL FIELDS SEARCHED (IPC)** D06M D06Q
Y	CN 110 284 330 A (UNIV ANHUI POLYTECHNIC) 27 September 2019 (2019-09-27) * paragraph [0040] - paragraph [0045]; claim 13 *	13	
Y	WO 2018/050827 A2 (NORDIC FLEX S L [ES]) 22 March 2018 (2018-03-22) * page 66, line 5 - line 11; figure 3 *	2-6	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	5 June 2023	Massella, Daniele

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

1

EPO FORM 1503 03.82 (P04C01)

page 1 of 2

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 23 15 1775

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
			D06M101/10
			TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	5 June 2023	Massella, Daniele

1

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 23 15 1775

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

05-06-2023

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 11378471 B2	05-07-2022	NONE	
US 2013199822 A1	08-08-2013	US 2013199822 A1	08-08-2013
		WO 2011146835 A2	24-11-2011
CN 110284330 A	27-09-2019	NONE	
WO 2018050827 A2	22-03-2018	EP 3513412 A2	24-07-2019
		FI 127417 B	31-05-2018
		WO 2018050827 A2	22-03-2018

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82