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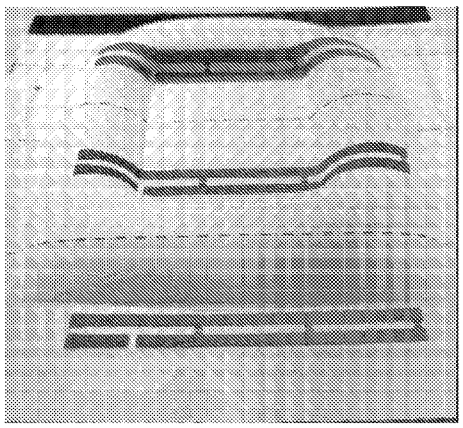

FIG. 5B

(57) Abstract: A thermoformable electronic substrate having a first substrate layer of 4-way stretch fabric that includes at least one conductive trace printed thereon and a second substrate layer of a thermoformable polymer or textile. The first substrate layer may be laminated to a surface of the second substrate layer via an extensible adhesive, heat, or both. The conductive trace is formed by printing a particle-free conductive ink on the first substrate layer either before or after lamination to the second substrate layer. The conductive traces may form connecting wires for standard electronic elements, or electronic elements such as resistive heaters, circuits, sensors such as thermal sensors, humidity sensors, proximity sensors, pressure sensors, and the like. The thermoformable electronic substrates may be thermoformed to create three dimensional parts useful in a wide range of industries.

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[Continued on next page]

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THERMOFORMABLE ELECTRONIC SUBSTRATES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit under 35 U.S.C. § 119(e) of prior U.S. Provisional Application Ser. No. 63/521,455, filed June 16, 2023, and U.S. Provisional Application Ser. No. 63/605,891, filed December 4, 2023, the entire contents of which are incorporated herein.

TECHNICAL FIELD

[0002] This invention pertains generally to thermoformable substrates having conductive patterns printed thereon, and methods for forming those substrates and three-dimensional surfaces utilizing those substrates.

BACKGROUND

[0003] Thermoforming is a process utilizing heat and either vacuum or high gas pressure to form a softened thermoplastic film onto a mold form of desired shape and size to form a three-dimensional (3D) molded part. It is a widely used technology in forming thermoplastics for packaging and consumer products. Recently, the integration of printed electronics into the thermoforming process is starting to be explored. The printing of conductive metal traces on planar thermoformable plastic substrates followed by thermoforming to manufacture 3D parts has limitations due to the mismatch in mechanical and physical properties of the polymeric substrate and metal trace. The draw requirements of the thermoforming process increase trace cracking potential, leading to a reduced or catastrophic failure in electrical performance. The larger the draw height required to meet the design of a product, the more susceptible the traces will become to failure.

[0004] For example, US Pat. No. 10,544,317 discloses screen printing inks comprising metal particles or flakes and polymers on a polycarbonate substrate to form a circuit, which is then encapsulated by a dielectric layer. Upon thermoforming, the printed polycarbonate substrate was found to have a maximum elongation of 20 to 45% before the conductive trace showed reduced conductivity (e.g., trace cracking), wherein the elongation range depended on the polymer in the ink: vinyl-polyurethane inks and polyester-based inks showed reductions in conductivity for deformations of about 20-25% elongation and up to 45% elongation, respectively.

[0005] US Pat. Application Pub. No. 2014/0037941 also discloses screen printing inks comprising silver particles or flakes and polymers on a polycarbonate substrate to form a circuit, which was then thermoformed to provide a 3D part. Of note, the ink was found to require a specific

mixture of urethane and polyhydroxyether resins to maintain adherence, and thus conductivity, of the circuit to the polycarbonate substrate. An encapsulant was found to improve thermoforming performance of the underlying circuit. This application does not provide any data related to conductivity of the thermoformed articles, or the degree of substrate1`1 deformation before failure, i.e., loss of conductivity. Rather, the degree of crazing of the underlying polycarbonate substrate is the only metric considered for measure of success or failure.

[0006] US Pat. No. 7,506,436 discloses metalizing a sheet of a thermoformable polymer with an admixture of conductive metal particles and a resin, and thermoforming the metalized thermoformable polymer to form a 3D part, in this case an enclosure for shielding a semiconductor device such as from electromagnetic frequencies. No disclosure is provided regarding forming conductive traces on a thermoformable substrate, or the sheet resistance of the metalized substrate before or after thermoforming.

[0007] Other solutions to this problem include droplet-based deposition of electronic inks on a multi-axis system to print complex conformal circuits directly onto a 3D substrate (Adams et al., Conformal printing of electrically small antennas on three-dimensional surfaces. *Adv Mater.* 2011 Mar 18;23(11):1335-40), and laser structuring on molded plastic to electroless plate conductive traces on the 3D surface (Ratautas et al., Laser-Induced Selective Electroless Plating on PC/ABS Polymer: Minimization of Thermal Effects for Supreme Processing Speed. *Polymers* 2020 Oct 21;12(10):2427). Not only are these approaches difficult to adopt, but the necessary equipment is expensive to own and requires specialized training to print 3D surfaces. Moreover, extrusion of conductive ink on 3D surfaces requires complex control of ink rheology and extrusion angle.

[0008] An alternative approach is manual placement of copper tapes on 3D objects. However, this approach is difficult to implement for complex circuitry and suffers from high manual labor cost.

[0009] Accordingly, there is a need for thermoformable substrates and methods of producing robust 3D printed electronic devices and articles that is economical and uses common place processing equipment.

SUMMARY

[0010] Disclosed herein are thermoformable printed electronic substrates, methods of forming those substrates, methods for using those substrates to provide three-dimensional (3D) printed electronic components, and the 3D printed electronic components formed using those methods.

[0011] Accordingly, the present disclosure provides a thermoformable printed electronic substrate having a first substrate layer comprising a stretchable textile having at least one conductive trace printed thereon with a conductive ink; and a second substrate layer comprising a thermoformable substrate such as a thermoformable polymeric substrate or a thermoformable textile substrate, wherein the first substrate layer is laminated to the second substrate layer via an extensible adhesive, heat, or both. The at least one conductive trace may be printed on a top side of the stretchable textile of the first substrate layer, wherein a bottom side of the stretchable textile faces the second substrate layer. Alternatively, the at least one conductive trace may be printed on the bottom side of the stretchable textile that faces the second substrate layer. The thermoformable printed electronic substrate may further comprise a thermoplastic polymer sheet or foam laminated to the top side of the first substrate layer.

[0012] The present disclosure further provides 3D articles comprising the thermoformable printed electronic substrate according to the present disclosure. The first substrate layer of the thermoformable printed electronic substrate may be on an exterior or interior surface of the 3D article. Further, the 3D printed article may comprise a polymeric coating over the first substrate layer to encapsulate the at least one conductive trace. The polymeric coating may be a dielectric coating.

[0013] Exemplary 3D articles include at least automotive air ducts, door panels, head liners, dashboard panels, trunk liners, and the like. Other exemplary 3D printed articles include at least clothing, such as hats, shoes, and accessories (e.g., purses and bags), headboards, wall coverings, seat cushions such as car, boat, or airplane seats, portable cushions or covers for seats or chairs, and the like. Further exemplary 3D printed articles include any traditional thermoformed part known in the art.

[0014] Exemplary printed electronics on the thermoformable substrates include any of resistive heaters; connecting wires for standard electronic elements; circuits; lighting; haptic devices; sensors such as thermal sensors, humidity sensors, proximity sensors, pressure sensors, force sensors, capacitive touch sensors; and the like.

[0015] The present disclosure also provides a method for forming the thermoformable printed electronic substrate. The method generally comprises depositing a particle free conductive ink on a first substrate layer to form at least one pattern, wherein the depositing is by inkjet or aerosol jet printing on the first substrate layer; curing the conductive ink in the at least one pattern to form at least one conductive pattern; and laminating the first substrate layer to a second substrate layer using an extensible liquid adhesive, an extensible adhesive tape, heat, or any combination thereof, wherein the first substrate layer is a stretchable textile, and

the second substrate layer is a thermoformable polymer sheet or thermoformable textile. The first substrate may be heated to a temperature of 30°C to 90°C during deposition of the particle free conductive ink. Curing the conductive ink to form the at least one conductive pattern may be by heating at a temperature of 100°C to 200°C for a time of less than 20 minutes, exposure to 2-20 pulses of pulsed light, exposure to infrared radiation, or any combination thereof. The method may further comprise laminating a thermoplastic polymer sheet or foam to the top side of the first substrate layer.

[0016] The present disclosure also provides a second method for forming the thermoformable printed electronic substrate. The second method comprises laminating a first substrate layer to a second substrate layer to form a composite, wherein the laminating uses an extensible liquid adhesive, an extensible adhesive tape, heat, or any combination thereof, and wherein the first substrate layer is a stretchable textile and the second substrate layer is a thermoformable polymer sheet or thermoformable textile; depositing a particle free conductive ink on the composite to form at least one pattern, wherein the depositing is by inkjet or aerosol jet printing on the first substrate layer; and curing the particle free conductive ink in the at least one pattern to form at least one conductive pattern, wherein curing is by heating at a temperature of 100°C to 200°C for a time of less than 20 minutes, exposure to 2-20 pulses of pulsed light, exposure to infrared radiation, or any combination thereof. Before curing but during deposition of the particle free conductive ink, the first substrate may be heated to a temperature of 30°C to 90°C. After laminating the first substrate layer to the second substrate layer, the composite may be cut to provide a desired shape, such as before depositing the particle free conductive ink, after depositing the particle free conductive ink, before curing the particle free conductive ink, or after curing the particle free conductive ink. Moreover, after depositing a particle free conductive ink on the composite to form at least one pattern, the method may include laminating a thermoplastic polymer sheet or foam to the first substrate layer of the composite.

[0017] The present disclosure also provides a method of forming a 3D article comprising a conductive pattern. The method includes registering a thermoformable printed electronic substrate according to the present disclosure with a 3D form, i.e., positioning the substrate over or under the 3D form; heating the thermoformable printed electronic substrate to a softening temperature of a second substrate layer thereof; and forcing at least portions of the thermoformable printed electronic substrate against the 3D form to provide the 3D article, wherein either the first substrate layer or the second substrate layer is in contact with the 3D form. The thermoformable printed electronic substrate may be heated after registering with the

3D form such as via contact with a heated 3D form and/or elevated temperature around the 3D form and/or exposure to infrared radiation (IR). The thermoformable printed electronic substrate may be heated prior to registering with the 3D form, such as in a thermal oven or via exposure to IR, and forced against a hot or cold 3D form.

[0018] When the second substrate layer is a thermoformable polymer sheet, forcing at least portions of the heated thermoformable printed electronic substrate against the 3D form may be via positive or negative pressure, or compaction, e.g., compaction between mated portions or halves of the 3D form. When the second substrate layer is a thermoformable textile, this may be accomplished via compaction.

[0019] According to certain aspects, the second substrate layer may have been previously formed as a 3D article, and the first substrate layer may be caused to conform to the shape (interior or exterior) of the 3D article via positive or negative pressure, or compaction, e.g., compaction of the first substrate layer onto or into the previously formed 3D article (i.e., previously thermoformed second substrate layer). The first substrate layer may be laminated to the second substrate layer to form the composite 3D article, wherein the laminating may be via an extensible liquid adhesive, an extensible adhesive tape, heat, or any combination thereof.

[0020] For any of the substrates, articles, or methods disclosed herein, the stretchable textile of the first substrate layer is generally a 4-way stretch fabric, such as a blend of polyester and polyether-polyurea copolymer, or a blend of nylon and polyether-polyurea copolymer. The second substrate layer may be a thermoformable textile such as a composite natural fiber non-woven mat or web, such as mats or webs of natural fibers (e.g., plant or animal derived fibers) and synthetic polymer(s). Alternatively, the second substrate layer may be a thermoformable polymeric substrate, such as a polycarbonate, polybutylene terephthalate (PBT), polyethylene terephthalate (PET), polyethylene terephthalate glycol-modified (PETG), acrylonitrile-butadiene-styrene (ABS), polymethyl methacrylate (acrylic), acrylic capped ABS, cellulose acetate butyrate (CAB), ethylene vinyl acetate (EVA), high impact polystyrene, expanded polyvinyl chloride (PVC), acrylic-PVC, polystyrene modified poly(p-phenylene oxide) or polyphenylene ether.

[0021] For any of the substrates, articles, or methods disclosed herein, the conductive ink comprises a particle-free metal complex composition that includes a solvent and at least one metal complex, wherein the metal complex comprises at least one metal, at least one first ligand that is a sigma donor to the metal and volatilizes upon heating the metal complex, and at least one second ligand that is different from the first ligand and volatilizes upon heating the metal complex. For example, the particle-free metal complex composition may comprise a

silver amine carboxylate and at least one polar protic solvent selected from the group consisting of water, an alcohol, an amine, an amino alcohol, and a polyol. The conductive ink conformally coats fibers of the 4-way stretch fabric.

[0022] For any of the substrates, articles, or methods disclosed herein, the at least one conductive pattern may include at least one bus, wherein the at least one bus electrically connected to the conductive pattern and configured to provide connection to a controller and a power source.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] Aspects, features, benefits, and advantages of the embodiments herein will be apparent with regard to the following description, appended claims, and accompanying drawings. In the following figures, like numerals represent like features in the various views. It is to be noted that features and components in these drawings, illustrating the views of embodiments of the present disclosure, unless stated to be otherwise, are not necessarily drawn to scale.

[0024] **FIGS. 1A-1E** illustrate aspects of the prior art nanoparticle inks printed on a non-woven textile, where **FIGS. 1A** and **1B** are two different magnifications of scanning electron micrograph (SEM) images of a single layer of nanoparticle silver ink printed on Evolon®; **FIG. 1C** is a cross sectional view SEM image of the same textile, wherein the fibers are colored green and the nanoparticle silver ink is shown in red; **FIG. 1D** shows the distribution of the nanoparticle silver ink throughout the textile shown in **FIG. 1C** (i.e., only the nanoparticle silver ink is shown); and **FIG. 1E** shows resistance readings for 2 to 5 layers of nanoparticle inks printed on Evolon® or modified Evolon®.

[0025] **FIGS. 2A** and **2B** are schematic diagrams showing the coating of textile fibers by a nanoparticle ink of the prior art and conformal coating of textile fibers by the particle-free inks of the present disclosure, respectively.

[0026] **FIG. 3** illustrates knit textiles screen-printed with conductive materials of the prior art under different amounts of strain (i.e., stretch of the textile).

[0027] **FIGS. 4A-4D** illustrate cross-sectional views of various implementations of the thermoformable printed electronic substrates according to the present disclosure.

[0028] **FIG. 5A** illustrates conductive traces printed on 4-way stretch fabric laminated to a thermoformable polymer sheet to form a thermoformable printed electronic substrate according to methods of the present disclosure.

[0029] **FIG. 5B** illustrates the thermoformable printed electronic substrate of **FIG. 5A** after thermoforming according to methods of the present disclosure.

[0030] **FIG. 5C** illustrates conductive traces printed on 4-way stretch fabric laminated to a thermoformable textile to form a thermoformable printed electronic substrate according to methods of the present disclosure.

[0031] **FIG. 6** illustrates an inkjet printer setup useful in methods of the present disclosure.

[0032] **FIG. 7A** shows a woven textile having a molecular ink of the present disclosure conformally coated on a portion thereof (coated at left; uncoated at right), and **FIGS. 7B** and **7C** are SEM images of the coated portions of the textile (150x and 800x magnification, respectively).

[0033] **FIGS. 8A and 8B** are cross sectional view SEM images of a textile having a molecular ink of the present disclosure printed thereon (perspective and side views, respectively at 70,000x), and **FIG. 8C** is an SEM image at high magnification (250,000x) showing the conductive trace includes nanoparticles.

[0034] **FIG. 9** shows a proton nuclear magnetic resonance (^{1}H-NMR) scan of an exemplary metal complex (ethylenediaminosilver(I) isobutyrate in D_2O) of the present disclosure, and (upper right) the structure of an exemplary metal complex of a molecular ink of the present disclosure.

[0035] **FIG. 10** shows a proton nuclear magnetic resonance (^{1}H-NMR) scan of an exemplary molecular ink comprising a particle free solution of a metal complex dissolved in a solvent (ethylenediaminosilver(I) isobutyrate dissolved in polar protic solvents and in D_2O) of the present disclosure.

[0036] **FIG. 11** shows a graph of the resistance (ohms) after multiple wash cycles for a conductive trace on a textile using inks and methods in accordance with certain aspects of the present disclosure.

[0037] **FIG. 12** shows a graph of the change in resistance with increased strain (stretch) for a conductive trace on a textile using inks and methods in accordance with certain aspects of the present disclosure.

[0038] **FIG. 13** shows a graph of the change in resistance with increased bending cycles for a conductive trace on a textile using inks and methods in accordance with certain aspects of the present disclosure.

[0039] **FIG. 14** shows a graph of resistivity for molecular inks comprising varied ratios of silver and copper complexes according to aspects of the present disclosure.

[0040] **FIGS. 15** and **16** show graphs of sheet resistance as a function of cure time for molecular inks according to aspects of the present disclosure.

[0041] **FIG. 17** shows a current-voltage graph for resistive films printed using molecular ink according to aspects of the present disclosure.

DETAILED DESCRIPTION

[0042] In the following description, the present disclosure is set forth in the context of various alternative embodiments and implementations involving molecular inks and methods for printing the molecular inks on stretchable textiles, such as 4-way stretch fabrics, to form conductive and resistive traces, coatings, and patterns (used interchangeably and referred to herein as "conductive traces") thereon. Also provided are methods of forming thermoformable printed electronic substrates having the stretchable textiles laminated thereon, thermoformable printed electronic substrates produced by these methods, three-dimensional (3D) articles formed with the thermoformable printed electronic substrates, and methods of thermoforming the thermoformable printed electronic substrates to produce 3D articles of manufacture. While the following description discloses numerous exemplary embodiments, the scope of the present patent application is not limited to the disclosed embodiments, but also encompasses combinations of the disclosed embodiments, as well as modifications to the disclosed embodiments.

[0043] Deposition of particle free conductive inks onto a flat thermoformable substrate has not previously been known or possible for a wide range of substrates. For example, particle-free conductive inks are not compatible with certain polymers, such as polypropylene and polycarbonate, and thus will not adhere to those polymer substrates. Some prior art solutions included use of inks comprising particulate or flaked conductive metals and a polymer binder, wherein the binder was chosen for compatibility with the substrate. These inks are generally viscous and only compatible with printing methods such as screen printing, thus limiting their use in forming certain electronic components. Moreover, the prior art inks and methods generally only allowed for a small level of deformation of the thermoformable substrate before the conductive traces formed from the inks became discontinuous and thus non-conductive.

[0044] Disclosed herein are methods for forming a thermoformable printed electronic substrate that uses conventional polymer processing equipment, such as roll laminators, heated presses, thermoforming equipment, inkjet or aerosol jet printers, and injection mold machines. Additionally, the novel molecular inks and methods for printing those inks onto stretchable textile substrates that are then laminated to a thermoformable polymer or thermoformable

textile provide a thermoformable printed electronic substrate useful to produce 3D parts having large deformations (e.g., stretch) and bend angles. For example, the particle free molecular inks, which are compatible with the stretchable textiles, need not be compatible with the thermoformable polymer or thermoformable textile. Moreover, the molecular inks may be configured for printing by a wide range of methods. For example, the molecular inks may be printed by methods such as ink jet or aerosol jet and are thus suitable for printing very thin conductive traces that are useful for production of a wide range of electronic components.

[0045] A novel and unique aspect of the presently disclosed conductive traces is that they are formed using molecular inks that comprise particle-free compositions of stoichiometric metal complexes dissolved in a solvent. This affords printing of traces that are narrow and may be precisely deposited. When printed on a stretchable textile substrate, such as the 4-way stretch fabrics disclosed herein, these molecular inks conformally coat fibers of the substrate and are resistant to degradation by the standard strains and forces exerted upon such substrates, e.g., bending, stretching, twisting, washing, abrasion, etc. As such, the molecular inks and electronic elements formed using the methods of the present disclosure provide dramatic improvements over those disclosed in the prior art.

[0046] Direct print methods are frequently used to form conductive patterns. The conductive inks of the prior art, however, often do not show satisfactory results. For example, inkjet printing with nanoparticle inks has proven challenging due to clogging of the nozzle and either too little interaction with the textile surface, e.g., pooling, or too much interaction with the textile surface, e.g., spreading due to capillary effects. As shown in **FIGS. 1A** and **1B**, for example, nanoparticle inks printed on nonwoven textiles such as Evolon® can pool, failing to coat the fibers to the extent required to form a conductive pattern. Even after multiple layers are applied, such as the 6 layers of ink shown in **FIGS. 1C** and **1D**, scanning electron micrograph images show that the ink is pooled into islands separated by non-coated areas. For example, **FIGS. 1C** and **1D** show the Evolon® non-woven fiber includes the ink discontinuously on the top (particles or discontinuous film; **FIG. 1C**) and throughout the thickness of the textile via capillary spreading (**FIG. 1D**).

[0047] As shown in **FIG. 1E**, because these nanoparticle inks fail to form a continuous pattern, they demonstrate extremely high resistance (i.e., fail to form conductive traces). Moreover, additional coating layers of the nanoparticle inks does not reduce the resistance of these printed patterns. Modification of the textile to decrease surface resistance is possible, such as up to 2 orders of magnitude, but still does not form conductive patterns (**FIG. 1E** at right). The dots on the background in **FIGS. 1C** and **1D** represent clustered silver particles with

little silver-to-silver fusion or connectivity (see **FIG. 2A**), hence the poor conductivity of silver nanoparticle films. The poor conductivity is further worsened by the low temperature limitation of most textile substrates, such as fabrics, which makes it impossible to systematically fuse silver particles with the elevated temperatures often required for nanoparticle ink curing.

[0048] Moreover, patterns formed on textiles with nanoparticle inks generally show poor flexibility during use of the textile (e.g., multiple wear and/or wash cycles). As illustrated in **FIG. 3**, strain such as by stretching a screen-printed woven textile leads to breaks in the conductive pattern, rendering the pattern non-conductive over time. In fact, as little as 10% strain on the textile can lead to an observable increase in breaks in the printed pattern and loss of conductivity.

[0049] The inventive processes disclosed herein circumvent many of these difficulties by directly printing a pattern on the flexible substrate (e.g., stretchable textiles such as 4-way stretch fabrics, woven or non-woven textiles, or flexible polymeric substrates) using molecular inks that comprise particle-free compositions of a metal complex dissolved in a solvent, and thus provide highly scalable and automated methods for producing printed flexible electronics that maintain integrity through multiple types of stress and strain. The methods generally comprise using a direct printing process to deposit the molecular ink on the flexible substrate, which is then cured to produce a conductive pattern thereon. As such, the conductive patterns may be formed on the flexible substrate, such as a textile, in a manner that is easily integrated into current manufacturing processes, and more importantly, is easily scalable and can be highly automated. Moreover, the methods disclosed herein provide conformal coating of the molecular ink on the textile fibers of a textile flexible substrate (**FIG. 2B**) that allows for greatly improved conductivity and longevity of the conductive trace. As used herein, the term "conformal" shall be taken to mean a coating that covers at least the surface of a textile, fiber, or substrate, and which follows the contours of the surface.

Thermoformable printed electronic substrates

[0050] The presently disclosed molecular inks and methods for printing those inks can be used to form electronic elements on stretchable substrates, such as 4-way stretch fabrics. With reference to **FIGS. 4A-4D**, a thermoformable printed electronic substrate will be described that includes a thermoformable substrate layer (second substrate layer **8**) having laminated thereon a stretchable fabric layer (first substrate layer **6**).

[0051] With specific reference to **FIGS. 4A** and **4B**, a molecular ink **4** according to the present disclosure is printed on the first substrate layer **6**, such as by methods disclosed herein. The first substrate layer may be a stretchable textile or fabric. Organic and inorganic substrates

can be used, such as stretchable substrates comprising organic or synthetic fibers. Preferred are 4-way stretch fabrics, such as those comprising a blend of polyester and polyether-polyurea copolymer, or a blend of nylon and polyether-polyurea copolymer.

[0052] The textiles of the first substrate layer may be pretreated with a reactive gas, such as an O_2 plasma or corona, which may improve deposition of the molecular inks thereon and may reduce sheet resistance. Additionally, the textiles may be prewashed and dried prior to deposition or printing of the molecular inks disclosed herein.

[0053] The first substrate layer **6** may be laminated to the second substrate layer **8** using an adhesive, heat, or both.

[0054] The second substrate layer **8** may be a composite natural fiber non-woven mat or web. These are a combination of natural derived fibers, e.g., plant and/or animal, and synthetic polymers. The synthetic polymers may include polypropylene, polyethylene, thermoplastic olefin (TPO), and acrylic. The synthetic polymer may include both thermoplastics and cross-linkable thermoplastics. Suitable natural plant fibers include wood, hemp, cotton, coconut, flax, jute, bamboo, wheat straw, kenaf, and sisal fibers. Suitable natural animal fibers include at least wool. Other natural fibers can include glass fibers. The weight ratio of natural fiber to synthetic polymer may vary but is generally 0.1:1 to 1:0.1, such as 0.5:1 to 1:0.5, or 1:1. The composite mat or web may be formed by impregnating the natural fiber mat or web with an aqueous polymer dispersion followed by drying; or commingling natural fibers and synthetic polymer fibers. The non-woven mats or webs of commingled fibers are typically formed by a needle punching process to a thickness of 0.25 to 0.50 inch.

[0055] The second substrate layer may be a woven or knit textile comprising a thermoformable polymer, such as polyester or nylon fabrics. The second substrate layer may be a foam, such as an ethylene-vinyl acetate (EVA) foam, polyurethane (PU) Foam, polyethylene (PE) foam, cross-linked closed cell Polyolefin (IXPE) foam, and the like. The second substrate layer may be a rubber foam, such as neoprene or a thermoplastic elastomer. While specific examples are provided, other thermoformable textiles are possible and within the scope of the present invention.

[0056] Alternatively, the second substrate layer **8** may be any thermoformable polymer known in the industry. Exemplary thermoformable polymers include any of polycarbonate, polybutylene terephthalate, polyethylene terephthalate, polyethylene terephthalate glycol-modified (PETG), acrylonitrile-butadiene-styrene (ABS), polymethyl methacrylate (acrylic), acrylic capped ABS, cellulose acetate butyrate (CAB), ethylene vinyl acetate (EVA), high impact polystyrene, expanded polyvinyl chloride (PVC), acrylic-PVC, polystyrene modified

poly(p-phenylene oxide) or polyphenylene ether (e.g., Noryl® by SABIC). According to certain aspects, the thermoformable polymer may be a polycarbonate or polycarbonate blend, such as any of those provided under the trade names of Lexan® by SABIC, Makrolon® and Makrofol® by Covestro, and the like. When the second substrate layer **8** is a thermoformable polymer, it may be in the form of a sheet. Exemplary thermoformable polymer sheets may have a thickness of 2-200 mil, such as 2-50mil, or 2-20mil.

[0057] Exemplary adhesives include at least liquid adhesives and adhesive tapes, wherein the adhesive may be extensible, such as a rubber or acrylic based adhesive. Hot melt adhesives are also possible. Temperatures used for heat lamination will depend on the composition of the thermoformable substrate layer **8**. For example, when the substrate layer **8** is a thermoformable polymer sheet, temperatures useful for heat lamination are generally below the melting temperature of the polymer, such as at or above the glass transition temperature of the polymer but below the melting temperature. For example, the first substrate layer **6** may be heat laminated to a polycarbonate second substrate layer **8** at a temperature at or above the glass transition temperature (softening temperature) of about 140°C, but below the melt temperature of 288-316°C, such as the temperature at which polycarbonate flows, i.e., about 155°C. The first substrate layer **6** may be heat laminated to a polycarbonate second substrate layer **8** at a temperature of 140-220°C, such as 145-200°C, or 145-180°C, or even 145-170°C.

[0058] As shown in FIG. **4A**, the first substrate layer **6** may be laminated to the second substrate layer **8** with the printed side of the first substrate layer (i.e., top surface of the fabric comprising the molecular ink **4**) facing upward, while a bottom non-printed side (i.e., bottom surface of the fabric) faces the second substrate layer **8**. Alternatively, the first substrate layer **6** may be laminated to the second substrate layer **8** with the printed side of the first substrate layer (i.e., top surface of the fabric) facing the second substrate layer **8**, such as shown in **FIG. 4B**.

[0059] In some implementations, an additional layer **7** may be bonded, such as by lamination (heat or adhesive) to the first substrate layer **6** as shown in **FIGS. 4C** and **4D**. The additional layer **7** may be a thermoplastic polymer sheet or foam. The additional layer **7** may be bonded to the first substrate layer **6** with the molecular ink **4** facing outward and away from the second substrate layer **8**, such as shown in **FIG. 4C**. Alternatively, the additional layer **7** may be bonded to the first substrate layer **6** with the molecular ink **4** facing inward toward the second substrate layer **8**, such as shown in **FIG. 4D**.

[0060] The additional layer **7** may a polymer as listed for the second substrate layer **8** hereinabove or may be a different polymer. When the second substrate layer **8** is a

thermoformable polymer, inclusion of the first substrate layer **6** between the two polymer layers, i.e., the additional and second layers (**7**, **8**), allows lamination and thermoforming of otherwise incompatible polymer sheets, wherein the stretchable textile acts as a tie layer between the incompatible polymers.

[0061] The thermoformable printed electronic substrate may be formed by first depositing a particle free conductive ink **4** on the first substrate layer **6** to form at least one pattern. The ink may be deposited by any method disclosed herein, but preferred methods include inkjet printing and aerosol jet printing. The ink may be printed on the first substrate layer as the first substrate layer is heated to a temperature of 30°C to 90°C, such as on a heated platen positioned below the first substrate layer. Alternatively, the ink may be printed on a first substrate layer at ambient temperatures, such as 10°C to 40°C, or 10°C to 30°C.

[0062] The ink in the pattern may then be cured by any method disclosed herein to form at least one conductive pattern. Preferred methods of curing the molecular ink **4** include heating, such as at a temperature above 100°C, such as 100°C to 200°C, for a time of less than 20 minutes; or exposure to 2-20 pulses of pulsed light, such as photonic cure or exposure to infrared radiation, or any combination thereof.

[0063] This first substrate layer **6** may then be laminated to a second substrate layer **8** using an adhesive, such as an extensible adhesive, and/or heat. In certain preferred implementations, the first substrate layer **6** is a 4-way stretch fabric such as a blend of polyester and polyether-polyurea copolymer, or a blend of nylon and polyether-polyurea copolymer, and the second substrate layer is either a thermoformable textile or a thermoformable polymer sheet such as a thermoformable polycarbonate, polycarbonate blend, or acrylic PVC sheet.

[0064] According to certain alternative aspects of the method, the molecular ink **4** in the pattern on the first substrate layer **6** may be cured after the first substrate layer **6** has been laminated onto the second substrate layer **8**. Further yet, the molecular ink **4** in the pattern on the first substrate layer **6** may be cured by the heat of the thermoforming process, such as at the temperature indicated hereinabove (e.g., above 100°C but below the melt temperature of the second substrate layer).

[0065] Alternatively, the thermoformable printed electronic substrate may be formed by laminating a first substrate layer **6** to a second substrate layer **8** using an adhesive, such as an extensible adhesive, and/or heat, thus forming a composite. The molecular ink **4** may then be deposited on a surface of the first substrate layer **6** to form at least one pattern on the composite, which may then be cured to form at least one conductive pattern, and thus the thermoformable printed electronic substrate.

[0066] Either method may further include laminating an additional layer **7**, such as a thermoplastic polymer sheet or foam, to the first substrate layer. The thermoplastic polymer may be any of the thermoformable polymers listed herein above for the second substrate layer.

[0067] In these methods, each of the substrates and adhesives may comprise any of those elements disclosed herein. Further, each of the method steps of laminating the substrates together and depositing and curing the ink may be according to any of the methods disclosed herein.

[0068] According to certain aspects of the present disclosure, the molecular inks disclosed herein may be printed directly on the second substrate layer, such as when the second substrate layer comprises a thermoformable textile (e.g., non-woven mat or web composed of natural fibers or a mixture of natural and synthetic fibers). In this configuration, the second substrate layer, i.e., thermoformable textile, may be thermoformed to form the 3D article. Additional layers, such as protective coatings, thermoplastic polymer films or sheets, foam, and the like may be laminated to the thermoformable textile before thermoforming as described herein.

Electronic elements and devices formed on the thermorformable printed electronic substrates

[0069] The molecular inks of the present disclosure and methods for depositing those inks on the stretchable substrate of the first substrate layer to form highly conductive traces having little to no ink bleed allow for production of a wide range of electronic elements or devices. For example, the at least one conductive trace of the first substrate layer may form a conductive pattern that is configured as a sensor, heater, haptic device, capacitive touch device, lighting, circuit, and the like. Exemplary sensors include temperature sensors, moisture sensors, humidity sensors, pressure sensors, force sensors, strain sensors, capacitive touch sensor, proximity sensor, and the like. The first substrate layer may further comprise at least one bus, such as printed using the methods disclosed herein, that is electrically connected to the conductive pattern and configured to provide connection to a controller and/or a power source.

[0070] The conductive patterns on the first substrate layer may withstand at least 50 wash cycles, such as at least 70 wash cycles, or even 100 wash cycles with air drying (*see* **FIG. 11** and examples). The resistance of these conductive patterns increase only slightly after multiple wash cycles, such as by less than 50% after 50 washes, or less than 30% after 50 washes, or less than 15% after 50 washes, or less than 70% after 100 washes, or less than 60% after 100 washes, or less than 40% after 100 washes, or less than 30% after 100 washes, or less than 20% after 100 washes, wherein a wash cycle is defined as in according to AATCC 61-

2013 (laundering). As shown in **FIG. 11**, a protective coating may improve the washability of the flexible electronics disclosed herein.

[0071] The conductive patterns on the first substrate layer may be abrasion resistant (up to 500 cycles by standard ASTM testing methods) and may be sweat resistant (moisture resistant).

[0072] The conductive patterns on the first substrate layer may be strain resistant. For example, knit textiles comprising the conductive traces may be stretched by up to 50%, or up to 100%, without connection loss, generally showing only a slight decrease in conductivity with an increase in stretching of the textile substrate (*see* **FIG. 12** and examples).

[0073] The conductive patterns on the first substrate layer may be bendable, showing less than a 10% loss in conductivity after up to 10,000 bend cycles using standard ASTM testing methods (see **FIG. 13**).

3D parts formed using the thermorformable printed electronic substrates

[0074] The thermoformable printed electronic substrate may be formed into a 3D part or article of manufacture using thermoforming methods known in the art. For example, a thermoformable printed electronic substrate of the present disclosure may be placed within a thermoforming machine, which may include registering the substrate in a specific orientation or position. For example, the thermoformable printed electronic substrate may be positioned so that either the first substrate layer or the second substrate layer is forced into contact with a 3D form. The thermoformable printed electronic substrate may be heated to at least a glass deformation temperature of the polymer of the second substrate layer (i.e., layer of thermoformable polymer sheet). At least a portion of the thermoformable printed electronic substrate may be forced against the 3D form, such as by gas pressure and/or a vacuum, to form the 3D part or article of manufacture. Temperatures and times for heating depend on the polymer of the second substrate layer, and the pressures exerted, positive and/or negative, may depend on the polymer, the 3D form, and the thermoforming equipment. Once the 3D part has cooled, it may be removed from the 3D form.

[0075] An exemplary thermoformable printed electronic substrate is shown before thermoforming in **FIG. 5A**, and after thermoforming in **FIG. 5B**. Of note, the thermoformable printed electronic substrates produced using the molecular inks and methods disclosed herein may withstand deformations such as stretch of at least 25%, such as at least 30%, or 35%, or 40%, or 50%, or 60%, or 70%, or 80%, or 90%, or 100%. The thermoformable printed electronic substrates may withstand bend angles of at least 20°, such as at least 30°, or at least 40°, or 50°, or 60°, or 70°, or 80°, or 90°, or 100°.

[0076] Thermoforming methods may further include using the 3D part as a mold insert to an injection molding machine, and backfilling with a polymer. In cases where the conductive traces are on a surface of the first substrate layer, such as shown in **FIG. 4A**, the backfilling may encapsulate the conductive traces. However, such encapsulation may not be required as the conductive traces formed using the molecular inks and methods disclosed herein have excellent wear performance, e.g., bendability, washability, strain resistance, etc.

Molecular inks

[0077] The molecular inks of the present disclosure include a particle-free metal complex composition comprising at least one metal complex dissolved in at least one solvent. Such particle-free metal complex compositions and molecular inks have been described in US Patent Application Publication No. 2019/0249026 and 2020/0369061.

[0078] The metal complex can be mononuclear, dinuclear, trinuclear, and higher. For example, the metal complex may be a neutral metal complex comprising at least one metal, at least one first ligand, and at least one second ligand. The metal complex may be as described in US Patent Application Publications 2011/0111138, 2013/0236656, and 2020/0369061. The metal complex may comprise a first metal complex having at least one first metal, and a second metal complex having at least one second metal. The metal complex may be as described in any of US Patent Nos. 9,487,669; 9,920,212; 10,738,211; and 11,118,078.

[0079] For example, a neutral metal complex may be formed by first forming a complex between the metal (M) and the second ligand (L_2), such as by reacting a metal, metal salt, or metal oxide with the second ligand. The metal-second ligand complex may then be reacted with an excess of the first ligand (L_1) to form the neutral metal complex. The stoichiometric reaction ratio between the first ligand and the metal-second ligand complex can be, for example, at least 10:1, such as at least 13:1, or at least 15:1, or at least 20:1. When formulated in this way, the reaction mixture remains substantially or totally free of particles and progresses to completion forming a metal complex having stoichiometric amounts of the first and second ligands and the metal.

[0080] The excess, unreacted first ligand may be removed to provide the metal complex having stoichiometric amounts of the metal, first ligand, and second ligand (i.e., free of unliganded first ligand). For example, the excess, unreacted first ligand may be removed by vacuum evaporation of the complex and may include one or more wash steps with an appropriate solvent, to yield a final dry powder having stoichiometric amounts of the metal, first ligand, and second ligand. For silver metal complexes, this powder is typically white.

[0081] The resulting purified metal complexes are substantially or totally free of particles (particle-free) including nanoparticles and microparticles and are highly soluble in various solvents. This differs greatly from prior art complexes that do not include stoichiometric amounts of the metal, first ligand, and second ligand and/or may include residual unliganded first ligand, and accordingly generally include particles such as nanoparticles and/or microparticles (see additional discussion in the Examples). Printing of these prior art nanoparticle inks on certain textiles has demonstrated that they often do not penetrate the textile, but rather pool on top of the textile, as observed in the scanning electron microscopy images shown in **FIGS. 1A-1D**, and the schematic in **FIG. 2A**, and thus do not form conductive traces (*see* **FIG. 1E**). The molecular inks of the present disclosure are capable of conformally coating fibers of a textile substrate (*see* **FIG. 2B**) and form highly conductive traces.

[0082] The molecular inks may optionally further include at least one conductive filler material. Exemplary filler materials include at least conductive polymers, metal oxides, and carbon-based materials, such as carbon nanotubes (CNTs), graphene, and graphite. The conductive filler material can be preferentially selected from commercially available conductive polymers or carbon-based materials. Possible conducting filler materials include carbon black, graphite, polypyrrole (PPy), poly[3,4-ethylenedioxythiophene] (PEDOT), polyacetylene, polythiophene (PT), graphene, polyphenylene, CNTs, polyaniline (PANI), and polyphenylene ethylene.

[0083] Among the different types of conductive polymers that have been applied to textiles, PANI, PT and PPy provide high electrical conductivity and simple processing. PPy and PANI, in particular, provide excellent stability under environmental conditions, good conductivity, ease of fabrication onto flexible substrates such as fabrics, simple synthesis methods, and corrosion resistance. A general concern around the use of certain polymeric fillers in the presently disclosed molecular inks is poor mechanical properties. However, in those instances such concerns can be mitigated by incorporating polymer additives and binders such as nitrocellulose, which is characterized by its thermoplastic behavior, fast solvent evaporation, good compatibility with a wide range of materials, excellent processability and good mechanical properties. Thus, the molecular inks comprising a conductive filler may optionally comprise an additional binder material.

[0084] The molecular inks may optionally comprise one or more surfactants. The surfactants may comprise anionic, cationic, nonionic, or amphoteric surfactants, which may be present in the amount of 0.001-5 wt. %, such as 0.001-3 wt. %, or 0.01-2 wt. %, or not more than 0.1 wt. %, such as 0.001-0.1 wt.%, based on the total weight of the ink. Exemplary

surfactants may be those useful to reduce the surface tension of the molecular inks, such as silicone-based surfactants (i.e., silyl surfactant). Exemplary surfactants of particular use include polydimethyl siloxanes and modified polydimethyl siloxanes, e.g., polyether-modified polydimethylsiloxane.

[0085] The molecular inks may be formulated by dissolving the at least one purified metal complex, i.e., complex that is free of any unreacted first ligand, in a hydrocarbon solvent to form the particle-free metal complex composition, and adding any optional components, such as the conductive filler(s), surfactant(s), additional solvents, and binder material(s). Alternatively, the molecular inks may be formulated by dissolving the at least one purified metal complex, i.e., complex that is free of any unreacted first ligand, and any optional components, such as the conductive filler(s), surfactant(s), and any binder material(s), in an organic solvent system such as a hydrocarbon solvent system.

[0086] The molecular inks may be formulated by dissolving the at least one purified metal complex, i.e., complex that is free of any unreacted first ligand, in at least one polar protic solvent to form the particle-free metal complex composition, and adding any optional components, such as the conductive filler(s), surfactant(s), additional solvents, and binder material(s). Alternatively, the molecular inks may be formulated by dissolving the at least one purified metal complex, i.e., complex that is free of any unreacted first ligand, and any optional components, such as the conductive filler(s), surfactant(s), and any binder material(s), in at least one polar protic solvent.

[0087] In general, polar protic solvents can have high polarity and high dielectric constants. Polar protic solvents may comprise, for example, at least one hydrogen atom bound to an oxygen or a nitrogen. Polar protic solvents may comprise, for example, at least one acidic hydrogen. Polar protic solvents may comprise, for example, at least one unshared electron pair. Polar protic solvents may display, for example, hydrogen bonding.

[0088] Polar protic solvents may be particularly useful for depositing the molecular inks on certain substrates since hydrocarbon solvent(s) may not be compatible with the substrate and/or may not be recommended in some situations. Moreover, polar protic solvents may provide a more environmentally friendly ink solution.

[0089] Examples of polar protic solvents include water, linear or branched alcohols, amines, amino alcohols, and hydroxyl-terminated polyols including glycols. The polar protic solvent may also be, for example, ethylene and higher glycols, as well as alcohols. Examples of polar protic solvents include water, methanol, ethanol, n-propanol, isopropanol, n-butanol, acetic acid, formic acid, and ammonia.

[0090] The polar protic solvent may comprise, for example, water and at least one amine solvent. The amine solvent may have a molecular weight of, for example, about 200 g/mol or less, or about 100 g/mol or less. The amine solvent may be, for example, at least one monodentate amine, at least one bidentate amine, and/or at least one polydentate amine. The amine solvent may be, for example, at least one primary amine or at least one secondary amine. In one embodiment, the amine solvent may comprise at least one alkyl group bonded to at least one primary or secondary amine. The amine solvent may comprise at least two primary or secondary amine groups connected by a linear or branched alkyl group. The amine solvent may comprise at least two linear or branched alkyl groups connected by at least one secondary amine. Advantages of the amine solvent include, for example, improved solubility and thus higher possible concentrations of the metal complex in the solvent, as well as lower decomposition temperatures for the metal complex.

[0091] The solvent may be a mixed solvent system comprising, for example, two or more polar protic solvents, such as at least one alcohol, at least one amine, and optionally, a surfactant. For example, a mixed solvent system may comprise at least one alkyl alcohol, at least one diol, at least one amine, at least one thiolalkyldiol, and at least one surfactant, such as a silyl surfactant, wherein the at least one alkyl alcohol, the at least one diol, and the at least one thiolalkyldiol are not the same. Exemplary alkyl alcohols of the mixed solvent system may comprise 1-6 carbons atoms, such as at least methanol, ethanol, 1-propanol, 2-propanol, n-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 2-methyl-1-butanol, and 2-methyl-2-butanol. Exemplary diols of the mixed solvent system include at least ethylene glycol, 1,2-hexanediol, diethylene glycol, triethylene glycol, 1,3-propanediol, 1,3-butanediol, 1,2-butanediol, 2,3-butanediol, propylene glycol, dipropylene glycol, tripropylene glycol, trimethylene glycol, and 1,4-butanediol. Exemplary amines of the mixed solvent system include at least ammonium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide, ethylenediamine, propylene diamine, 1,2-diaminopropane, and diethyl ethylenediamine. Exemplary thiolalkyldiols of the mixed solvent system include at least thiodiglycol, 1,4-dithiane-2,5-diol, and 3,6-diathiaoctane-1,8-diol.

[0092] An exemplary mixed solvent system may comprise 15 to 25 wt.% of the at least one alkyl alcohol; 10 to 15 wt.% of the at least one diol; 1 to less than 3 wt.% of the at least one amine, 1 to 5 wt.% of the at least one thiolalkyldiol, and less than 0.1 wt.% of the surfactant (such as 0.001 to 0.1 wt.%), based on the total weight of the ink composition. Such a mixed solvent system may be preferred for certain metal complexes, such as a gold complex, which

may be included in this solvent system at 5 to 50 wt.%, such as 5 to 25 wt.%, or 5 to 15 wt.% based on the total weight of the ink composition.

[0093] The molecular inks can be prepared by mechanical mixing of the at least one polar protic solvent(s) and the at least one metal complex (e.g., an amine silver carboxylate, an amine copper carboxylate), and any of the optional components, such as the conductive fillers, surfactants, and any binders.

[0094] When included, the conductive filler can be blended with the particle-free metal complex, such as a particle-free silver precursor, in various weight ratios. Exemplary weight ratios include 50:50 metal complex : conductive filler, such as 60:40 metal complex : conductive filler, or 70:30 metal complex : conductive filler, or 80:20 metal complex : conductive filler, or 90:10 metal complex : conductive filler, or even 99:1 metal complex : conductive filler, and other ratios in-between.

[0095] As indicated, the molecular inks may comprise at least one conductive polymer. According to specific aspects, the ink may comprise a mixture of polypyrrole (PPy) and polyaniline (PANI). Formation of interpenetrated PANI/PPy networks play a decisive role in enhancing the conductive polymer film integrity and offer good film conformality during printing.

[0096] Certain conducting organic polymers are known to be excellent hosts for metal nanoparticles where cured nanoparticles may be embedded in the polymer matrix. In the past, PANI- or PPy-coated textiles have been used as substrates for a second coating with another conductive polymer such as PEDOT, PPy or PANI. In this case, such precoated textiles can be used to seed surfaces for silver printing which afford reduced temperature curing. In fact, the PPy-aided silver metalation can yield silver particles with different shapes and sizes in the nanometer and micrometer range. In addition to tuning the particle size of cured silver, the low temperature used for curing silver-printed textiles may not decompose the conductive fillers or seed layer.

[0097] The present inventors have recognized the potential of PPy to reduce amine silver carboxylates to metallic silver and use this potential as a new route to lower temperature curing of particle-free silver inks. Thus, the blending of conductive fillers in the molecular inks can enhance the performance of flexible electronic elements printed using such inks through improved mechanical, thermal, electrical, and other processing properties. The blending approach can minimize fabrication cost and promote easy process scale-up and commercialization by enabling sheet-to-sheet and roll-to-roll processing.

[0098] An exemplary molecular ink according to the present disclosure may comprise 10-40wt% of the at least one conductive filler material mixed with a metal complex at any of the above indicated ratios, 2-10wt% of alcohol or amine, 2-15wt% of glycol, 10-25wt% of a conductive filler solubilizer, and 40-70wt% of water. An exemplary filler solubilizer includes at least N-methyl-2-pyrrolidone.

[0099] To enhance the textile coating homogeneity, multiple printing cycles can be repeated from 1 to 20, as necessary. The printed textile can be cured or dried in between prints to avoid textile saturation. The resistance of the coated textile is optimally within 0.01 - 500 Ω/□, such as 0.01 - 300 Ω/□, or even 0.01 - 100 Ω/□ based on the film thickness and printed textile.

[0100] The viscosity of hydrogen bonding solvents is inherently greater than non-hydrogen bonding solvents such as hydrocarbons. Further the elevated solvent boiling points (due to energetically greater intermolecular forces) and polar ink nature render them capable and competent systems for the formation of thin films and structures of greater quality than strictly hydrocarbon or aromatic hydrocarbon delivery systems due to slower controlled drying times, surface tensions, and surface wetting properties. Thus, mixed solvent systems can provide superior application, solubility, and performance for the presently disclosed molecular inks.

[0101] The molecular inks of the present disclosure may be formulated to include hydrogels and/or polymers, such as polyacrylic acids, having lower molecular weights, and which may function as viscosity modifiers. For example, the compositions may include up to 5 wt.% of a hydrogel and/or polymer, such as up to 4 wt.%, or up to 3 wt.%, or up to 2 wt.%, or up to 1 wt.%, or up to 0.5 wt.%, or up to 0.1 wt.%, or up to 0.05 wt.%. The compositions may include hydrogels and/or polymers at from 0.01 wt.% to 5 wt.%, such as 0.01 wt.% to 4 wt.%, or 0.01 wt.% to 3 wt.%, or 0.01 wt.% to 2 wt.%, or 0.01 wt.% to 1 wt.%. The polymer may be a conductive polymer, such as any of the polyacetylenes, polyanilines, polyphenylenes, polypyrenes, polypyrroles, polythiophenes, etc. known in the art.

[0102] The metal complexes described herein may have a solubility in at least one polar protic solvent at 25° C of at least 50 mg/ml, or at least 100 mg/ml, or at least 150 mg/ml, or at least 200 mg/ml, or at least 250 mg/ml, or at least 300 mg/ml, or at least 400 mg/ml, or at least 500 mg/ml, or at least 1,000 mg/ml, or at least 1,500 mg/ml, or even or at least 2,000 mg/ml.

[0103] The amount of organic solvent in the molecular inks disclosed herein can be, for example, less than 30 wt. %, less than 20 wt. %, less than 10 wt. %, less than 5 wt. %, less

than 3 wt. %, less than 1 wt. %, less than 0.1 wt. % or less than 0.01 wt. %. The molecular ink formulations may be substantially or totally free of organic solvent.

[0104] The viscosity of the ink formulations measured at 25°C can be, for example, about 800 cps or less, about 500 cps or less, about 250 cps or less, or about 100 cps or less. According to certain other aspects, the viscosity of the ink formulations measured at 25°C can be, for example, about 50 cps or less, 40 cps or less, 30 cps or less, 25 cps or less, 20 cps or less, or even 10 cps or less. According to yet other aspects, the ink formulations have a viscosity of about 2 cps to about 20 cps, or about 2 cps to about 15 cps, or about 2 cps to about 10 cps.

[0105] The viscosity of the ink formulations measured at 25°C can be, for example, about 800 cps or more, such as about 1500 cps or more, about 2,500 cps or more, about 5,000 cps or more, or even about 10,000 cps or more.

[0106] The molecular inks can be formulated for a total metal complex concentration of 3 g/ml to 0.1 g/ml, 2 g/ml to 0.1 g/ml, such as 1.5 g/ml to 0.1 g/ml, or 1 g/ml to 0.1 g/ml, or 2 g/ml to 0.4 g/ml, or 1.5 g/ml to 0.4 g/ml. The molecular inks can be formulated for a pH in the range of 7 to 12. The molecular inks can be formulated for a viscosity of at least 2cP such as at least 5cP, or at least 10cP.

[0107] Analysis of the molecular ink formulations, in either of the organic or polar protic solvent systems, has shown that the amounts of the metal, and first and second ligands, in the ink solutions are stoichiometric (*see* Examples).

[0108] The molecular ink formulations may be substantially or totally free of particles, microparticles, and nanoparticles, and metal particles, such as metal microparticles and metal nanoparticles. In particular, the molecular ink formulations comprising the metal complex may be substantially or totally free of nanoparticles and/or metal nanoparticles before deposition or printing, and during deposition or printing. The molecular ink may be substantially or totally free of particles, including nanoparticles and/or metal nanoparticles, after deposition but before reduction to metal (e.g., before curing). For example, the level of nanoparticles can be less than 1 wt. %, less than 0.1 wt. %, or less than 0.01 wt. %, or less than 0.001 wt. %. The level of metal nanoparticles can be less than 1 wt. %, less than 0.1 wt. %, or less than 0.01 wt. %, or less than 0.001 wt. %. One can examine the composition for particles using methods known in the art including, for example, SEM and TEM, spectroscopy including UV-Vis, dynamic light scattering, plasmon resonance, and the like. Nanoparticles can have diameters of, for example, 1 nm to 500 nm, or 1 nm to 100 nm. Microparticles can have diameters of, for example, 0.5 μm to 500 μm, or 1 μm to 100 μm.

[0109] Upon cure, the ink forms a continuous conductive trace on the substrate, e.g., flexible substrate, and may include metal nanoparticles formed *in situ* during cure (see **FIGS. 8A-8B**). The metal nanoparticles may have diameters of 1-500nM, such as 5-100nM, or 10-50nM, or even 20-40nM (see **FIG. 8C**).

Metal complex

[0110] The metal complex may comprise a metal useful for forming electrically conducting lines, particularly those metals used in the semiconductor and electronics industries. Exemplary metals include at least silver, gold, copper, platinum, ruthenium, nickel, cobalt, palladium, zinc, iron, tin, indium, and alloys thereof. The metal complexes may comprise a single metal center or two metal centers.

[0111] For example, the metal complex may be a neutral metal complex comprising at least one metal, at least one first ligand, and at least one second ligand. The first ligand may be adapted to volatilize when heated without formation of a solid product. For example, the first ligand may volatize upon heating at a temperature of, for example, 250°C or less, or 200°C or less, or 150°C or less. Heating can be done in the presence or absence of oxygen. The first ligand may be a reductant for the metal. The first ligand may be in neutral state, such as neither an anion nor a cation.

[0112] The first ligand may be a monodentate ligand, or a polydentate ligand including, for example, a bidentate or a tridentate ligand. The first ligand may be a thioether, such as tetrahydrothiophene, a phosphine, or an amine compound. In certain examples, the first ligand may be a thioether, such as a thioether having the formula R_1-S-R_2, wherein R_1 and R_2 may be independently selected from C_1-C_3 alkyl or may form a saturated heterocyclic compound with the sulfur. Exemplary thioethers include at least dimethyl sulfide, diethyl sulfide, dipropyl sulfide, diisopropyl sulfide, ethyl methyl sulfide, and tetrahydrothiophene.

[0113] In certain examples, the first ligand may comprise an amine compound having at least two primary amine groups. Primary amines are stronger reducing agents than alcohols and can form homogenous solutions with polar protic solvents. Moreover, the first ligand may comprise two primary amine end groups and no secondary amine group, or one primary amine end group and one secondary amine end group. In this latter example, the secondary amine end group may be substituted with a linear alkane or a polar group, such as a hydroxy or alkoxy. In yet another example, the first ligand may comprise two primary amine end groups and one secondary amine group. The first ligand may be an amine including an alkyl amine. The alkyl groups can be linear, branched, or cyclic. Bridging alkylene can be used to link multiple nitrogen together. In the amine, the number of carbon atoms can be, for example, 15 or less, or

10 or less, or 5 or less. In particular examples, the first ligand is ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, diaminocyclohexane, or diethyl ethylenediamine.

[0114] The molecular weight of the first ligand, may be, for example, about 1,000 g/mol or less, or about 500 g/mol or less, or about 250 g/mol or less.

[0115] The second ligand is different from the first ligand and may also volatilize upon heating the metal complex. For example, the second ligand may release carbon dioxide, as well as volatile small organic molecules. The second ligand may be adapted to volatilize when heated without formation of a solid product. The second ligand may volatize upon heating at a temperature of, for example, 250°C or less, or 200°C or less, or 150°C or less. Heating can be done in the presence or absence of oxygen. The second ligand can be anionic. The second ligand may be self-reducing.

[0116] The second ligand may be a carboxylate. The carboxylate may comprise a linear, branched, or cyclic alkyl group. In one embodiment, the second ligand does not comprise an aromatic group. The second ligand may be an amide represented by —N(H)—C(O)—R, wherein R is a linear, branched, or cyclic alkyl group, with 10 or fewer carbon atoms, 8 or fewer carbon atoms, 6 or fewer carbon atoms, or 5 or fewer carbon atoms. The second ligand can also be an N-containing bidentate chelator. In particular examples, the second ligand may be isobutyrate, oxalate, malonate, fumarate, maleate, formate, glycolate, lactate, citrate, or tartrate.

[0117] The molecular weight of the second ligand, including the carboxylate, may be, for example, about 1,000 g/mol or less, or about 500 g/mol or less, or about 250 g/mol, or about 150 g/mol or less or less.

[0118] The second ligand may be a halide such as fluoride, chloride, bromide, iodide, or astatide.

[0119] Thus, the metal complex may comprise at least one metal, at least one first ligand, and at least one second ligand, wherein the metal may be silver, gold, platinum, or copper. Exemplary first ligands include amines and sulfur containing compounds, and exemplary second ligands include carboxylic acids, dicarboxylic acids, tricarboxylic acids, and halides. Exemplary solvents include one or more polar protic solvents, such as at least two polar protic solvents selected from the group comprising at least water, alcohols, amines, amino alcohols, polyols, and combinations thereof.

[0120] According to certain other aspects, the metal complex may comprise at least one first metal complex having at least one first metal, at least one second metal complex having at least one second metal, at least one third metal complex having at least one third metal, and

so forth, wherein each metal complex may comprise stoichiometric amounts of a metal and first and second ligands. For example, the metal complex may comprise two neutral metal complexes formed as detailed above (i.e., having stoichiometric amounts of a metal and first and second ligands).

[0121] According to certain other aspects of the present disclosure, the metal complex may be configured to provide a metal alloy (e.g., after curing in the textile substrate). The metal complex may comprise at least one first metal complex, wherein the first metal complex comprises a first metal and at least one first ligand and at least one second ligand, different from the first ligand; and at least one second metal complex, which is different from the first metal complex, and comprises a second metal and at least one first ligand and at least one second ligand, different from the first ligand, for the second metal; and at least one solvent. The (i) the selection of the amount of the first metal complex and the amount of the second metal complex, (ii) the selection of the first ligands and the selection of the second ligands for the first and second metals, and (iii) the selection of the solvent may be adapted to provide a homogeneous composition.

[0122] According to yet other aspects, the metal complex may comprise at least one first metal complex having at least one first metal in an oxidation state of (I) or (II), and at least two ligands, wherein at least one first ligand is an amine and at least one second ligand is a carboxylate anion; at least one second metal complex, which is different from the first metal complex, wherein the second metal complex is a neutral complex comprising at least one second metal in an oxidation state of (I) or (II), and at least two ligands, wherein at least one first ligand is a sulfur compound and at least one second ligand is the carboxylate anion of the first metal complex.

[0123] According to certain other aspects of the present disclosure, the metal complex may comprise at least one first metal complex, wherein the first metal complex is a neutral, dissymmetrical complex comprising at least one first metal in an oxidation state of (I) or (II), and at least two ligands, wherein at least one first ligand is an amine and at least one second ligand is a carboxylate anion; at least one second metal complex, which is different from the first metal complex, wherein the second metal complex is a neutral, dissymmetrical complex comprising at least one second metal in an oxidation state of (I) or (II), and at least two ligands, wherein at least one first ligand is sulfur compound and at least one second ligand is the carboxylate anion of the first metal complex; at least one organic solvent, and wherein the atomic percent of the first metal is about 20% to about 80% and the atomic percent of the second metal is about 20% to about 80% relative to the total metal content.

[0124] Exemplary metals for use in these metal alloys include Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Hg. In particular, coinage metals can be used including silver, gold, and copper. Precious metals can be used including gold, iridium, osmium, palladium, platinum, rhodium, ruthenium, and silver. In other preferred embodiments, platinum, nickel, cobalt, and palladium can be used. Still further, lead, iron, tin, ruthenium, rhodium, iridium, zinc, and aluminum can be used. Other metals and elements can be used as known in the art.

[0125] The first metal complex is a silver, gold, copper, platinum, nickel, iridium, or rhodium complex. For example, the first metal complex may be a silver complex. The second metal complex is a silver, gold, copper, platinum, nickel, iridium, or rhodium complex. For example, the second metal complex may be a gold complex. Examples of binary combinations of metals to form binary alloys include at least Ag-Au, Pt-Rh, Au-Cu, Zn-Cu, Pt-Cu, Ni-Al, Cu-Al, Pt-Ni, and Pt-Ir.

[0126] The metal complexes of the metal alloy can comprise a plurality of ligands including two or more ligands, or just two ligands. There can be, for example, a first ligand and a second ligand, different from each other. The first ligand can provide sigma electron donation, or dative bonding. The first ligand can be in a neutral state, not an anion or cation. Examples of the first ligand include amines, oxygen-containing ligands, and sulfur-containing ligands including oxygenated ethers and thioethers, including cyclic thioethers. Asymmetrical or symmetrical amines can be used. The amines can comprise, for example, at least two primary or secondary amine groups. Monodentate ligands can be used. Polydentate or multidentate ligands can be used. Alkylamino ligands can be used.

[0127] The second ligand can be different from the first ligand and can volatilize upon heating the metal complex. For example, it can release carbon dioxide, as well as volatile small organic molecules such as propene, in some embodiments. The second ligand can be a chelator with minimum number of atoms that can bear an anionic charge and provide a neutral complex. The second ligand can be anionic. For example, the second ligand can be a carboxylate, including a carboxylate comprising a small alkyl group. The number of carbon atoms in the alkyl group can be, for example, ten or less, or eight or less, or five or less. The molecular weight of the second ligand can be, for example, about 1,000 g/mol or less, or about 250 g/mol or less, or about 150 g/mole or less.

[0128] The metal complexes of the present disclosure can be substantially or totally free of particles, including nanoparticles and microparticles, when in the dried state (powder)

or when formulated as an ink in at least one solvent (i.e., particle-free composition comprising the metal complex and at least one solvent).

Tuning resistivity of the conductive traces

[0129] The high solubility of the metal complex in the solvent systems disclosed herein provide cured continuous conductive films or traces having high conductivity / low resistance. For example, a silver ink according to the present disclosure provides traces having a resistance of less than 1 Ω, wherein the trace comprises at least 90% metal, such as at least 95% metal, or 96% metal, or 97% metal, or 98% metal, or 99% metal, or even as much as 99.5% metal.

[0130] The resistivity of the conductive traces may be tuned by addition of a second metal complex in the molecular ink. For example, the present inventors have found that molecular inks comprising at least a second metal complex may provide conductive traces having increased resistivity. The molecular inks capable of forming such resistive coatings may comprise a first metal complex and a second metal complex. Exemplary combinations of metal complexes comprise any combination of silver, gold, platinum, and copper complexes, such as silver complexes and copper complexes, or silver complexes and gold complexes, etc.

[0131] The molecular inks may comprise various ratios of the first and second metal complexes, such as 1-99 wt. % or the first metal complex and 99-1 wt.% of the second metal complex. As a specific example, the molecular inks may comprise 99-75 wt. % silver complex, such as a silver amine carboxylate, and 1-25 wt. % of a copper complex, such as a copper amine carboxylate, based on the total weight of metal complex in the molecular ink.

[0132] Exemplary mixed metal molecular inks having increased resistivity include those comprising 99-75 wt. % of amine silver carboxylate (e.g., silver diamine carboxylate such as silver diamine isobutyrate or silver diamine oxalate) and 1-25 wt. % of amine copper carboxylate (e.g., copper diamine carboxylate), based on the total weight of metal complex in the molecular ink; and may further comprise a solvent system having one or more polar protic solvents, i.e., water and an amine as indicated hereinabove, and optionally, a surfactant.

Direct printing and deposition methods

[0133] Methods known in the art can be used to deposit the presently disclosed molecular inks including, for example, pipetting, inkjet printing, lithography or offset printing, gravure or gravure offset printing, flexographic printing, microdispersion direct write printing, screen printing or rotary screen process printing, offset printing, stencil printing, drop casting, slot die, roll-to-roll, stamping, roll coating, spray coating, flow coating, extrusion printing, and aerosol delivery such as spraying or pneumatic or ultrasonic aerosol jet printing. One can adapt the ink formulation and the substrate with the deposition method.

[0134] The disclosed molecular inks may be deposited by direct printing methods such as pipetting, stencil printing, rolling, spraying, inkjet printing, or aerosol jet . In certain examples, the molecular inks are deposited using inkjet or aerosol jet printing.

[0135] The disclosed molecular inks may be printed directly onto a surface of the flexible substrate, e.g., surface of a woven or non-woven textile or polymeric film.

[0136] Certain flexible substrates may benefit from pre-treating. For example, for textile substrates, pre-treatment such as prewashing the textile and optionally treating by oxygen plasma, corona, and/or chemical etch (e.g., acidic, caustic). Accordingly, the molecular inks of the present disclosure may be printed on the textile substrate after it has been pretreated by oxygen plasma, corona, and/or chemical etch.

[0137] Certain flexible substrates may benefit from addition of a coating. For example, cellulose based substrates such as paper and/or cotton textiles may need a coating to reduce ink bleed and enhance conductivity of traces formed thereon. That is, the cellulose or cotton-based substrates may be coated with a transparent layer, such as a polyurethane coating prior to printing the conductive pattern.

[0138] One can adapt the viscosity of the disclosed molecular inks to the deposition method. For example, viscosity can be adapted for inkjet or aerosol jet printing. Viscosity of the ink formulations measured at 25°C can be, for example, about 500 cps or less, such as 200 cps or less, or 50 cps or less, or even 25 cps or less. Viscosity of the ink formulations measured at 25°C can be, for example, at least 50 cps. Viscosity of the ink formulations measured at 25°C can be, for example, about 50 cps or less, such as about 25 cps or less. According to certain other aspects, the viscosity of the ink formulations measured at 25°C can be, for example, about 2 cps to about 20 cps, or about 2 cps to about 10 cps. Viscosity of the ink formulations may be tuned through selective ratios of polar protic solvents (e.g., ratio of water to amine).

[0139] Alternatively, the viscosity of the disclosed molecular inks can be formulated, for example, to be greater than 15 cps, or 20 cps, or even 25 cps, such as by addition of binders, resins, or other additives or solids that may thicken or increase the viscosity of the ink formulation. For example, one can adapt the concentration of dissolved solids in the ink to about 2,000 mg/ml, or 1,500 mg/ml or less, about 1,000 mg/ml or less, about 500 mg/mL or less, about 250 mg/mL or less, about 100 mg/mL or less, about 50 mg/mL or less, or about 10 mg/mL or less.

[0140] Additives may also be included to adapt the wetting properties of the disclosed molecular inks. Additives such as, for example, surfactants, dispersants, colorant (e.g., dye), and/or binders can be used to control one or more ink properties as desired. For example, a

hydrophilic binder may aid in wetting certain textiles, and thus may aid in providing a conductive trace that conformally coats the textile fibers (i.e., improve conductivity of the conductive trace). For example, the molecular ink formulations may include up to 10 wt.% of one or more additives, such as up to 8 wt.%, or up to 6 wt.%, or up to 4 wt.%, or up to 2 wt.%, or up to 1 wt.%, or up to 0.1 wt.%, or up to 0.05 wt.%. The compositions may include additives at from 0.001 wt.% to 5 wt.%, such as 0.001 wt.% to 4 wt.%, or 0.001 wt.% to 3 wt.%, or 0.001 wt.% to 2 wt.%, 0.001 wt.% to 1 wt.%, or 0.001 wt.% to 0.1 wt.%, based on the weight of the ink formulation.

[0141] According to certain aspects, molecular ink formulations of the present disclosure may be substantially or totally free of additives such as surfactants, dispersants, colorant (e.g., dye), and/or binders.

[0142] Nozzles can be used to deposit the precursor, and the nozzle diameter can be, for example, less than 200 micrometers, or even less than 100 micrometers, or even less than 50 micrometers. The absence of particulates can help with prevention of nozzle clogging. The nozzle may deposit the ink in droplets, wherein a drop size may be less than 200 micrometers, such as less than 100 micrometers, or less than 50 micrometers, or even less than 30 micrometers. The nozzle may deposit the ink in droplets, wherein a drop volume is less than 100 picoliter (pL), or less than 50 pL, or less than 25 pL, or even less than 15 pL, or even less than 5 pL. The drops may be deposited at a density greater than 30 drops per inch, such as greater than 60 drops per inch, or greater than 90 drops per inch, or greater than 200 drops per inch, or greater than 500 drops per inch, or greater than 1,000 drops per inch, or greater than 1,500 drops per inch, or greater than 2,500 drops per inch, or greater than 4,000 drops per inch, or greater than 6,000 drops per inch.

[0143] While specific numbers are listed herein for the size and density of the droplets, volume of the droplets, and the nozzle size, these values may vary depending on the printing method chosen, the printer chosen (e.g., nozzle configuration), the viscosity of the molecular ink, and the coverage desired.

[0144] The molecular inks may be printed on flexible substrates at ambient conditions, such as at standard room temperatures and pressures.

[0145] The flexible substrate may be heated before and/or during deposition of the ink. For example, the flexible substrate may be heated to temperatures of 40°C to 90°C. With reference to **FIG. 6**, an exemplary inkjet printer **10** is shown which includes a heated platen **12** and a nozzle assembly **14**. In use, the molecular inks of the present disclosure may be loaded to the printer **10** so that droplets of the ink may be deposited. The platen **12** may be heated to

temperatures of at least 30°C, such as at least 35°C, or at least 40°C, or at least 45°C, or at least 50°C, or at least 55°C. The platen **12** may be heated to temperatures of up to 90°C, such as up to 85°C, or up to 80°C, or up to 75°C, or up to 70°C, or up to 65°C, or up to 60°C, or up to 55°C. Any upper and lower temperature may be combined to define a temperature range for heating the platen during printing, such as 30°C to 90°C during printing, or 40°C to 80°C, and the like.

[0146] Thus, according to certain methods of the present disclosure, the molecular inks may be deposited on a substrate such as a textile that is heated at low temperatures during deposition, followed by a curing step that converts the metal complex in the ink formulation to a metallic structure, wherein the curing step may be by any of the curing steps detailed herein.

[0147] According to certain other methods of the present disclosure, the disclosed molecular inks may be deposited on a substrate such as a textile at ambient temperatures (and pressures), followed by a curing step that converts the metal complex in the ink formulation to a metallic structure, wherein the curing step may comprise any of the curing steps detailed herein.

[0148] The printed textile or fabric can be cured or dried in between prints to avoid fabric saturation. The resistance of the coated fabric is generally within 0.01 - 500 Ω/□ based on the trace dimension (e.g., thickness), molecular ink composition, and printed flexible substrate, e.g., fabric.

[0149] An exemplary silver ink formulation may include a silver complex having stoichiometric amounts of first and second ligands, dissolved in two or more polar protic solvents, such as water and any of an alcohol and/or amine. Generally, such an ink solution is formulated to include the silver complex at 250 mg/ml or greater, such as 500 mg/ml. These solutions are clear. Heating the textile during deposition of the molecular ink may reduce the ink bleed outside of the printed region. For example, the conductive traces formed using the inks and methods of the present disclosure may exhibit an ink bleed of less than 0.5 mm, such as less than 0.4 mm, or less than 0.3 mm, or less than 0.2 mm, or even less than 0.1 mm. As used herein, the term "ink bleed" may be taken to mean a measure of the precision of the ink deposition and is referred to in terms of the distance from a defined edge (intended border) of a printed trace that the ink may extend.

[0150] An exemplary solution of 500mg/ml of an ink composition according to aspects of the present disclosure may have a viscosity of about 5-15 cps at 25°C, a density of about 1.0-1.3 g/mL, a pH of at least 10-13, a surface tension of about 15-34 dyne/cm, and a silver content of about 15-25wt.%. Ink jet printing of such an ink may include depositing the ink as droplets of between 5-200 micrometers at 60-6,000 drops per inch to a flexible substrate heated

at between 30°C to 90°C on the platen **12** (**FIG. 6**), such as 65 micrometers at 1270 drops per inch. The textile may then be cured.

[0151] Curing may be accomplished by heating the substrate to a temperature of greater than 100°C but less than 200°C for a time of 1 to 30 minutes, such as for between 2-20 minutes at 140°C, or 10 minutes at 140°C. Curing may also be accomplished by exposing the substrate to infrared radiation for a time of less than 30 minutes, such as for between 2-20 minutes, or 10 minutes. The textile may be cured by photonic curing technology using a photonic source such as a radiation source in the electromagnetic spectrum including, but not limited, to ultraviolet, visible, infrared, microwaves, or combinations thereof. The poor conductivity, low absorptivity and high thermal mass of the substrates used herein ensure the energy from a pulse from the photonic source heats the traces printed on the substrate with minimal energy transfer to the substrate or surrounding components (i.e., may cure the printed trace to form the conductive pattern with minimal heating of the substrate so that heat sensitive substrates remain substantially unaffected).

[0152] Exemplary line width resulting from this method may about 2mm and may show an ink bleed of less than 0.5 mm, such as less than 0.2mm, or even less than 0.1mm. Moreover, the pattern demonstrated a resistivity of less than 10Ω/□, such as less than 5Ω/□, or less than 1Ω/□, or from 0.1 Ω/□ to 0.9 Ω/□.

[0153] The conductive traces of the present disclosure may have sheet resistance values of less than 10.0 Ω/□, or less than 8.0 Ω/□, or less than 6.0 Ω/□, or less than 4.0 Ω/□, or less than 2.0 Ω/□, or less than 1.0 Ω/□, such as from 0.1 Ω/□ to 1.0 Ω/□. Certain applications of the conductive traces may benefit from increased sheet resistance, such as more than 2.0 Ω/□ or 10.0 Ω/□, such as resistive heaters.

[0154] Exemplary systems that may be used in methods of the present disclosure include Fujifilm Dimatix DMP 2850 and DMP 2931. Using this printer, the molecular inks of the present disclosure may be printed to textiles pre-heated on the platen using a drop size of 5-200 micrometers, or a drop volume of less than 100 pL, at 60-6,000 drops per inch. The textile may then be cured on the platen in the device, such as for 10 minutes at 140°C or 10 minutes exposure to infrared radiation or via photonic curing technology or may be removed to an oven or other area for curing, wherein the metal in the metal complex turns to a solid conductive metal. In preferred embodiments, the textile is removed from the platen and printer for curing. Curing may be by any method disclosed herein.

[0155] Key factors effecting the conductivity achievable by the presently disclosed inks and printing methods include compatibility of the ink chemistry with the surface energy of the textile, the textile size and structure (woven, non-woven), pretreatment of the textile, such as with O_2 plasma, and the curing methods, such as the *in situ* heating of the textile during printing which provides high resolution traces, and the low temperature curing after printing is complete (>100°C but < 200°C; *see* section below regarding curing). Thus, the presently disclosed inks and methods provide a large advantage over the prior art inks shown in **FIGS. 1A-1E**, wherein the particles of the ink may clog the nozzles of an inkjet device, and traces formed using the inks are generally non-conductive (i.e., show extremely high sheet resistance) and non-compatible with many textiles as they require high cure temperatures.

[0156] An exemplary textile printed as detailed above is shown in **FIGS. 7A-7C**. Shown in **FIG. 7A** is a close-up view of a woven textile substrate having a printed section (left) and a non-printed section (right), wherein printing was on a heated substrate using the molecular inks of the present disclosure. **FIGS. 7B** and **7C** show scanning electron microscopy images (SEM) of the printed textile taken by SEM (150x and 800x magnification). These images demonstrate that the heating the substrate during printing provides better "dying" of the fibers of the substrate. That is, the particle-free inks according to the present disclosure may better penetrate (e.g., soak into the fibers of the textile), or may more completely coat an outer surface (e.g., encapsulate or soak into an outer surface of the textile; conformal coating) of a heated textile substrate, acting as a dye on the textile substrate and improving the conductivity of patterns formed in the heated substrates. Prior art molecular inks, which comprise particles (nanoparticles, flakes, etc.), would not be able to penetrate the textile and were found to sit on top of the textile substrate as shown in **FIGS. 1A** and **1B**. This leaves the prior art inks more susceptible to removal by abrasion and other forces exerted on the textile substrate through standard wear and tear. Thus, the *in-situ* heating at low temperatures, such as 30°C to 90°C, promotes better coating around the fabric thread (i.e., conformal coating; *see* **FIG. 2B**).

[0157] The present inventors have found that *in situ* heating improves the sheet resistance values for textiles (knit, woven, and nonwoven such as Evolon®) printed with the molecular inks and cured according to the present disclosure for most textile substrate, as compared to printing in the absence of the *in-situ* heating. Printing on the substrate that is heated (*in-situ* heating) lowers the sheet resistance, in some cases several orders of magnitude over values measured from conductive traces and reduces the ink bleed. These results were consistent for all numbers of printed layers tested (number of layers in the conductive trace). Thus, methods of the present disclosure, which include heating of the textile during deposition

of the ink, such as by ink jet or aerosol jet printing, not only leads to improved trace resolution, but also improved conductivity of the trace.

[0158] Additionally, the sheet resistance values for knit and non-woven (Evolon®) textiles printed with the molecular inks according to the present disclosure were improved by pretreatment by oxygen plasma or corona. Accordingly, methods of the present disclosure, which include heating of the textile before and/or during deposition of the ink, such as by ink jet or aerosol jet printing, may also include pretreatment of the textile.

Curing the molecular inks

[0159] Once the disclosed molecular ink formulations have been printed onto a flexible substrate, at either ambient temperatures (<30°C) or elevated temperatures (e.g., 30°C to 90°C), they may be cured to form the conductive pattern (i.e., converted to a metallic structure). Curing can include heating the printed substrate and/or irradiating the printed substrate. In certain examples, the printed substrate may be cured by heating to a temperature of at least 100 °C, or at least 110°C, or at least 120°C, or at least 130°C, or at least 140°C, but less than 250°C, such as less than 220°C, or 200°C, or 180°C, or 160, or 150°C. Any combination of upper and lower cure temperature may define a temperature range for curing the ink. Curing may be at the noted temperatures for a time of less than 60 minutes, such as less than 30 minutes, or less than 15 minutes. In a particular example, the printed substrate is heated to 140°C for 10 minutes, or exposed to infrared radiation for 10 minutes, or pulsed with a photonic emission source, to form a conductive pattern with a resistance of less than 1 Ω/□.

[0160] Sheet resistance values for knit, woven, and nonwoven textiles, wherein the substrate was heated or not during deposition of the molecular inks (i.e., printed on the textile at ambient temperatures and cured; or printed on the textile at elevated temperatures and cured) were tested. The lowest sheet resistance was found for conductive traces on woven polyester, wherein the textile was at ambient or elevated temperatures during printing, while both the knit and nonwoven textiles benefited from printing on a heated substrate.

[0161] In certain examples, the conductive trace on the textile substrate may be additionally, or alternatively, cured by exposure to pulsed light, such as by photonic curing, wherein the number of pulses ranges from 2 to 20. Alternatively, or in addition, curing may include irradiating the conductive trace on the textile substrate, such as by exposure to infrared radiation.

Protective coatings

[0162] The conductive traces on the 3D articles formed using the molecular inks disclosed herein may be coated with a protective coating, such as a dielectric coating. For

example, all or a portion of a trace may be coated with an aqueous dielectric polymer solution. Exemplary polymer solutions include at least acrylic and polyurethane polymers.

[0163] The protective coating can be deposited by painting, spraying, dipping, or printing (e.g., inkjet or aerosol jet, gravure, flexographic, or screen-printing techniques). For example, the viscosity measured at 25°C may be 2 to 40 centipoise for inkjet printing, or 100 to 400 centipoise for flexographic printing, or 50 to 300 centipoise for gravure printing. The viscosity of the polymeric solutions can be adjusted for the specific textile and deposition method by dilution with appropriate solvents and solvent mixtures. Such coatings may be cured by heat treatment, evaporation of solvents, irradiation (e.g., UV treatment), or any combination thereof. An exemplary coating includes an acrylic-based coating that is printed over the conductive trace and is cured by heating the textile to a temperature of at least 80°C, such as at least 90°C, or at least 100°C, but 160°C or less, such as 150°C or less, or 150°C or less for 30 minutes or less, such as 20 minutes or less.

[0164] An exemplary protective dielectric coating composition is disclosed in in U.S. Pat. Application Publication No. US 2020/0283653, which includes an aqueous binder, an inorganic nanoparticle having a particle size of less than 250nm, and one or more polar protic solvents. The aqueous binder may be a polyvinyl alcohol, a hydroxy cellulose, a hydrogel, or a combination thereof. The inorganic nanoparticle may be SiO_2 nanoparticles, Al_2O_3 nanoparticles, TiO_2 nanoparticles, ZrO_2 nanoparticles, nanoclay, or a combination thereof. The inorganic nanoparticle may be a colloidal particle. The inorganic nanoparticle may have a particle size of less than 100nm, or even less than 50nm. Accordingly, an exemplary protective dielectric coating composition may comprise 2-15 wt.% of an aqueous binder, 1-5 wt.% of a colloidal silica having a particle size of less than 100nm, and an aqueous solvent, wherein the composition has a viscosity measured at 25°C of 2 to 400 centipoise.

[0165] The coatings may be cured via heat, such as by exposure to temperatures of 250°C or less, such as 240°C or less, or 230°C or less, or 220°C or less, but at least 80°C, or at least 90°C, or at least 100°C, for 30 minutes or less, or by photonic curing. The dielectric coating composition may be dried before curing, such as at ambient temperatures of temperatures above ambient (30°C to 80°C). .

[0166] The coatings may improve washability of the conductive traces, as shown in **FIG. 11**, and may also improve abrasion resistance of the conductive traces (see **Table 5** in examples).

[0167] Additional conductive coatings may be provided over contact regions, such as at the contact points or pads of a trace. Such coatings may include conductive polymers and

may provide conductive contact with the printed trace while also protecting the trace from abrasion and/or during wash cycles.

Definitions and Abbreviations.

[0168] Various aspects of the molecular inks, traces printed using those inks, and printed electronic elements and devices disclosed herein may be illustrated by describing components that are coupled, attached, and/or joined. As used herein, the terms "coupled," "attached," and/or "joined" are interchangeably used to indicate either a direct connection between two components or, where appropriate, an indirect connection to one another through intervening or intermediate components. In contrast, when a component is referred to as being "directly coupled", "directly attached," and/or "directly joined" to another component, there are no intervening elements shown in said examples.

[0169] Various aspects of the molecular inks, traces, printed electronic elements and devices, and methods disclosed herein may be described and illustrated with reference to one or more exemplary implementations. As used herein, the term "exemplary" means "serving as an example, instance, or illustration," and should not necessarily be construed as preferred or advantageous over other variations of the devices, systems, or methods disclosed herein. "Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where the event occurs and instances where it does not. In addition, the word "comprising" as used herein means "including, but not limited to."

[0170] Relative terms such as "lower" or "bottom" and "upper" or "top" may be used herein to describe one element's relationship to another element illustrated in the drawings. It will be understood that relative terms are intended to encompass different orientations of the elements and/or devices disclosed herein in addition to the orientation depicted in the drawings. By way of example, if aspects of a thermoformable printed electronic substrate shown in the drawings are turned over, elements described as being on the "bottom" side of the other elements would then be oriented on the "top" side of the other elements as shown in the relevant drawing. The term "bottom" can therefore encompass both an orientation of "bottom" and "top" depending on the orientation of the drawing.

[0171] It must also be noted that as used herein and in the appended claims, the singular forms "a," "an," and "the" include the plural reference unless the context clearly dictates otherwise. For example, although reference is made to "a" substrate, "an" upper layer, "a" metal, "an" ink, and "the" metal complex, one or more of any of these components and/or any other components described herein can be used.

[0172] Moreover, other than in any operating examples, or where otherwise indicated, all numbers expressing, for example, quantities of ingredients used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and appended claims are approximations that may vary depending upon the desired properties to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0173] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

[0174] "Substantially free," as used herein, is understood to mean inclusive of only trace amounts of a constituent. "Trace amounts" are those quantitative levels of a constituent that are barely detectable and provide no benefit to the functional properties of the subject composition, process, or articles formed therefrom. For example, a trace amount may constitute 1.0 wt.%, 0.5 wt.%, 0.1 wt.%, 0.05 wt.%, or even 0.01 wt.% of a component of any of the particle-free ink formulations disclosed herein. "Totally free," as used herein, is understood to mean completely free of a constituent.

[0175] The terms flexible substrate and textile substrate are used interchangeably throughout the specification and may be understood to mean any woven or non-woven, organic, or synthetic substrate unless specifically indicated otherwise. Moreover, when a fiber is referred to, it may be part of a woven or non-woven flexible substrate unless specifically indicated otherwise.

[0176] Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art.

EXAMPLES

Production of a molecular ink

[0177] Exemplary molecular inks comprising silver complexes comprising a carboxylate second ligand (e.g., silver carboxylate) may be formed by reaction of a metal oxide

or metal-acetate and a carboxylic acid in a reaction that affords analytically pure compounds and proceeds in quantitative yields.

[0178] As example, silver acetate was reacted with a carboxylic acid (isobutyrate and cyclopropate). The elemental analysis of the two silver complexes were C, 24.59; H, 3.72 and C, 24.68; H, 2.56 for the isobutyrate and cyclopropate, respectively. Theoretical values are C, 24.64; H, 3.62 and C, 24.90; H, 2.61 for the isobutyrate and cyclopropate, respectively.

[0179] The metal-second ligand salt was then reacted with an excess of the first ligand to form the metal complex. In a typical preparation, silver isobutyrate was prepared as described above, and placed in a 25 mL one-neck 14/20 round bottom flask containing a Teflon coated magnetic stir bar. To this was added 13 eq. ethylenediamine (amounts as shown in **Table 1** below). The reaction proceeded for 2 h at room temperature with stirring, filtered to remove any particulates, and the unreacted ethylenediamine was removed by rotary evaporation at 40°C to yield a white powder. Additional wash steps can be included. The isolated metal complex - ethylenediamine silver isobutyrate – was then dissolved to at least 100 mg/ml in a mixture of polar protic solvents (water, propylene glycol, and isopropanol) to form a molecular ink that is clear (*see* **Table 2**).

Table 1

Diamine Amount (ethylenediamine)	Silver (I) Carboxylate Amount (Silver isobutyrate)	Yield
184g, 3059mmol, **13equiv.**	46g, 235mmol, **1 equiv.**	59g (99%)

Table 2

Isolated Metal Complex	Water	Propylene glycol	Isopropanol
2.20g (30%)	3.08g (42%)	0.77g (11%)	1.25g (17%)

Purity of the metal complex

[0180] Preparation of the metal complexes was found to require an excess of the first ligand reactant with the metal-second ligand (*see* table above; 13-fold excess second ligand used to produce the metal complex). As example, most silver (I) carboxylates are insoluble in most conventional solvents. A 1:1 reaction (1:1 silver isobutyrate: ethylenediamine) gave a dark colored product with a large amount of insoluble material, presumably unreacted silver (I) isobutyrate, when formulated in a polar protic solvent system. Thus, the metal complexes formed by the 1:1 reaction likely failed to promote complete conversion of all reactants to products and failed to form continuous conductive films on a substrate.

[0181] A 1:6 reaction (1:6 silver isobutyrate: ethylenediamine), on the other hand, formed crystals spontaneously from a filtered solution of the reaction. Moreover, while the metal complex did dissolve in the polar protic solvent system, the presence of excess unreacted diamine was found to have a significant impact on the density, viscosity, and surface tension of the ink formulations. The 1:6 product formulated as an ink shows poor sheet coverage and extremely high sheet resistance (>600,000 Ω/□).

[0182] The 1:13 reaction product listed in the table above, which was purified to remove excess unreacted amine (first ligand), showed excellent sheet coverage, and demonstrated a sheet resistance of less than 1Ω/□. The purified product, dissolved in a polar protic solvent system as shown in **Table 2**, showed a density of 1.12 g/mL, a viscosity of 8.55 cps, and a surface tension of 22.9 dyne/cm.

[0183] Accordingly, an important step in producing the molecular inks of the present disclosure is removal of any unreacted second ligand, especially in view of the large excess used to formulate the final metal complex. When purified as detailed above, the product (yield 99%) is colorless. Unpurified products, however, tend to be dark colored, which is likely associated with normal darkening of diamines when exposed to open air. In general, amines absorb moisture and carbon dioxide resulting in formation of unstable carbamates. Such speciation of amines may destabilize diaminosilver (I) carboxylates, which often results in premature silver metallization, dark coloration, and particle formation. Hence, removal of any residual amines is important to promote stability of diaminosilver (I) carboxylates, especially if concomitant preparation of zero-particulate diaminosilver (I) carboxylate compositions is required.

Stoichiometric ratio of ligands and metal in the metal complex

[0184] The metal complex was found to comprise stoichiometric amounts of the first and second ligands and the metal. Structural analysis using proton NMR showed that the ethylenediamine silver isobutyrate powder dissolved in D_2O consists of stoichiometric amounts of the ethylenediamine ligand coordinated to silver isobutyrate. A ^{1}H-NMR spectrum of the metal complex in D_2O (*see* **FIG. 9**; ^{1}H-NMR scan on a Bruker AV-360 spectrometer) showed the expected three proton-carbon (CH) peaks: one for the two ethylenediamine CH_2 groups (4 protons total), one for the single isobutyrate CH group (1 proton), and one for the two isobutyrate CH_3 groups (6 protons total). These were assigned as: 0.93 ppm isobutyrate CH_3, 2.25 ppm isobutyrate CH, and 2.81 ppm ethylenediamine CH_2. The proton integral ratio of 3.978 ethylenediamine CH_2: 0.928 isobutyrate CH: 6.151 isobutyrate CH_3 is consistent with 1

ethylenediamine: 1 silver isobutyrate, or stoichiometric amounts of the metal, and each of the ethylenediamine and isobutyrate ligands.

[0185] In order to verify that the metal complex, when dissolved in two or more polar protic solvents to form the ink, maintains a stoichiometric ratio of the first and second ligands and the metal, further ^{1}H-NMR experiments were performed for the metal complex dissolved in a mixture of three polar protic solvents as listed above (water, propylene glycol, isopropanol), and D_2O. The spectra in **FIG. 10** shows well-resolved peaks for the various polar protic solvents as well as the metal complex (ethylenediamine silver (I) isobutyrate), which are assigned as: 0.93 ppm (doublet, isobutyrate CH_3), 2.25 ppm (septet, isobutyrate CH), and 2.81 ppm (singlet, ethylenediamine CH_2).

[0186] The strong similarity between the chemical shifts of the metal complex in the NMR solvent (**FIG. 9**) and in the composition comprising the metal complex and two or more polar protic solvents (**FIG. 10**) suggests excellent compatibility between the metal complex and the polar protic solvent system. The ethylenediamine silver (I) isobutyrate proton ratios of 4.098 ethylenediamine CH_2 : 0.944 isobutyrate CH : 6.446 isobutyrate CH_3 are in good agreement with theoretical ratios of 4 ethylenediamine CH_2 : 1 isobutyrate CH : 6 isobutyrate CH_3; which demonstrates that dissolving the metal complex in a polar protic solvent carrier does not impact the coordination environment around the metal (i.e., silver). This result further corroborates the fact that the chemical composition of the metal complex remains unchanged when dissolved to form the ink composition (i.e., stoichiometry remains unchanged).

Formulation of molecular inks

[0187] Various polar protic solvent systems were tested to demonstrate the flexibility of the solvent choice for formulation of the molecular inks of the present disclosure (*see* **Tables 3** and **4** below). For example, a diamine silver (I) isobutyrate complex was formulated in solvent systems comprising at least two polar protic solvents. Representative ink formulations using different combinations of polar protic solvents, and data showing that the ink formulations produce continuous, highly conductive films (sheet resistance of 0.04-0.09 Ω/□) when formulated in the polar protic solvents are shown in **Tables 3** and **4**.

Table 3

Metal Complex Formulated in Polar Protic Solvent Systems							
composition	metal complex	water	Glycol		Glycol ether (dowanol)	Alcohol	
			ethylene glycol	propylene glycol		ethanol	isopropanol
A	2.20g	3.08g	-	0.77g	-	-	1.25g
B	2.01g	-	-	0.77g	-	-	4.25g
C	2.03g	4.27g	-	0.78g	-	-	-

D	2.03g	4.26g	0.75g	-	-	-	-
E	2.00g	3.00g	-	0.27g	-	-	1.75g
F	2.01g	3.07g	-	0.13g	-	-	1.91g
G	2.00g	3.06g	-	1.5g	-	-	0.51g
H	2.00g	3.02g	0.75g	-	-	-	1.26g
I	2.02g	3.03g	-	0.76g	-	1.26g	-
J	2.04g	3.03g	-	0.76g	1.26 g	-	-
K	2.09g	3.01g	-	0.51 g	0.76 g		0.76 g

Table 4

composition	Density (g/mL)	Viscosity (cP)	Surface Tension (dyne/cm)	Sheet Resistance (Ω/□)
A	1.12	8.55	22.9	0.05
B	0.937	10.8	23.3	0.04
C	1.15	4.60	25.3	0.08
D	1.15	3.77	24.7	0.08-0.09
E	1.09	6.99	23.6	0.06
F	1.08	6.71	22.7	0.06
G	1.14	8.83	23.3	0.05
H	1.11	7.02	23.5	0.08
I	1.11	21.3	23.8	0.06
J	1.14	8.25	23.5	0.9-01
K	1.12	8.21	22.7	005-0.06

Molecular inks comprising two different metal complexes

[0188] A molecular ink comprising two different metal complexes was formed, with the goal to provide a molecular ink that provides tunable resistivity of cured films formed therefrom. For example, a molecular ink comprising soluble silver complex and copper complex was formulated in a polar protic solvent system. The use of soluble metal complexes, i.e., metal complexes that provide molecular inks absent particles, circumvents agglomeration and settling issues related to commercial resistive inks based on particle dispersion, i.e., carbon, graphite, graphene. This provides a more reliable, robust manufacturing process since ink instability can lead to production down-time due to nozzle blockage, cause inconsistent or poor-quality prints, and potentially requiring replacement of a high-cost print-head.

[0189] The present inventors have found that the resistivity of the mixed metal complex molecular ink may be tunable by adjusting the ratio of two metal complexes. An exemplary mixed metal complex molecular ink according to the present disclosure comprises a silver complex and a copper complex, such as a silver diamine carboxylate complex and a copper

diamine carboxylate complex. According to certain aspects, the copper diamine carboxylate may be formed *in situ* from a copper carboxylate and diamine solvent. Using molecular inks comprising varied ratios of silver complex to copper complex to print a substrate, a gradient of resistivity, or different patterns of resistivity may be formed. For example, a heating device printed with molecular inks having a gradient of resistivity may form a gradient heat flux.

[0190] As shown in **FIG. 14**, the molecular ink comprising both silver complexes and copper complexes shows an exponential correlation between resistivity of a cured film and the weight percent copper complex relative to the total weight of the two metal complexes, e.g., silver complex and copper complex. The mixed metal complex molecular ink shown in **FIG. 14** comprise mixtures of silver diamine oxalate and copper diamine carboxylate that are printed on a Melinex ST505 polymer substrate using methods of the present disclosure and cured at 140°C for 30 minutes. By blending the two metal complexes, the film resistivity can be adjusted within a range of $3x10^{-5}$ to $6x10^{-3}$ ohm-cm as shown. This range encompasses values that have been reported for carbon ($3.5x10^{-3}$) and natural graphite ($1.2x10^{-4}$).

[0191] Film curing conditions were tested to find a temperature low enough to allow formation of resistive films on polymer substrates, such as PET and Kapton. The minimum thermal cure time required to form the resistive film was characterized by determining sheet resistance as a function of cure time at constant temperature. Two samples were tested under different cure conditions: (A) a film prepared with an ink containing 10 wt. % copper complex was coated on PET and cured at 140°C; and (B) a film prepared with an ink containing 15% copper complex was coated on Kapton and cured at 180°C. **FIG. 15** shows resistivity stabilizing around 160 ohm/sq after 20 minutes cure time for the film comprising 10 wt.% copper (sample A), while **FIG. 16** shows resistivity stabilizing around 50 ohm/sq after 15 minutes cure time for the film comprising 15 wt. % copper (sample B).

[0192] The flexibility, adhesion, and electrical properties for a cured film formed from a molecular ink comprising both silver and copper complexes were also tested. The film properties generated from the ink indicated good adhesion to both PET film and Kapton polyimide film. An adhesion rating of 5B, which indicates no removal of coating, resulted when tested by crosshatch tape test (ASTM D3359). A mandrel test with a 50 mm bend radius confirmed the coating was conformable without cracking or delamination of the resistive film. No change in resistivity was observed after the bend test.

[0193] Current-voltage plots for resistive films made with blends of reactive silver complex and copper complex showed that all the film resistors obey Ohm's law. For these measurements, 7 mm x 25 mm films were coated on PET, cured, then tested at ambient

conditions. **FIG. 17** shows a typical example in which the film was printed using an ink containing 15% copper complex. The calculated resistance for this film was 390 ohms, with a maximum power output of 3.3 watts, and maximum power density of 1.4 W/cm^2.

[0194] Inkjet printability was demonstrated for ink containing 10% by weight of copper complex. A test pattern consisting of five 50 mm long lines with widths of 50 microns, 100 microns, 500 microns, 1 mm, and 2 mm was printed on both PET and Kapton®. The printer used was a Susse IP410 industrial printer equipped with a Konica Minolta KM512-SHX print-head. Print conditions were 70°C print platen temperature, 150 mm/s print speed, 2161 x 1993 DPI. The ink was deposited in three layers, then cured at 140°C for 25 minutes. Electrical resistance, ohms, for the printed lines are listed in **Table 5**. Also shown in Table 5 are electrical resistance values measure for traces printed with a molecular ink comprising only silver metal complexes. In general, resistance decreased as line width increases. Average line broadening was 49 microns (see measured width listed for the silver ink) and resistance was reduced by 3 to 4 orders of magnitude.

Table 5

	Silver/Copper Ink		Silver Ink	
	PET	Kapton	Melinex	
Pattern width (μ)	Resistance (ohms)	Resistance (ohms)	Measured width (μ)	Resistance (ohms)
50	$1.5x10^6$	$4.0x10^6$	101	114
100	$7.8x10^4$	$1.5x10^4$	140	55
500	$4.4x10^4$	$6.0x10^3$	540	11.5
1000	$1.2x10^4$	$4.0x10^3$	1052	5.9
2000	$1.2x10^4$	$3.2x10^3$	2024	3.3

[0195] A three-zone heating device was assembled using three inks containing differing amounts of copper complex, 6.0 wt. %, 7.4 wt. %, and 9.0 wt. %, based on the total amount of silver complex and copper complex in the molecular ink. The molecular inks were coating on PET film and thermally cured at 140°C for 25 minutes. Cured films had sheet resistance of 3.5 ohm/sq, 5.0 ohm/sq, and 10.0 ohm/sq, respectively. Each zone was 1 inch x 2.5 inch, and the three zones were electrically connected at opposing ends using a silver paste bus bars. A potential of 5 volts was applied and the current was determined to be 570mA, 400 mA, and 200 mA for the three zones. Power density was calculated to be 0.18 W/cm^2, 0.12 W/cm^2, and 0.06 W/cm^2, respectively. The surface temperatures of the three zones after equilibration at ambient conditions were 111°C, 77°C, and 59°C. These data are summarized in **Table 6**.

Table 6

Resistive film zone	A	B	C
Copper complex, wt. %	6.0	7.4	9.0
Sheet resistance, ohm/sq	3.5	5.0	10.0
Voltage	5.0	5.0	5.0
Current, mA	570	400	200
Power density, W/cm^2	0.18	0.12	0.06
Surface temperature, °C	111	77	59

Washability of molecular inks

[0196] The molecular inks of the present disclosure were printed on various textiles to form conductive traces using ink jet printing methods as disclosed hereinabove. The trace remained uncoated or was coated with a transparent UV curable polyurethane coating. Sheet resistance for these patterns was tested according to AATCC 61-2013 (laundering). As shown in **FIG. 11,** only a slight change in the conductivity for the traces was observed after up to 50 washes. The coated trace shows good conductivity after as many as 100 wash cycles, while the native (uncoated) traces showed good conductivity after as many as 70 wash cycles. The control samples completely lost conductivity after only 5 wash cycles.

[0197] Analysis of various textiles according to AATCC 61-2013 demonstrated that a conductive trace comprising 8 layers of printed ink showed less than a 3 Ω increase in resistance after 100 wash cycles. When an abrasion resistant coating was included over the trace, the resistance only increased by less than 0.7 Ω.

Strain resistance

[0198] Woven fabrics were printed using inks and methods according to the present disclosure and subjected to strain resistance measurements. Shown in **FIG. 12** are results for electromechanical stretch testing under various amounts of stretching (0% to 230%). For conductive traces of the prior art, strain induces film cracking which reduces conductivity (see **FIG. 3**). Using inks and methods according to the present disclosure, the trace conductivity was little affected by the increased strain until the breakpoint of the textile (i.e., textile rips into two pieces). This unusual behavior is demonstrated by a very slight increase in the average spot temperature of the trace (as measured using FLIR; data not shown), where the spot temperature correlates to the amount of heat generated when electrons flow through a stretched conductive fabric; the higher the temperature, the more heated generated by the flowing electrons.

[0199] Bendability of the printed traces was also tested, as shown in **FIG. 13**, and only a small loss of conductivity (<10%) was observed for bending of a conductive trace printed on woven textiles using inks and methods of the present disclosure (10,000 x bends in the trace;

tested according to ASTM D522 -Mandel Bend Test). Nonwoven textiles showed reduced performance after 1,300 bends, which is likely a function of breakdown of the textile and not the conductive trace.

Abrasion resistance

[0200] A woven substrate was printed with a molecular ink according to the present disclosure and coated with an ablation resistance coating (Ablative Resistant Coating NSN 8030-00-164-4389) or left uncoated. Sheet resistance was measured for several textile samples after coating (control), 10X, 20X, and 30X rubbing (see **Table 7**).

Table 7

Sample	**Resistance Ω**				
	Before coating	After coating	After rubbing 10X	After rubbing 20X	After rubbing 30X
Uncoated	6-8	-	62-101	132-138	300-382
Coated	6-8	6-7	9-10	11-12	12-13

CLAIMS

1. A thermoformable printed electronic substrate comprising:
   a first substrate layer comprising a stretchable textile having at least one conductive trace printed thereon with a conductive ink; and
   a second substrate layer comprising a thermoformable substrate,
   wherein the first substrate layer is laminated to the second substrate layer via an adhesive, heat, or both.
2. The substrate of claim 1, wherein the stretchable textile of the first substrate layer is a 4-way stretch fabric.
3. The substrate of claim 2, wherein the conductive ink conformally coats fibers of the 4-way stretch fabric.
4. The substrate of claim 2, wherein the 4-way stretch fabric comprises a polyester and polyether-polyurea copolymer blend, or a nylon and polyether-polyurea copolymer blend.
5. The substrate of claim 1, wherein the thermoformable substrate of the second substrate layer comprises a thermorformable polymer sheet comprising polycarbonate, polybutylene terephthalate, polyethylene terephthalate glycol modified, acrylonitrile-butadiene-styrene, polymethyl methacrylate (acrylic), acrylic capped ABS, high impact polystyrene, polyvinyl chloride (PVC), or acrylic-PVC.
6. The substrate of claim 1, wherein the thermoformable substrate of the second substrate layer comprises a thermoformable textile.
7. The substrate of claim 6, wherein the thermoformable textile comprises non-woven mat or web formed as a composite of natural fibers and synthetic polymers.
8. The substrate of claim 7, wherein the synthetic polymers comprise a thermoplastic or cross-linkable thermoplastic.
9. The substrate of claim 7, wherein the natural fibers comprise wood, hemp, cotton, coconut, flax, jute, bamboo, wheat straw, kenaf, sisal, wool, glass, or any combination thereof, and wherein the synthetic polymers comprise polypropylene, polyethylene, thermoplastic olefin (TPO), acrylic, and any combination thereof.
10. The substrate of claim 1, wherein the at least one conductive trace of the first substrate layer forms a conductive pattern and at least one bus, the at least one bus electrically connected to the conductive pattern and configured to provide connection to a controller and a power source.

11. The substrate of claim 1, wherein the conductive ink comprises:
a particle-free metal complex composition comprising:
at least one metal complex comprising:
at least one metal,
at least one first ligand that is a sigma donor to the metal and volatilizes upon heating the metal complex, and
at least one second ligand that is different from the first ligand and volatilizes upon heating the metal complex; and
a solvent,
wherein the metal complex has a solubility measured at 25°C of at least 250 mg/ml in the solvent,
wherein the at least one metal, the at least one first ligand, and the at least one second ligand are provided in stoichiometric amounts in the conductive ink, and
wherein the conductive ink forms nanoparticles on the stretchable textile after curing to form the at least one conductive trace.

12. The substrate of claim 1, wherein the particle-free metal complex composition comprises a silver amine carboxylate and at least one polar protic solvent selected from the group consisting of water, an alcohol, an amine, an amino alcohol, and a polyol.

13. The substrate of claim 1, wherein the adhesive used to laminate the first substrate layer to the second substrate layer is an extensible liquid adhesive or an extensible adhesive tape.

14. The substrate of claim 1, wherein the at least one conductive trace is printed on a top side of the stretchable textile, wherein a bottom side of the stretchable textile faces the second substrate layer.

15. The substrate of claim 1, wherein the first substrate layer comprises a top side and a bottom side, wherein the at least one conductive trace is printed on the bottom side of the stretchable textile that faces the second substrate layer.

16. The substrate of claim 14 or 15, further comprising a thermoplastic polymer sheet or foam laminated to the top side of the first substrate layer.

17. A thermoformable printed electronic substrate comprising:
a first substrate layer comprising a 4-way stretch fabric having at least one conductive trace printed thereon with a particle-free conductive ink; and
a second substrate layer comprising a thermoformable substrate,

wherein the first substrate layer is laminated to the second substrate layer via an extensible liquid adhesive or an extensible adhesive tape, and

wherein the particle-free conductive ink comprises a silver amine carboxylate and at least one polar protic solvent and is absent hydrocarbons.

18. The substrate of claim 17, wherein the thermoformable substrate of the second substrate layer comprises a thermoformable textile.

19. The substrate of claim 18, wherein the thermoformable textile comprises non-woven mat or web formed as a composite of natural fibers and synthetic polymers.

20. The substrate of claim 19, wherein the synthetic polymers comprise a thermoplastic or cross-linkable thermoplastic.

21. The substrate of claim 19, wherein the natural fibers comprise wood, hemp, cotton, coconut, flax, jute, bamboo, wheat straw, kenaf, sisal, wool, glass, or any combination thereof, and wherein the synthetic polymers comprise polypropylene, polyethylene, thermoplastic olefin (TPO), acrylic, and any combination thereof.

22. The substrate of claim 17, wherein the thermoformable substrate of the second substrate layer comprises polycarbonate, polybutylene terephthalate, polyethylene terephthalate glycol modified, acrylonitrile-butadiene-styrene, polymethyl methacrylate (acrylic), acrylic capped ABS, high impact polystyrene, polyvinyl chloride (PVC), or acrylic-PVC.

23. The substrate of claim 17, wherein the 4-way stretch fabric comprises a blend of polyester and polyether-polyurea copolymer, or a blend of nylon and polyether-polyurea copolymer.

24. The substrate of claim 17, wherein the at least one conductive trace of the first substrate layer forms a conductive pattern and at least one bus, the at least one bus electrically connected to the conductive pattern and configured to provide connection to a controller and a power source.

25. The substrate of claim 17, wherein the at least one conductive trace is printed on a top side of the stretchable textile, wherein a bottom side of the stretchable textile faces the second substrate layer.

26. The substrate of claim 17, wherein the first substrate layer comprises a top side and a bottom side, wherein the at least one conductive trace is printed on the bottom side of the stretchable textile that faces the second substrate layer.

27. The substrate of claim 25 or 26, further comprising a thermoplastic polymer sheet or foam laminated to the top side of the first substrate layer.

28. A three-dimensional (3D) article comprising the thermoformable printed electronic substrate according to any one of claims 1 to 27.

29. The 3D article of claim 28, wherein the first substrate layer of the thermoformable printed electronic substrate is on an exterior surface of the 3D article.

30. The 3D article of claim 28, further comprising a polymeric coating over the exterior surface of the 3D article to encapsulate the at least one conductive trace.

31. The 3D article of claim 28, wherein the article is an automotive air duct, door panel, head liner, dashboard panel, or trunk liner, and wherein the electronic device is a resistive heater, connecting wire(s) for standard electronic elements, circuit, or sensor.

32. A method for forming a thermoformable printed electronic substrate, the method comprising:

depositing a particle free conductive ink on a first substrate layer to form at least one pattern, wherein the depositing is by inkjet or aerosol jet printing on the first substrate layer that is heated to a temperature of 30°C to 90°C;

curing the conductive ink in the at least one pattern to form at least one conductive pattern; and

laminating the first substrate layer to a second substrate layer using an extensible liquid adhesive, an extensible adhesive tape, heat, or any combination thereof,

wherein the first substrate layer is a stretchable textile, and the second substrate layer is a thermoformable polymer sheet or a thermoformable textile.

33. The method of claim 32, wherein curing the conductive ink to form the at least one conductive pattern is by heating at a temperature of 100 °C to 200°C for a time of less than 20 minutes, exposure to 2-20 pulses of pulsed light, exposure to infrared radiation, or any combination thereof.

34. The method of claim 32, wherein the particle free conductive ink comprises a silver amine carboxylate and at least one polar protic solvent and is absent hydrocarbons.

35. The method of claim 32, wherein the thermoformable polymer sheet of the second substrate layer comprises polycarbonate, polybutylene terephthalate, polyethylene terephthalate glycol modified, acrylonitrile-butadiene-styrene, polymethyl methacrylate (acrylic), acrylic capped ABS, high impact polystyrene, polyvinyl chloride (PVC), and acrylic-PVC.

36. The method of claim 32, wherein the thermoformable textile of the second substrate layer comprises a thermoformable non-woven mat or web formed as a composite of natural fibers and synthetic polymers.

37. The method of claim 33, wherein the natural fibers comprise wood, hemp, cotton, coconut, flax, jute, bamboo, wheat straw, kenaf, sisal, wool, glass, or any combination thereof, and wherein the synthetic polymers comprise polypropylene, polyethylene, thermoplastic olefin (TPO), acrylic, and any combination thereof.
38. The method of claim 32, wherein the stretchable textile is a 4-way stretch fabric.
39. The method of claim 38, wherein the 4-way stretch fabric comprises a blend of polyester and polyether-polyurea copolymer, or a blend of nylon and polyether-polyurea copolymer.
40. The method of claim 32, wherein the at least one conductive pattern includes at least one bus, wherein the at least one bus electrically connected to the conductive pattern and configured to provide connection to a controller and a power source.
41. The method of claim 32, wherein depositing the particle free conductive ink on the first substrate layer comprises inkjet or aerosol jet printing the particle free conductive ink on a top side of the first substrate layer, wherein a bottom side of the first substrate layer faces the second substrate layer.
42. The method of claim 32, wherein the first substrate layer comprises a top side and a bottom side, wherein depositing the particle free conductive ink on the first substrate layer comprises inkjet or aerosol jet printing the particle free conductive ink on the bottom side of the first substrate layer that faces the second substrate layer.
43. The method of claim 41 or 42, further comprising:
laminating a thermoplastic polymer sheet or foam laminated to the top side of the first substrate layer.
44. A method for forming a thermoformable printed electronic substrate, the method comprising:
laminating a first substrate layer to a second substrate layer to form a composite, wherein the laminating uses an extensible liquid adhesive, an extensible adhesive tape, heat, or any combination thereof, and wherein the first substrate layer is a stretchable textile and the second substrate layer is a thermoformable polymer sheet or thermorformable textile;
depositing a particle free conductive ink on the composite to form at least one pattern, wherein the depositing is by inkjet or aerosol jet printing on the first substrate layer while the composite is heated to a temperature of 30°C to 90°C; and
curing the particle free conductive ink in the at least one pattern to form at least one conductive pattern, wherein curing is by heating at a temperature of 100 °C to

200°C for a time of less than 20 minutes, exposure to 2-20 pulses of pulsed light, exposure to infrared radiation, or any combination thereof.

45. The method of claim 44, further comprising, after laminating the first substrate layer to the second substrate layer: cutting the composite to provide a desired shape, wherein the cutting may be before depositing the particle free conductive ink, after depositing the particle free conductive ink, before curing the particle free conductive ink, or after curing the particle free conductive ink.

46. The method of claim 44, wherein the particle free conductive ink comprises a silver amine carboxylate and at least one polar protic solvent and is absent hydrocarbons.

47. The method of claim 44, wherein the thermoformable polymeric substrate of the second substrate layer comprises polycarbonate, polybutylene terephthalate, polyethylene terephthalate glycol modified, acrylonitrile-butadiene-styrene, polymethyl methacrylate (acrylic), acrylic capped ABS, high impact polystyrene, polyvinyl chloride (PVC), or acrylic-PVC.

48. The method of claim 44, wherein the thermoformable textile of the second substrate layer comprises a thermoformable non-woven mat or web formed as a composite of natural fibers and synthetic polymers.

49. The method of claim 48, wherein the natural fibers comprise wood, hemp, cotton, coconut, flax, jute, bamboo, wheat straw, kenaf, sisal, wool, glass, or any combination thereof, and wherein the synthetic polymers comprise polypropylene, polyethylene, thermoplastic olefin (TPO), acrylic, and any combination thereof.

50. The method of claim 44, wherein the stretchable textile is a 4-way stretch fabric.

51. The method of claim 50, wherein the 4-way stretch fabric comprises a blend of polyester and polyether-polyurea copolymer, or a blend of nylon and polyether-polyurea copolymer.

52. The method of claim 44, wherein the at least one conductive pattern includes at least one bus, wherein the at least one bus electrically connected to the conductive pattern and configured to provide connection to a controller and a power source.

53. The method of claim 44, further comprising, depositing a particle free conductive ink on the composite to form at least one pattern: laminating a thermoplastic polymer sheet or foam laminated to the first substrate layer of the composite.

54. A thermoformable printed electronic substrate formed by the method according to any one of claims 32 to 53.

55. A method of forming a 3D article comprising a conductive pattern, the method comprising:

registering a thermoformable printed electronic substrate according to any one of claims 1 to 27 onto a 3D form;

heating the thermoformable printed electronic substrate to at least a softening temperature of the second substrate layer of the thermoformable printed electronic substrate;

forcing at least portions of the heated thermoformable printed electronic substrate against the 3D form to form the 3D article; and

removing the 3D article from the platen when cooled.

56. The method of claim 55, wherein forcing at least portions of the heated thermoformable printed electronic substrate against the 3D form is by positive or negative pressure.

57. The method of claim 55, wherein forcing at least portions of the heated thermoformable printed electronic substrate against the 3D form is by compaction between opposing surfaces of the 3D form.

58. The method of claim 55, wherein the first substrate layer of the heated thermoformable printed electronic substrate is in contact with the 3D form.

59. The method of claim 55, wherein the second substrate layer of the heated thermoformable printed electronic substrate is in contact with the 3D form.

60. The method of claim 59, further comprising: using the 3D part as a mold insert to an injection molding machine, and backfilling with a polymer.

61. A 3D article formed by the method according to any one of claims 55 to 60.

62. The 3D article of claim 61, wherein the article is an automotive air duct, door panel, head liner, dashboard panel, or trunk liner, and wherein the electronic device is a resistive heater, connecting wire(s) for standard electronic elements, circuit, or sensor.

FIG. 1A PRIOR ART

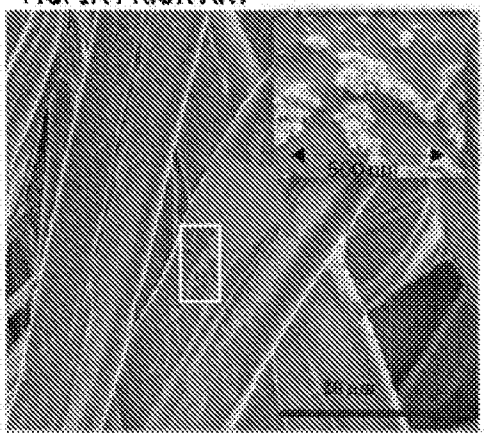


FIG. 1B PRIOR ART

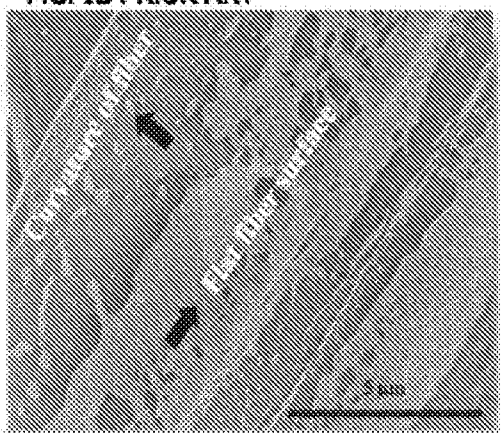


FIG. 1C PRIOR ART

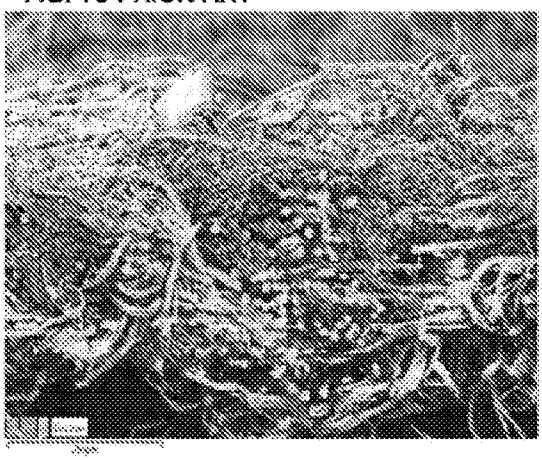
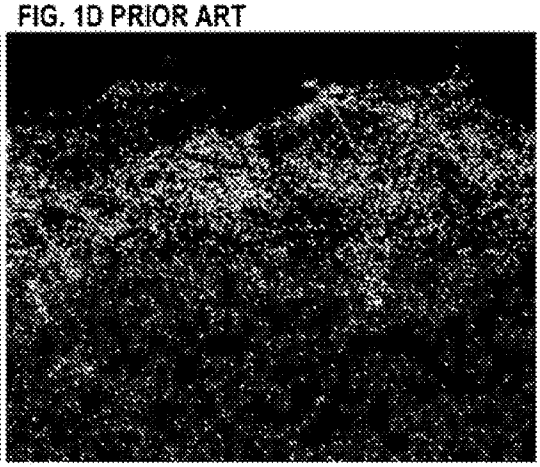


FIG. 1D PRIOR ART



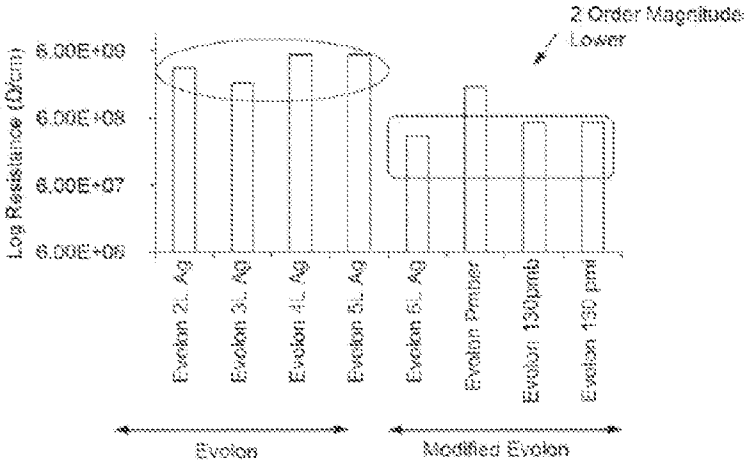


FIG. 1E PRIOR ART

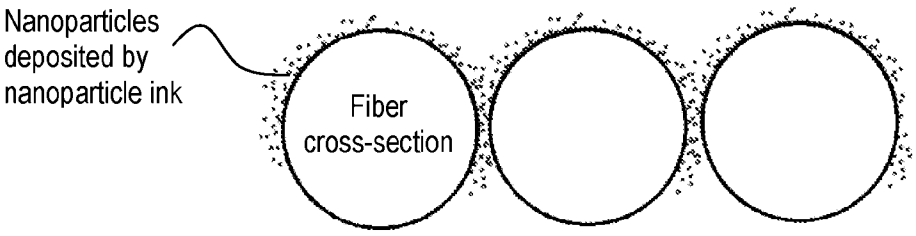


FIG. 2A (Prior Art)

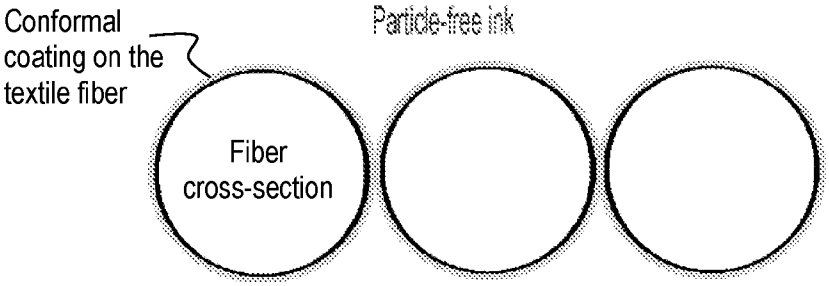


FIG. 2B

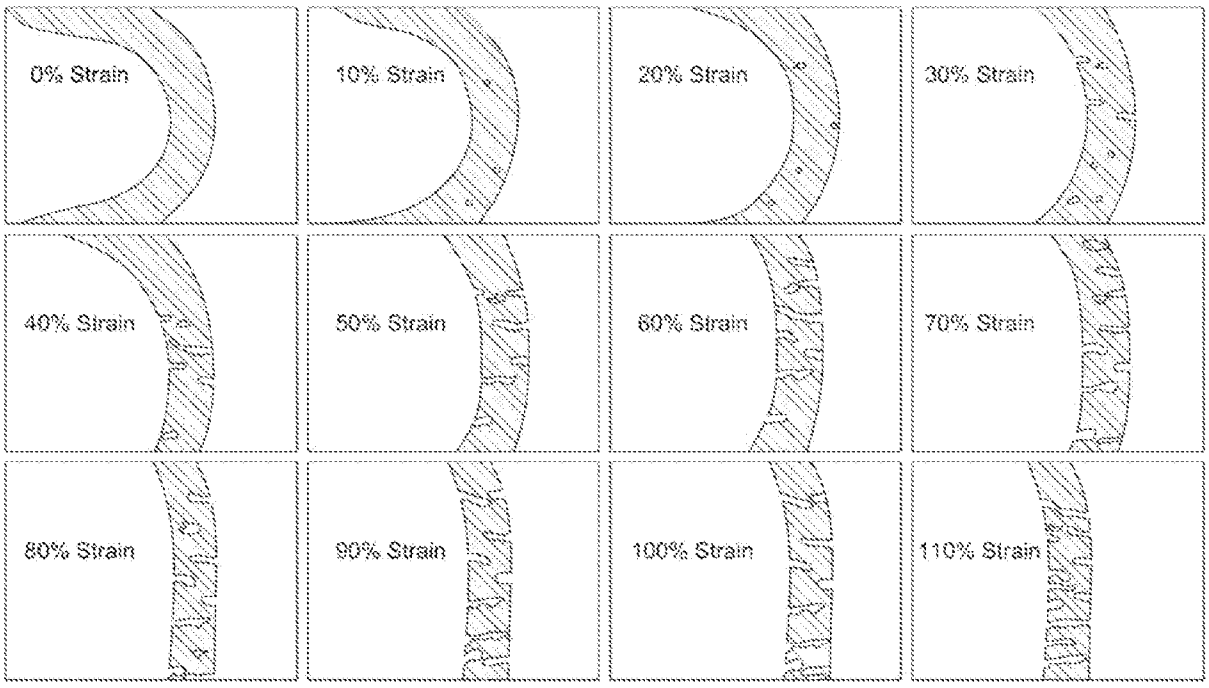


FIG. 3 (PRIOR ART)

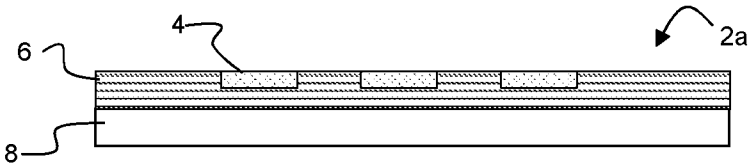


FIG. 4A

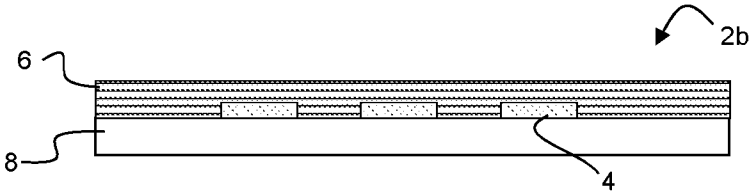


FIG. 4B

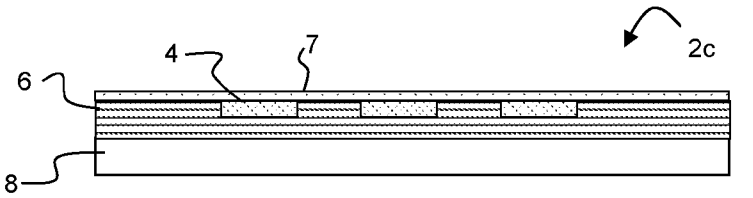


FIG. 4C

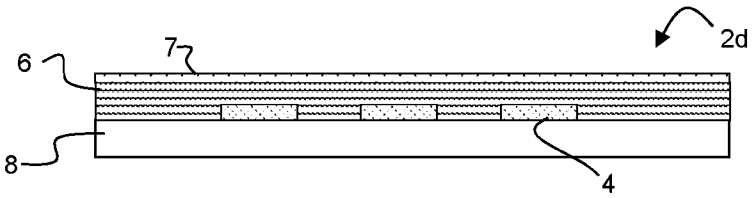


FIG. 4D

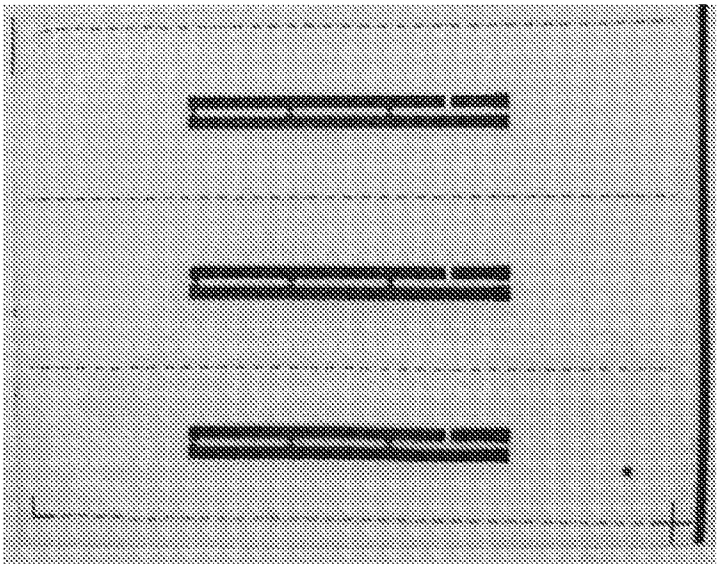


FIG. 5A

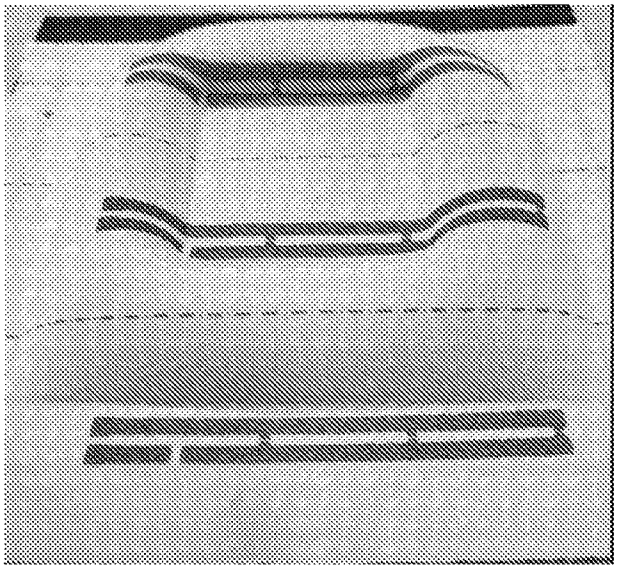


FIG. 5B

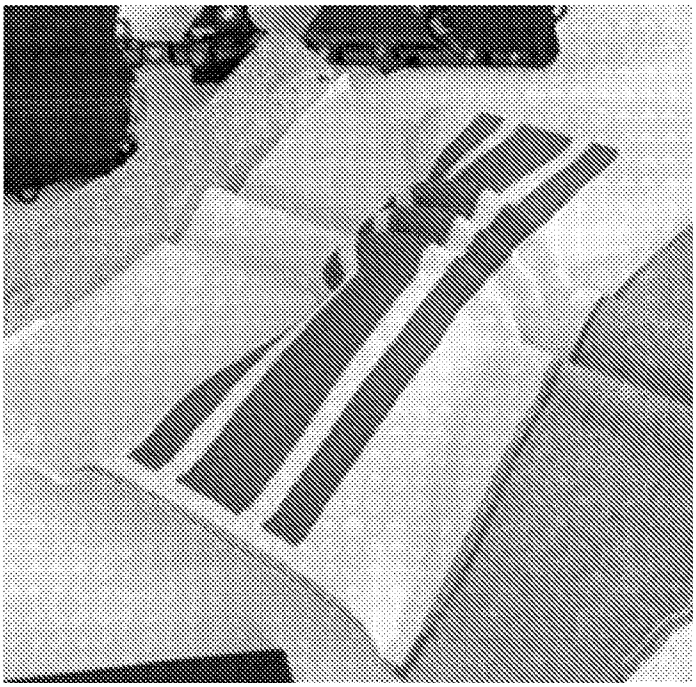


FIG. 5C

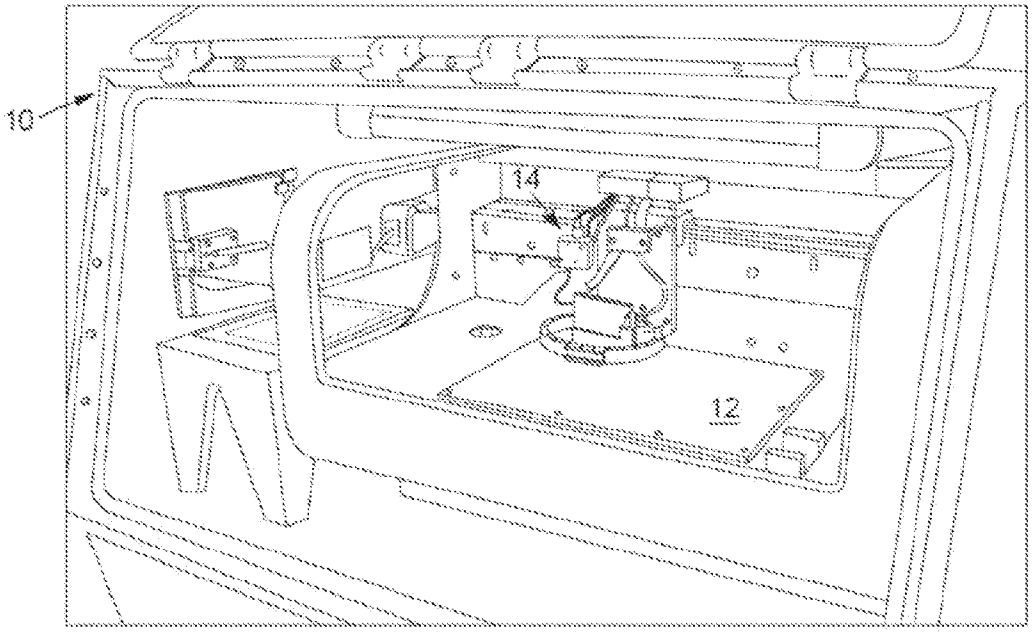


FIG. 6

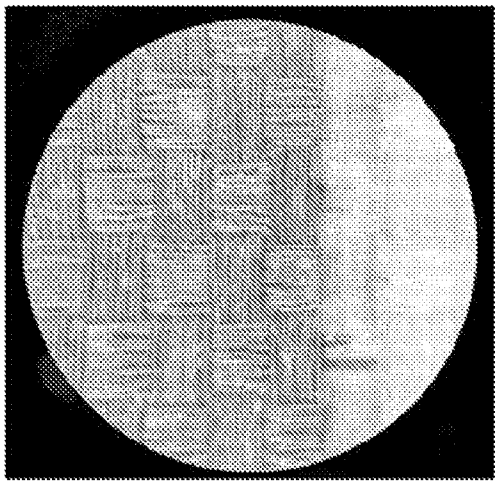


FIG. 7A

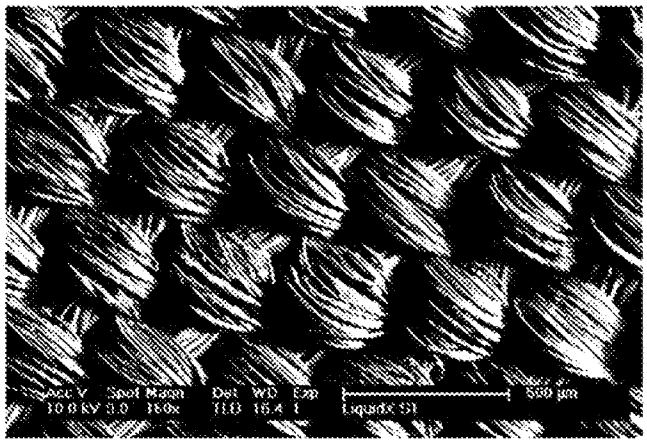

Acc.V Spot Magn Det WD Exp
10.0 kV 3.0 150x TLD 15.4 1
LiquidX S1
500 µm

FIG. 7B

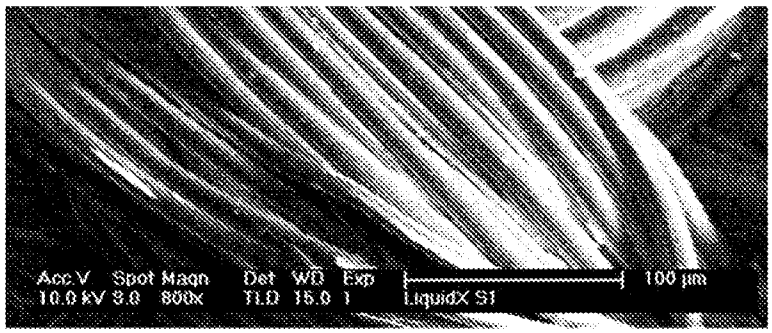

Acc.V Spot Magn Det WD Exp
10.0 kV 3.0 800x TLD 15.0 1
LiquidX S1
100 µm

FIG. 7C

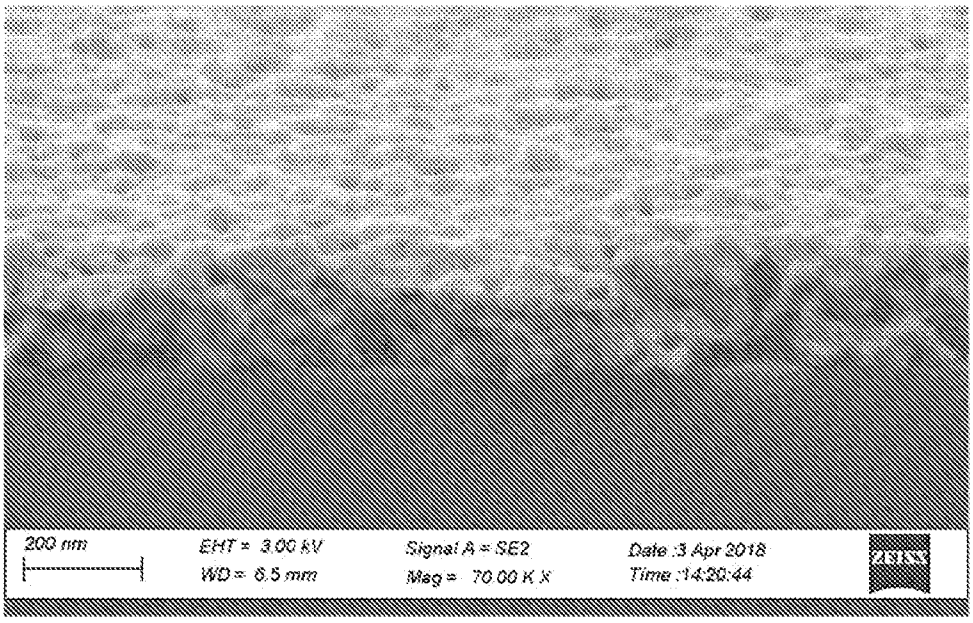

200 nm
EHT = 3.00 kV
WD = 6.5 mm
Signal A = SE2
Mag = 70.00 K X
Date :3 Apr 2018
Time :14:20:44
ZEISS

FIG. 8A

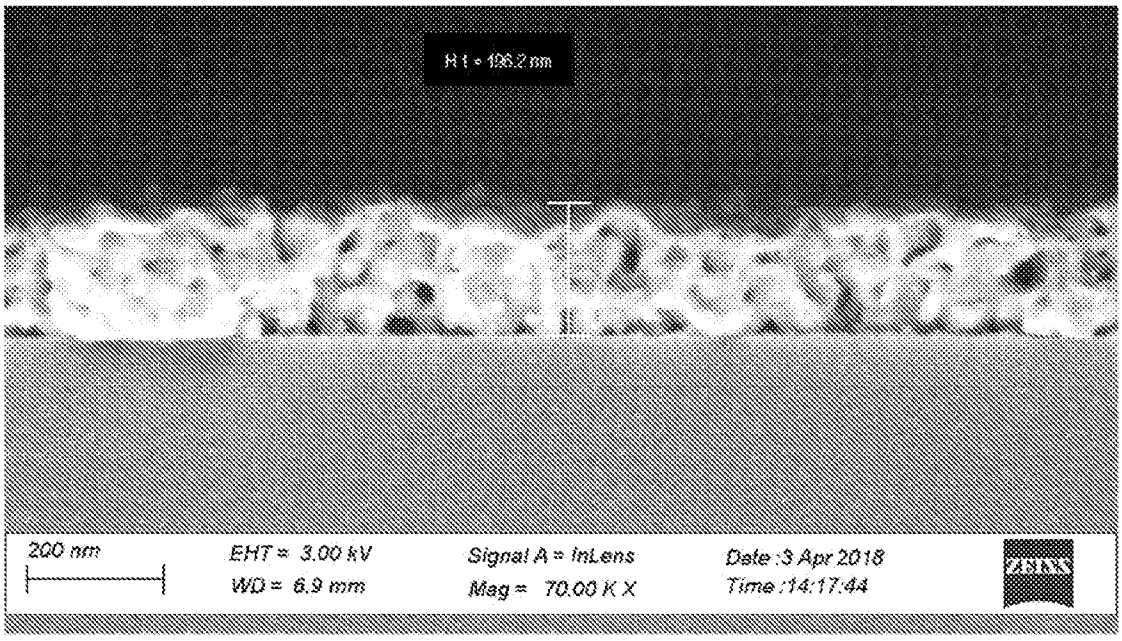

Ht = 196.2 nm
200 nm
EHT = 3.00 kV
WD = 6.9 mm
Signal A = InLens
Mag = 70.00 K X
Date :3 Apr 2018
Time :14:17:44
ZEISS

FIG. 8B

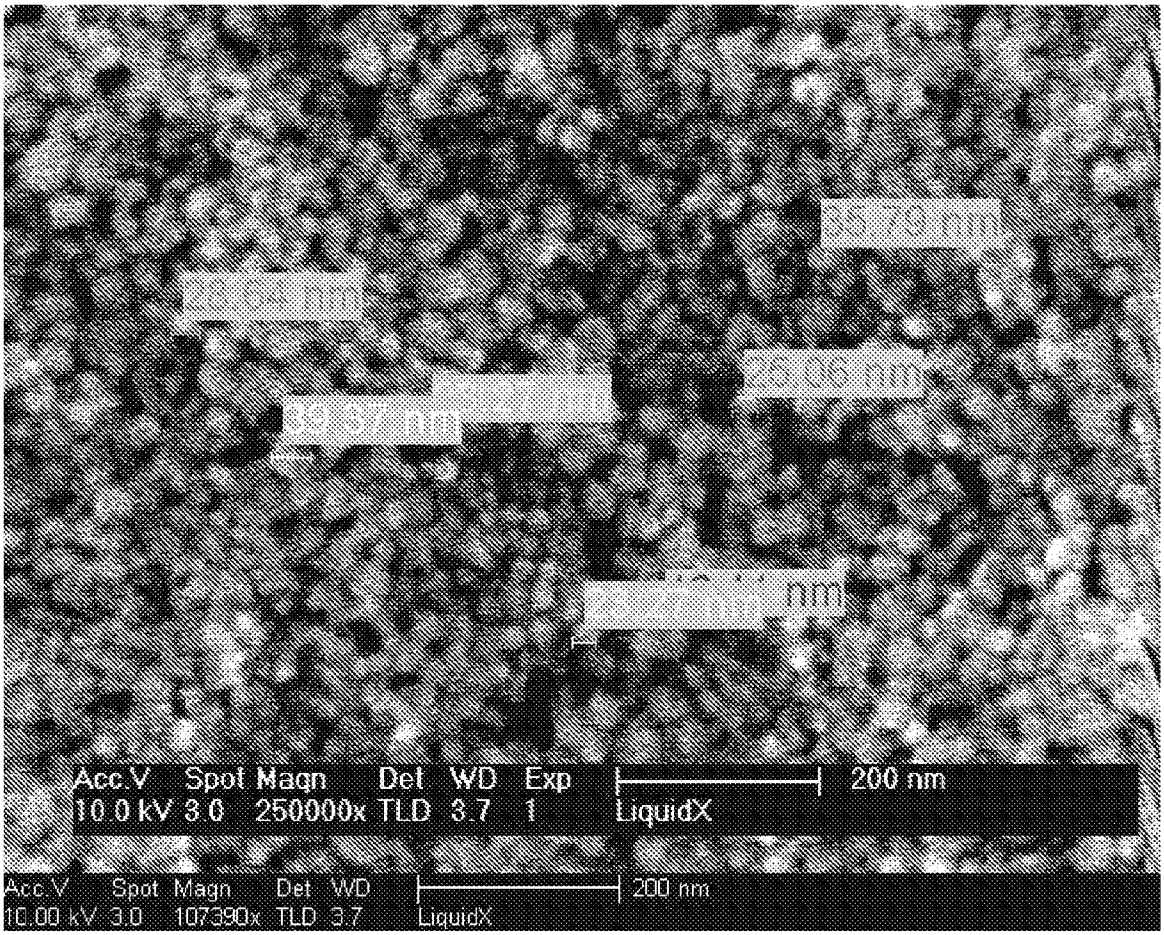

Acc.V Spot Magn Det WD Exp 200 nm
10.0 kV 3.0 250000x TLD 3.7 1 LiquidX
Acc.V Spot Magn Det WD 200 nm
10.00 kV 3.0 107390x TLD 3.7 LiquidX

FIG. 8C

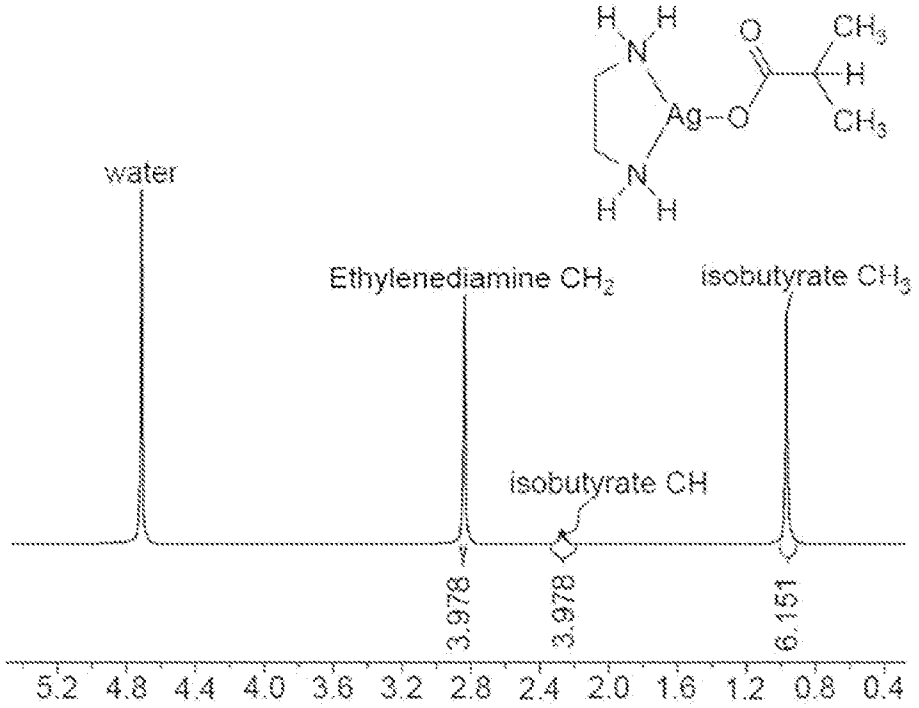

water
Ethylenediamine CH2
isobutyrate CH3
isobutyrate CH
3.978
3.978
6.151
5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4

FIG. 9

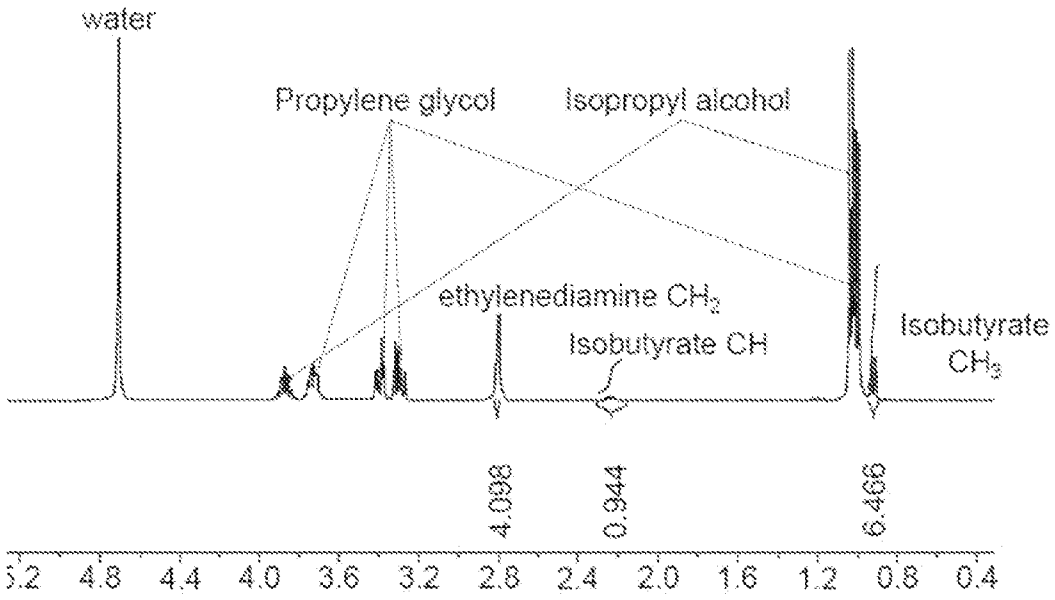

water
Propylene glycol
Isopropyl alcohol
ethylenediamine CH2
Isobutyrate CH
Isobutyrate CH3
4.098
0.944
6.466
5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4

FIG. 10

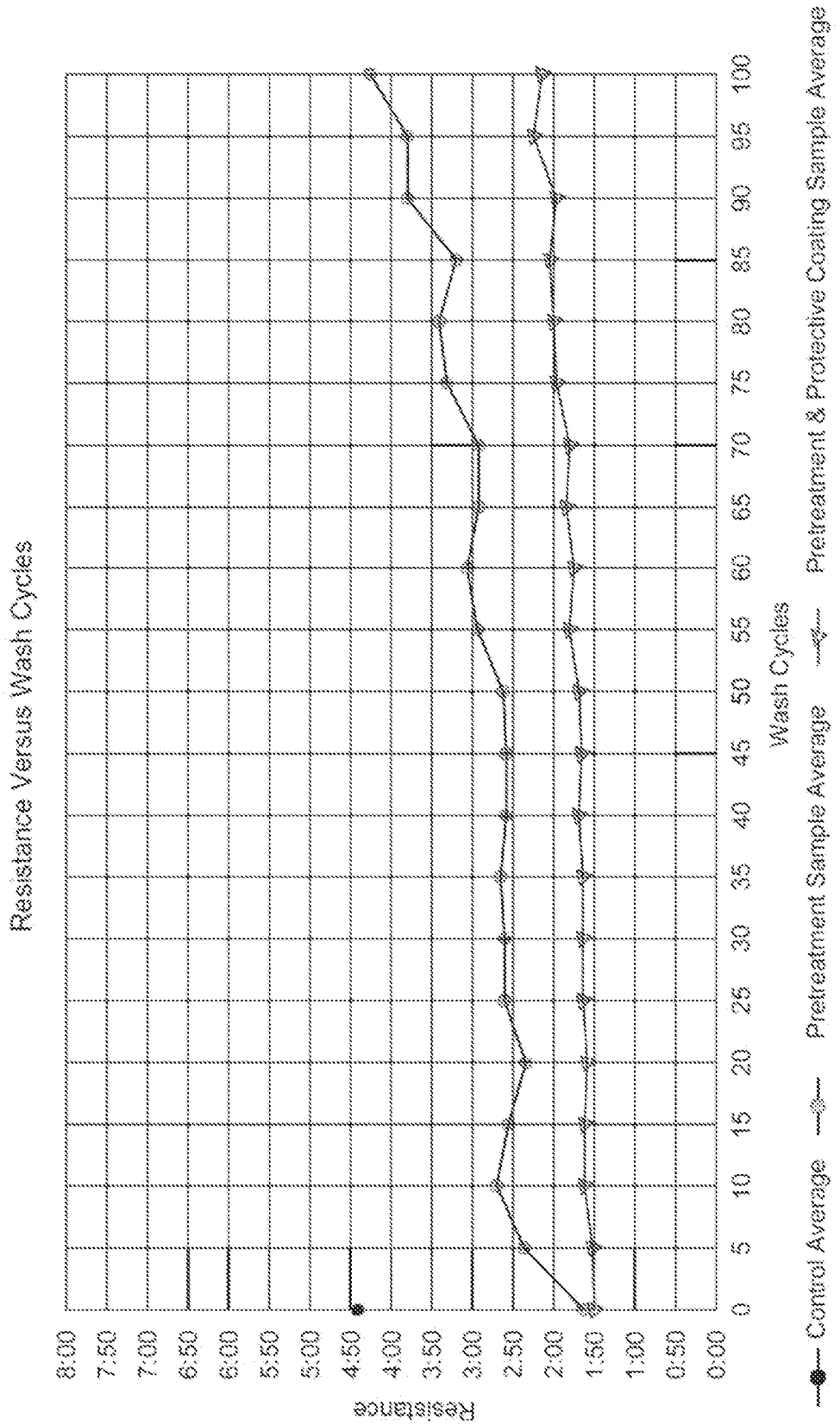

Resistance Versus Wash Cycles
Resistance
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
Wash Cycles
Control Average
Pretreatment Sample Average
Pretreatment & Protective Coating Sample Average

FIG. 11

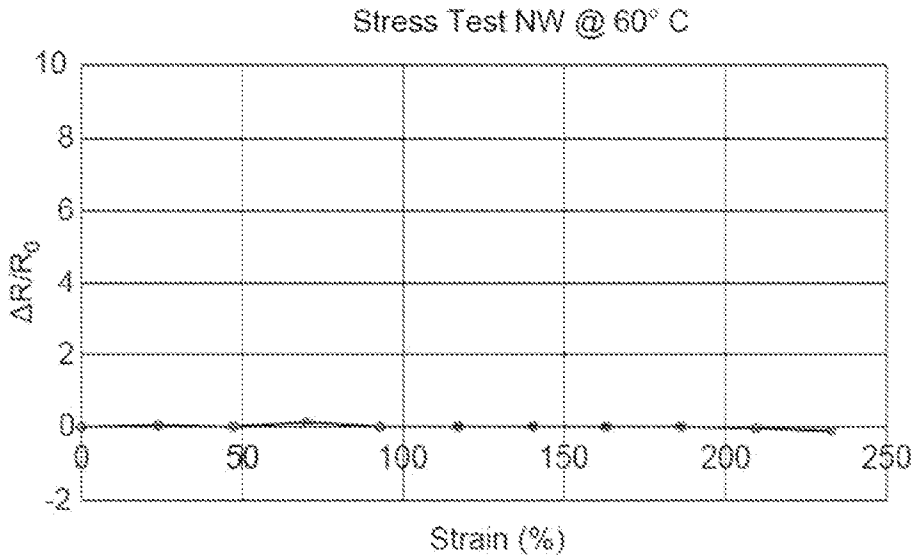

Stress Test NW @ 60° C
10
8
6
4
2
0
-2
ΔR/R0
0
50
100
150
200
250
Strain (%)

FIG. 12

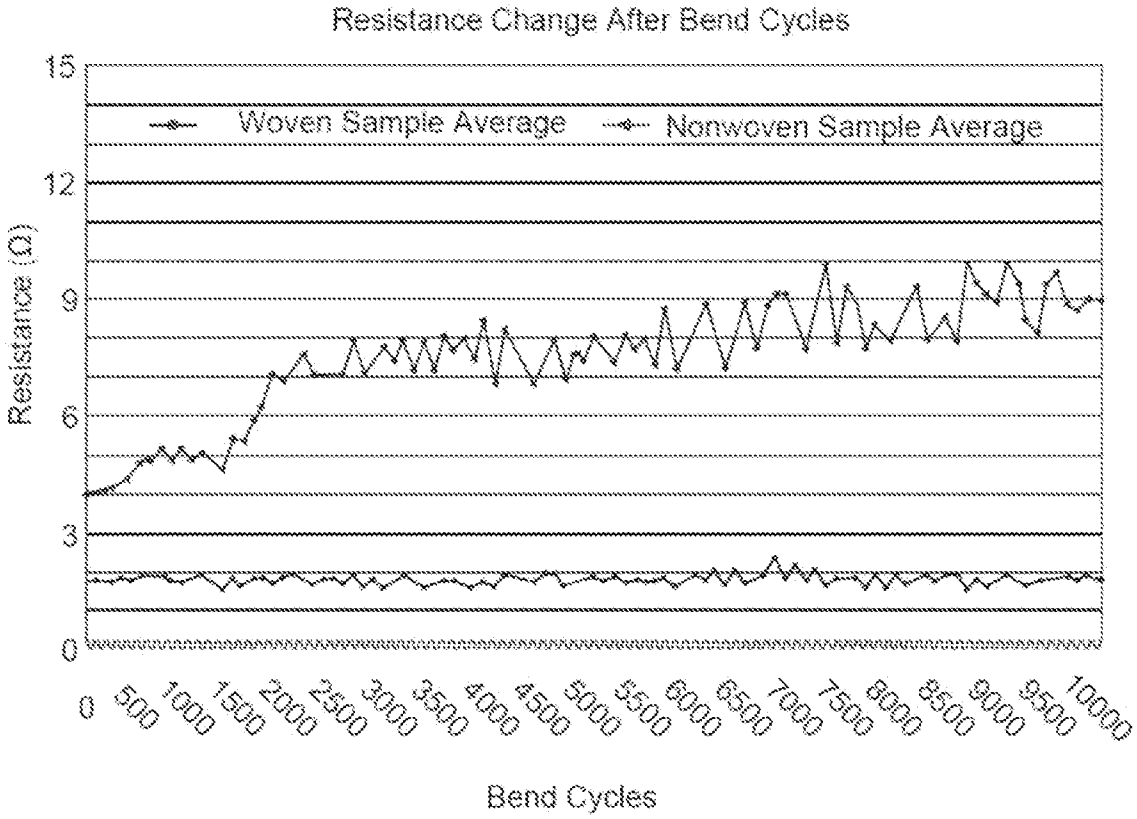

Resistance Change After Bend Cycles
Woven Sample Average
Nonwoven Sample Average
15
12
9
6
3
0
Resistance (Ω)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
7500
8000
8500
9000
9500
10000
Bend Cycles

FIG. 13

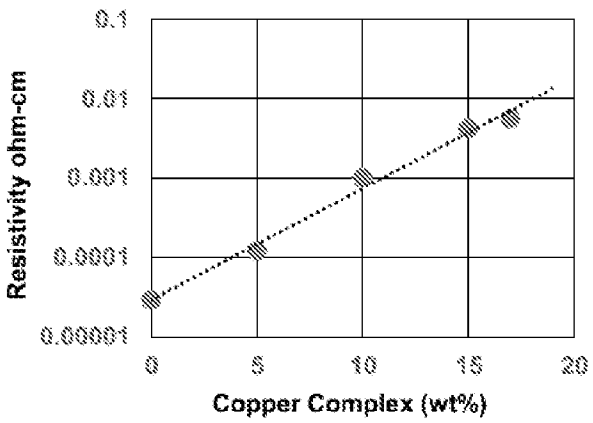


FIG. 14

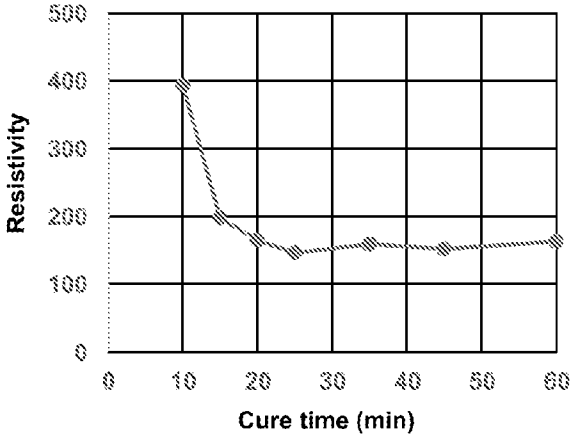


FIG. 15

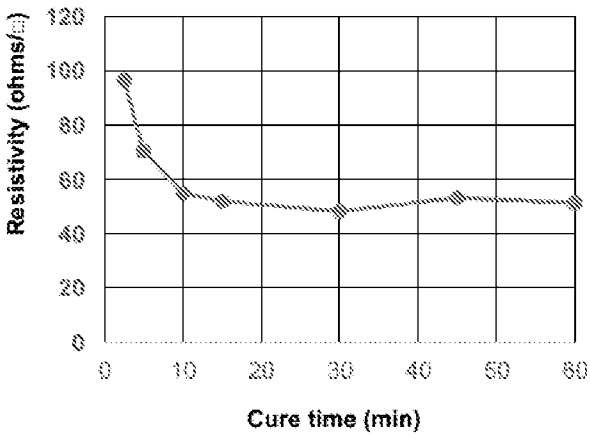


FIG. 16

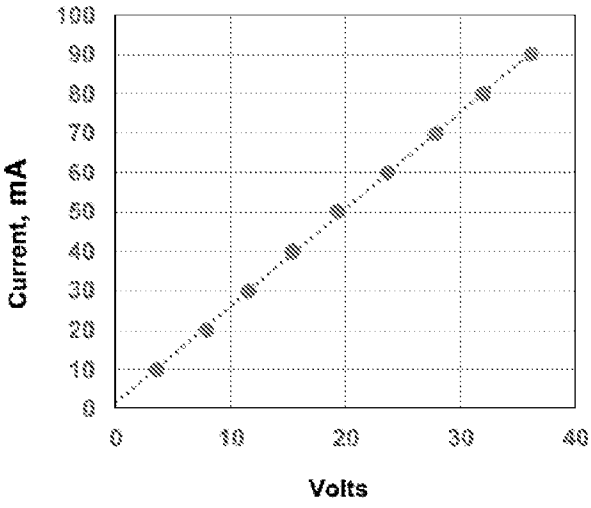


FIG. 17