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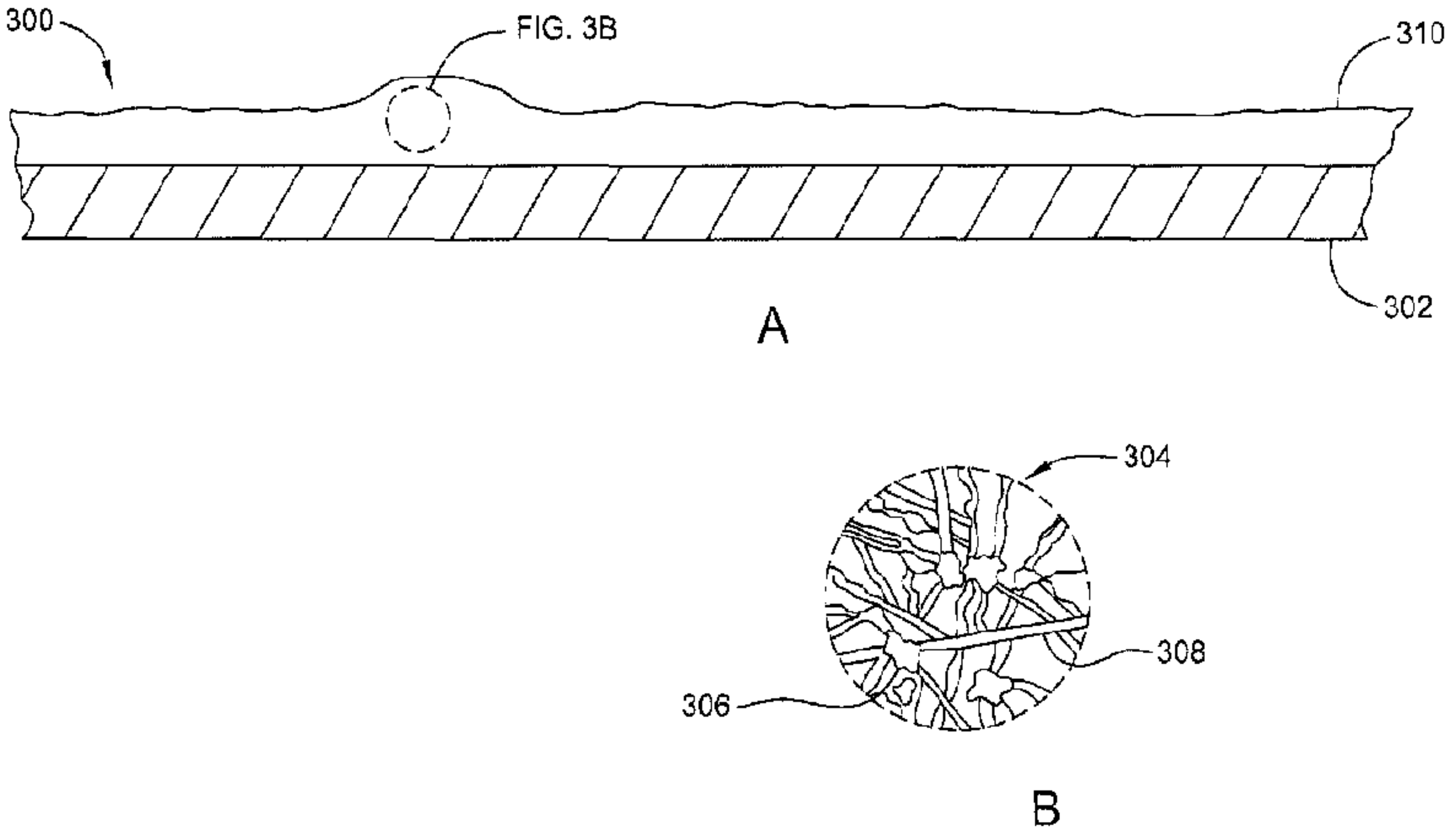
(54) **Titre :** COUCHES INTERMEDIAIRES NON TISSEES FAITES DE POLYMERES A NANOPARTICULES
(54) **Title:** NONWOVEN INTERLAYERS MADE USING POLYMER-NANOPARTICLE POLYMERS



(57) **Abrégé/Abstract:**

A method of manufacturing a composite structure is provided. The method includes positioning a polymer-nanoparticle-enhanced interlayer adjacent to a first fiber layer. The polymer-nanoparticle-enhanced interlayer comprises at least one polymer and derivatized nanoparticles included in the molecular backbone of the at least one polymer, wherein the nanoparticles are derivatized to include functional groups. The method further includes positioning a second fiber layer adjacent to the polymer-nanoparticle-enhanced interlayer attached to the first fiber layer. The first fiber layer and the second fiber layer are infused with resin. The resin is cured to harden the composite structure.

ABSTRACT

A method of manufacturing a composite structure is provided. The method includes positioning a polymer-nanoparticle-enhanced interlayer adjacent to a first fiber layer. The polymer-nanoparticle-enhanced interlayer comprises at least one polymer and derivatized nanoparticles included in the molecular backbone of the at least one polymer, wherein the nanoparticles are derivatized to include functional groups. The method further includes positioning a second fiber layer adjacent to the polymer-nanoparticle-enhanced interlayer attached to the first fiber layer. The first fiber layer and the second fiber layer are infused with resin. The resin is cured to harden the composite structure.

NONWOVEN INTERLAYERS MADE USING POLYMER-NANOPARTICLE POLYMERS

TECHNICAL FIELD

The implementations described herein generally relate to composite structures, and more particularly, to polymer-nanoparticle-enhanced interlayers for use in composite structures.

BACKGROUND

Fiber-reinforced-resin materials, or "composite" materials as they are commonly known, are frequently used for aerospace, automotive and marine applications because of high strength-to-weight ratios, corrosion resistance, and other favorable properties. Conventional composite materials typically include glass, carbon, or polyaramid fiber “plies” in woven and/or non-woven configurations. The fiber plies can be manufactured into composite parts by laminating them together with an uncured matrix material (e.g., an epoxy resin). The laminate can then be cured with the application of heat and/or pressure to form the finished part.

Composite parts can be manufactured from "prepreg" materials, or from dry fiber plies assembled into a “preform.” Prepreg is ready-to-mold material in a cloth, mat, roving, tape or other form that has been pre-impregnated with matrix material (e.g., epoxy resin) and stored for use in an uncured or semi-cured state. The prepreg sheets are laid-up on a mold surface in the shape of the finished part. Pressure is then applied to compact the prepreg sheets, and heat can be applied to complete the curing cycle. A preform is different from a prepreg assembly in that a preform is an assembly of dry fabric and/or fibers which have been prepared for resin infusion on a mold surface. The preform plies are usually tacked and/or stitched together or otherwise stabilized to maintain their shape before and during final processing. Once the preform has been stabilized, the layers can be infused with resin using liquid-molding. The part can then be cured with the addition of pressure and/or heat.

The fiber material in composite parts provides relatively high strength in the direction of the fibers. Impact resistance, however, is generally determined by the properties of the cured matrix. One way to enhance impact resistance is to add particles of, for example, a thermoplastic material to the matrix. The thermoplastic material can inhibit crack propagation through the part resulting from, for example, foreign-object debris, which is typically not visible to the naked eye.

Another way to increase the impact resistance and fracture toughness of composite parts is to enhance the structural properties of the bond-line between alternating layers of composite materials (i.e., the interlayer properties). To date, some in industry have used interlayers or "toughening veils" inside laminate composites to enhance the structural properties of the bond-line. Specifically, the toughening veil is intended to add toughness to the components meaning the ability to absorb energy and deform without fracturing. Existing toughening veils often lack stiffness, strength and the ability to maintain compression and shear strength at elevated temperatures, especially after exposure to moisture.

Therefore there is a need for toughening veils with improved stiffness, strength and the ability to maintain compression and shear strength at elevated temperatures.

SUMMARY

The implementations described herein generally relate to composite structures, and more particularly, to polymer-nanoparticle-enhanced interlayers for use in composite structures. According to one implementation described herein, a method of manufacturing a composite structure is provided. The method includes positioning a polymer-nanoparticle-enhanced interlayer adjacent to a first fiber layer. The polymer-nanoparticle-enhanced interlayer comprises at least one polymer and derivatized nanoparticles included in the molecular backbone of the at least one polymer. The nanoparticles are derivatized to include one or more functional groups. The method further includes positioning a second fiber layer adjacent to the polymer-nanoparticle-enhanced interlayer attached to the first fiber layer. The first fiber layer and the second fiber layer are infused with resin. The resin is cured to harden the composite structure. The first fiber layer and the second fiber layer may be nonwoven fiber layers and the polymer-nanoparticle enhanced interlaye is a nonwoven polymer sheet.

In another implementation described herein, a laminate composite structure is provided. The laminate composite structure includes a first fiber layer, a second fiber layer and a polymer-nanoparticle-enhanced interlayer positioned between the first fiber layer and the second fiber layer. The polymer-nanoparticle-enhanced interlayer includes at least one polymer and derivatized nanoparticles included in the molecular backbone of the at least one polymer. The nanoparticles are derivatized to include one or more functional groups. The laminate composite structure further includes matrix material infused into the first and second fiber layers.

In yet another implementation described herein, a laminiate composite structure is provided. The laminate composite comprises one or more woven or non-woven plies and at lest one nonwoven toughening veil. The at least one nonwoven toughening veil comprises spun fibers which are formed by functionalizing a plurality of nanoparticles and combining the plurality of nanoparticles with at least one monomer.

In yet another implementation described herein a method of manufacturing a laminate composite is provided. The method comprises functionalizing a plurality of nanoparticles. The plurality of nanoparticles are combined with at least one monomer to form a combined material. The combined material is spun to create a nonwoven toughening veil. The nonwoven toughening veil is added to a plurality of woven fiber plies to form a laminate composite.

The polymer-nanoparticle-enhanced interlayers are suitable for use in, among other things, both prepregs and preforms.

In one embodiment there is provided a method of manufacturing a composite structure. The method involves positioning a polymer-nanoparticle-enhanced interlayer adjacent to a first fiber layer. The polymer-nanoparticle-enhanced interlayer includes at least one polymer having a molecular backbone and derivatized nanoparticles incorporated into the molecular backbone. The derivatized nanoparticles are derivatized to include one or more functional groups. The derivatized nanoparticles are selected from a group consisting of: nanographite, nanographene, graphene fibers, carbon black, carbon nanofibers and combinations thereof. The method further involves positioning a second fiber layer adjacent to the polymer-nanoparticle-enhanced interlayer.

In another embodiment there is provided a laminate composite structure including a first fiber layer, a second fiber layer, and a polymer-nanoparticle-enhanced interlayer positioned between the first fiber layer and the second fiber layer. The polymer-nanoparticle-enhanced interlayer includes at least one polymer having a molecular backbone and derivatized nanoparticles incorporated into the molecular backbone. The derivatized nanoparticles are derivatized to include one or more functional groups. The derivatized nanoparticles are selected from a group consisting of: nanographite, nanographene, graphene fibers, carbon nanofibers and combinations thereof. The laminate composite structure further includes resin infused into the first and second fiber layers.

The features, functions, and advantages that have been discussed can be achieved independently in various implementations or may be combined in yet other implementations, further details of which can be seen with reference to the following description and drawings.

BRIEF DESCRIPTION OF ILLUSTRATIONS

So that the manner in which the above-recited features of the present disclosure can be understood in detail, a more particular description of the disclosure, briefly summarized above, may be had by reference to implementations, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical implementations of this disclosure and are therefore not to be considered limiting of its scope, for the disclosure may admit to other equally effective implementations.

FIG. **1** illustrates a flow diagram of an exemplary aircraft production and service method;

FIG. **2** illustrates a block diagram of an exemplary aircraft;

FIG. **3**A illustrates a cross-sectional side view of a polymer-nanoparticle-enhanced interlayer assembly attached to a fiber layer in accordance with an implementation described herein;

FIG. **3**B illustrates an enlarged, cross-sectional side view of the polymer-nanoparticle-enhanced interlayer assembly of FIG. **3**A;

FIG. **4** illustrates a cross-sectional side view of a polymer-nanoparticle-enhanced interlayer assembly attached to a fiber layer in accordance with another implementation described herein;

FIG. **5** illustrates a partially cut-away isometric view of the polymer-nanoparticle-enhanced interlayer assembly of FIG. **3**A;

FIG. **6**A illustrates an isometric view of a first composite laminate having a polymer-nanoparticle-enhanced interlayer assembly configured in accordance with an implementation described herein;

FIG. **6**B illustrates an isometric view of a second composite laminate having a polymer-nanoparticle-enhanced interlayer assembly configured in accordance with another implementation described herein;

FIG. **7** illustrates an enlarged, cross-sectional isometric view of a portion of the composite laminates of FIG. **6**A and FIG. **6**B;

FIG. **8** is a flow diagram illustrating a method for manufacturing composite parts in accordance with an implementation of the disclosure; and

FIG. **9** is a flow diagram illustrating a method of manufacturing a composite structure in accordance with another implementation of the disclosure.

To facilitate understanding, identical reference numerals have been used, wherever possible, to designate identical elements that are common to the Figures. Additionally, elements of one implementation may be advantageously adapted for utilization in other implementations described herein.

DETAILED DESCRIPTION

The following disclosure describes polymer-nanoparticle-enhanced interlayers for composite structures, methods for producing polymer-nanoparticle-enhanced interlayers, and methods for manufacturing composite parts for aircraft and other structures with polymer-nanoparticle-enhanced interlayers. Certain details are set forth in the following description and in FIGS. **1A-9** to provide a thorough understanding of various implementations of the disclosure. Other details describing well-known structures and systems often associated with composite parts and composite part manufacturing are not set forth in the following disclosure to avoid unnecessarily obscuring the description of the various implementations.

Many of the details, dimensions, angles and other features shown in the Figures are merely illustrative of particular implementations. Accordingly, other implementations can have other details, dimensions, angles and features without departing from the spirit or scope of the present disclosure. In addition, further implementations of the disclosure can be practiced without several of the details described below.

The implementations described herein generally relate to composite structures, and more particularly, to polymer-nanoparticle-enhanced interlayer for use in composite structures. Compression-strength retention in composites toughened from nonwoven veils has been lower than desired, primarily due to large decreases in stiffness with increasing temperature in the veil. It is believed that a veil polymer with increased stiffness and/or improved stiffness retention with increasing temperature will improve property retention while still providing increased toughness against impact. Polymers without stiff chain segments tend to soften significantly with increasing temperature. Polymers made with stiff backbones to improve their property retention with temperature generally are very difficult to process except at very high temperatures and, even in most cases, the ability to process may be very low. Incorporation of functionalized, stiff, nanoscale particles directly into the polymer chain used for producing nonwoven toughening veils should provide a balance of improved stiffness and processability to provide the desired properties of improved toughness with minimal adverse effects on other composite properties. It is believed that only a very small amount of functionalized nanoparticles is required to stiffen the polymers as incorporation of such particles directly into the polymer backbone should increase stiffness above what would be expected from the rule of mixtures because the stiffness is imparted directly, not through van der Waals interactions with the nanoparticles.

Certain implementations described herein provide polymers for use in fabricating nonwoven toughening veils. The polymers are formed from a mixture of one or more monomers with functionalized nanoparticles to provide increased stiffness and strength relative to polymers without the incorporation of nanoparticles. This increased stiffness provides improved composite material property retention, especially compression and shear strengths at elevated temperatures, for composites toughened with polymer-based nonwoven fabrics. This improvement allows for improved toughness while minimizing the reduction in other properties that occurs using conventional toughening methods.

Referring more particularly to the drawings, implementations of the disclosure may be described in the context of an aircraft manufacturing and service method **100** as shown in FIG. **1** and an aircraft **202** as shown in FIG. **2**. During pre-production, method **100** may include specification and design **104** of the aircraft **202** and material procurement **106**. During production, component and subassembly manufacturing **108** and system integration **110** of the aircraft **202** takes place. Thereafter, the aircraft **202** may go through certification and delivery **112** in order to be placed in service **114**. While in service by a customer, the aircraft **202** is scheduled for routine maintenance and service **116** (which may include modification, reconfiguration, refurbishment, and so on).

Each of the processes of method **100** may be performed or carried out by a system integrator, a third party, and/or an operator (e.g., a customer). For the purposes of this description, a system integrator may include without limitation any number of aircraft manufacturers and major-system subcontractors; a third party may include without limitation any number of venders, subcontractors, and suppliers; and an operator may be an airline, leasing company, military entity, service organization, and so on.

As shown in FIG. **2**, the aircraft **202** produced by exemplary method **100** may include an airframe **218** with a plurality of systems **220** and an interior **222**. Examples of high-level systems **220** include one or more of a propulsion system **224**, an electrical system **226**, a hydraulic system **228**, and an environmental system **230**.

Apparatus and methods embodied herein may be employed during any one or more of the stages of the production and service method **100**. For example, components or subassemblies corresponding to production process **108** may be fabricated or manufactured in a manner similar to components or subassemblies produced while the aircraft **202** is in service. Also, one or more apparatus implementations, method implementations, or a combination thereof may be utilized during the production stages **108** and **110**, for example, by substantially expediting assembly of or reducing the cost of an aircraft **202**. Similarly, one or more of apparatus implementations, method implementations, or a combination thereof may be utilized while the aircraft **202** is in service, for example and without limitation, to maintenance and service **116**.

FIG. **3**A illustrates a cross-sectional side view of a polymer-nanoparticle-enhanced interlayer assembly **300**. In the illustrated implementation, the polymer-nanoparticle-enhanced interlayer assembly **300** includes a polymer-nanoparticle-enhanced interlayer **310** attached to a fiber layer **302**. The fiber layer **302** can include various types of fiber materials known in the art including unidirectional, woven, nonwoven, braided, and/or warp-knit fibers (e.g., carbon, glass, polyaramide) in multiple orientations. For example, in one implementation, the fiber layer **302** can include carbon fibers in a bi-directional weave. In another implementation, the fiber layer **302** can include unidirectional carbon fibers.

In some implementations, the polymer-nanoparticle-enhanced interlayer **310** may be attached to the fiber layer **302** using mechanical means. Exemplary mechanical means include stitching as described below with regards to FIG. **5**. Various methods for stitching the polymer-nanoparticle-enhanced interlayer **310** to the fiber layer **302** are described in detail in U.S. Patent No. **8,246,882**.

In some implementations, the polymer-nanoparticle-enhanced interlayer **310** may be directly attached to the fiber layer **302** by directly bonding the polymer-nanoparticle-enhanced interlayer **310** to the fiber layer **302**. Exemplary bonding methods include melt-bonding. Melt-bonding may be achieved by elevating the temperature of the polymer-nanoparticle-enhanced interlayer **310** so that at least a portion of the polymer material melts and thereby bonds to the fiber layer **302**. Melt-bonding of interlayers to fiber layers is described in detail in U.S. patent application Pub. No. **2004-0219855**.

FIG. **3**B illustrates an enlarged, cross-sectional side view of the polymer-nanoparticle-enhanced interlayer **310** of FIG. **3**A. The polymer-nanoparticle-enhanced interlayer **310** includes at least one polymer **304** with derivatized nanoparticles **306** that are derivatized to include one or more functional groups. The derivatized nanoparticles are included in the molecular backbone of the at least one polymer. The at least one polymer **304** may be in the form of thermoplastic fibers that are spunbonded, spunlaced, or mesh fabric. As depicted in FIG. **3**B, the derivatized nanoparticles are embedded in polymer or thermoplastic fibers **308** of the at least one polymer **304**.

The polymer or thermoplastic fibers **308** may be made from two or more materials. In some implementations, the two or more materials may be used to form a bi-component fiber, tri-component fiber or higher component fiber to create the interlayer fabric.

In some implementations, the fibers making up the interlayer have diameters from about **1** to about **100** microns (e.g., from about **10** to about **75** microns; from about **10** to about **30** microns; from about **1** to about **15** microns).

In some implementations, the polymer-nanoparticle-enhanced interlayer **310** may be formed on a substrate (not shown). The substrate can include, without limitation, carbon fibers, glass fibers, ceramic fibers (e.g., alumina fibers) and/or other flexible materials that can withstand the relatively high temperatures often necessary for processing. The substrate can also include, without limitation, polyamide, polyimide, polyester, polybutadiene, polyurethane, polypropylene, polyetherimide, polysulfone, polyethersulfone, polyphenylsulfone, polyester-polyarylate (e.g., Vectran®), polyaramid (e.g., Kevlar®), polybenzoxazole (e.g., Zylon®), Viscose (e.g., Rayon®), etc. The substrate can further include a binder (e.g., a thermoplastic resin; not shown) if necessary.

The polymer-nanoparticle-enhanced interlayer **310** may be formed using any suitable method known in the art. Such methods can include extrusion methods, for example, melt-spinning, wet-spinning, dry-spinning, gel-spinning and electrospinning. The method of making the polymer interlayer typically includes mixing one or more monomers with functionalized nanoparticles. In some implementations, the nanoparticles may be functionalized prior to mixing with the monomers. In some implementations, the nanoparticles may be functionalized while mixing the one or more monomers with the nanoparticles.

The at least one polymer may include any polymer that provides a balance of improved stiffness and processability with minimal adverse effects on other composite properties. Other polymers that are melt-spinnable may also be used. Exemplary polymers or homopolymers that the at least one polymer **304** may be comprised of include carboxymethyl cellulose (CMC), Nylon-**6**, **6**, polyacrylic acid (PAA), polyvinyl alcohol (PVA), polylactic acid (PLA), polyethylene-co-vinyl acetate, PEVA/PLA, polymethyacrylate (PMMA)/tetrahydroperfluorooctylacrylate (TAN), polyethylene oxide (PEO), polyamide (PA), polyamide **11** (e.g., Nylon-**11**), polyamide **12** (e.g., Nylon-**12**), polycaprolactone (PCL), polyethyl imide (PEI) polycaprolactam (e.g., Nylon **6**), polyethylene (PE), polyethylene terephthalate (PET), polyolefin, polyphenyl ether (PPE), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), polyvinylidene fluoride (PVDF), poly(vinylidenefluoride-co-hexafluoropropylene (PVDF-HFP), polyvinyl-pyridine, polylactic acid (PLA), polypropylene (PP), polybutadiene, polybutylene (PB), polybutylene terephthalate (PBT), polyimide (PI), polycarbonate (PC), polytetrafluoroethylene (PTFE), polystyrene (PS), polyester (PE), Acrylonitrile butadiene styrene (ABS), poly(methyl methacrylate) (PMMA), polyoxymethylene (POM), polyurethane (PU), polyetherimide (PEI), polysulfone, polyethersulfone (PES), polyphenylsulfone (PPSU), polyester-polyarylate (e.g., Vectran®), polyarimid (e.g., Kevlar®), polybenzoxazole (e.g., Zylon®), Viscose (e.g., Rayon®), polyamide-imide (PAI), polyphenylene sulfide (PPS), polyetherketone (PEK), polyetheretherketone (PEEK), polyarylamide (PARA), polyketone, polyphthalamide, polyphenylenether (PPE), polyethylene terephthalate (PET), Styrene-acrylonitrile (SAN), polyacrylonitrile (PAN), Styrene-butadiene rubber (SBR), Ethylene vinyl acetate (EVA), Styrene maleic anhydride (SMA), and the like, and combinations thereof.

In some implementations, the polymer or thermoplastic fibers may be selected from among any type of fiber that is compatible with the thermosetting resin used to form the fiber-reinforced composite material. For example, the thermoplastic fibers of the interlayer may be selected from the group consisting of polyamide, polyimide, polyamideimide, polyester, polybutadiene, polyurethane, polypropylene, polyetherimide, polysulfone, polyethersulfone, polyphenylsulfone, polyphenylene sulfide, polyetherketone, polyethertherketone, polyarylamide, polyketone, polyphthalamide, polyphenylenether, polybutylene terephthalate and polyethylene terephthalate.

Nanoparticles, from which the derivatized nanoparticles are formed, are generally particles having an average particle size in at least one dimension, of less than one micrometer (μm). As used herein "average particle size" refers to the number average particle size based on the largest linear dimension of the particle (sometimes referred to as "diameter"). Particle size, including average, maximum, and minimum particle sizes, may be determined by an appropriate method of sizing particles such as, for example, static or dynamic light scattering (SLS or DLS) using a laser light source. Nanoparticles may include both particles having an average particle size of **250** nm or less, and particles having an average particle size of greater than **250** nm to less than **1** μm (sometimes referred to in the art as "sub-micron sized" particles). In one implementation, a nanoparticle may have an average particle size of about **0.01** to about **500** nanometers (nm), specifically **0.05** to **250** nm, more specifically about **0.1** to about **150** nm, more specifically about **0.5** to about **125** nm, and still more specifically about **1** to about **75** nm. The nanoparticles may be monodisperse, where all particles are of the same size with little variation, or polydisperse, where the particles have a range of sizes and are averaged. Nanoparticles of different average particle size may be used, and in this way, the particle size distribution of the nanoparticles may be unimodal (exhibiting a single distribution), bimodal exhibiting two distributions, or multi-modal, exhibiting more than one particle size distribution.

Nanoparticles that may be used with the implementations disclosed herein include, for example, single or multiwalled nanotubes, nanographite, nanographene, graphene fibers, silica nanoparticles, carbon black, carbon fibers, and the like, and combinations thereof.

The nanoparticles used herein are derivatized to include one or more functional groups such as, for example, carboxy (e.g., carboxylic acid groups), epoxy, ether, ketone, amine, hydroxy, alkoxy, alkyl, aryl, aralkyl, alkaryl, lactone, functionalized polymeric or oligomeric groups, and the like, and combinations thereof. The nanoparticles are derivatized to introduce chemical functionality to the nanoparticle. For example, for carbon nanotubes, the surface and/or edges of the carbon nanotubes may be derivatized to increase stiffness of the polymer interlayer.

In one implementation, the nanoparticle is derivatized by, for example, amination to include amine groups, where amination may be accomplished by nitration followed by reduction, or by nucleophilic substitution of a leaving group by an amine, substituted amine, or protected amine, followed by deprotection as necessary. In another implementation, the nanoparticle can be derivatized by oxidative methods to produce an epoxy, hydroxy group or glycol group using peroxide, or by cleavage of a double bond by for example a metal-mediated oxidation such as a permanganate oxidation to form ketone, aldehyde, or carboxylic acid functional groups.

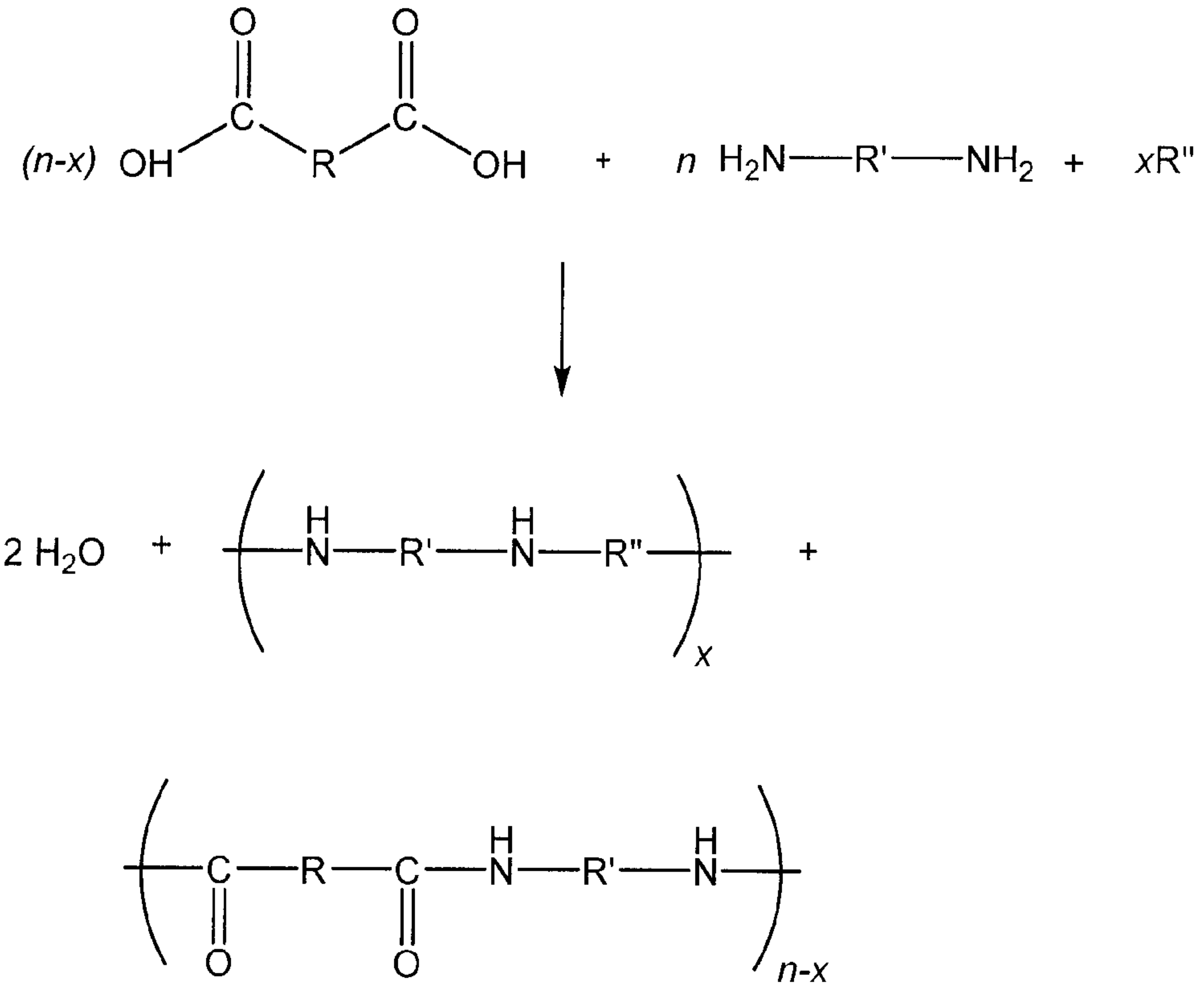
In another implementation, the nanoparticle can be further derivatized by grafting certain polymer chains to the functional groups. For example, polymer chains such as acrylic chains having carboxylic acid functional groups, hydroxy functional groups, and/or amine functional groups; polyamines such as polyethyleneamine or polyethyleneimine; and poly(alkylene glycols) such as poly(ethylene glycol) and poly(propylene glycol), may be included by reaction with functional groups.

The functional groups of the derivatized nanoparticles may be selected such that the derivatized nanoparticles will be incorporated into the polymer comprising the interlayer thereby producing a polymer chain that contains the nanoparticles within the polymer chain to impart improved properties such as higher stiffness.

The nanoparticles can also be blended in with other, more common filler particles such as carbon black, mica, clays such as e.g., montmorillonite clays, silicates, glass fiber, carbon fiber, and the like, and combinations thereof.

In one implementation, the nanoparticles are present in the amount of about **0.001** to about **10** wt. % based on the total weight of the polymer-nanoparticle-enhanced interlayer. In another implementation, the nanoparticles are present in the amount of about **0.01** to about **5** wt. % based on the total weight of the polymer-nanoparticle-enhanced interlayer. In yet another implementation, the nanoparticles are present in the amount of about **0**.**01** to about **1** wt. % based on the total weight of the polymer-nanoparticle-enhanced interlayer.

The exemplary sequence below illustrates the incorporation of derivatized nanoparticle R" into a polymer backbone, for example, the backbone of a polyamide to form an exemplary polymer-nanoparticle enhanced interlayer via a polycondensation reaction. Non-polyamide polymers may be used with appropriate modifications in nanoparticle functionalization using the same general scheme.



In some implementations, R and R' may be independently selected from divalent alkyls, divalent aryls, and substituted groups thereof. For example, for Nylon-**6**,**6**, R is C_4H_8 and R' is C_6H_{12}.

R” is a functionalized nanoparticle. R” may be any of the functionalized nanoparticles previously described herein. In some implementations, R” is functionalized with either amine or carboxyl groups. In some implementations R” is selected from the group of carbon black functionalized with carboxyl groups, graphene functionalized with carboxyl groups and carbon nanotubes functionalized with carboxyl groups. R” may be present in the amounts previously described herein. It is believed that addition of a small percentage of nanoparticles that have been functionalized with, for example, amine and/or carboxylic acid groups will participate in the above reaction to become part of the polymer backbone.

In some implementations x is from about **0.001** to about **10** wt. % (e.g., from about **0.01** to about **5** wt. %; from about **0.01** to **1** wt. %) based on the total weight of the polymer-nanoparticle-enhanced interlayer. n may be any percentage sufficiently high for providing a film-forming polymer.

FIG. **4** illustrates a cross-sectional side view of a polymer-nanoparticle-enhanced interlayer assembly **400** in accordance with another implementation described herein. The polymer-nanoparticle-enhanced interlayer assembly **400** includes a polymer-nanoparticle-enhanced interlayer **310** attached to the fiber layer **302** via an optional bond layer **402**. The bond layer **402** can include, for example, without limitation, a melt-bondable adhesive, such as a thermosetting or thermoplastic resin (e.g., a nylon-based or polyester-based resin), or other suitable adhesive known in the art.

In the illustrated implementation of FIG. **4**, the polymer-nanoparticle-enhanced interlayer **310** is attached to the fiber layer **302** by bonding (e.g., by melt-bonding) the bond layer **402** to the fiber layer **302**. Melt-bonding may be achieved by elevating the temperature of the bond layer **402** so that the material (e.g., the thermoplastic resin) melts and thereby bonds to the fiber layer **302**.

FIG. **5** illustrates a partially cut-away isometric view of the polymer-nanoparticle-enhanced interlayer assembly **300** of FIG. **3**A. In the illustrated implementation, the polymer-nanoparticle-enhanced interlayer **310** is stitched (e.g., knit-stitched or sewed) to the fiber layer **302** with thread **520**. The thread **520** extends through the polymer-nanoparticle-enhanced interlayer **310** and the fiber layer **302**. The stitching can be in various patterns, densities, and/or stitch-lengths depending on the nature of the fiber layer **302**, the polymer-nanoparticle-enhanced interlayer **310**, the thread **520**. For example, in the illustrated implementation, the thread **520** forms a tricot stitch. In other implementations, however, other stitch patterns can be used including, for example, without limitation, a lock stitch, a chain stitch, etc. The thread **520** can be selected from a variety of suitable materials in various thicknesses including, for example, without limitation, polyesters, phenoxies, polyamides, and copolyamides.

The knitting or sewing step can be manually or automatically carried out prior to use of the polymer-nanoparticle-enhanced interlayer assembly **300** in a preform, or after the initial layup of the fiber layer **302** in a preform. Various methods for stitching the polymer-nanoparticle-enhanced interlayer **310** to the fiber layer **302** are described in detail in U.S. Patent No. **8**,**246**,**882**. Although the polymer-nanoparticle-enhanced interlayer **310** is stitched to the fiber layer **302** with thread **520** in FIG. **5**, in other implementations, the polymer-nanoparticle-enhanced interlayer **310** can be attached to the fiber layer **302** with other types of fasteners. For example, in another implementation, the polymer-nanoparticle-enhanced interlayer **310** can be attached to the fiber layer **302** with mechanical fasteners, such as, without limitation, plastic rivets, inserts, staples, etc.

FIG. **6**A is an isometric view of a first composite laminate **630**a having a polymer-nanoparticle-enhanced interlayer assembly **400** configured in accordance with one implementation described herein. FIG. **6**B is an isometric view of a second composite laminate **630**b having a polymer-nanoparticle-enhanced interlayer assembly **300** configured in accordance with another implementation. With reference to FIG. **6**A, the first composite laminate **630**a includes a plurality of interlayer assemblies **600** (identified individually as a first interlayer assembly **600**a and a second interlayer assembly **600**b) assembled on a mold surface **640**. In the illustrated implementation, the interlayer assemblies **600** are at least generally similar in structure and function to the interlayer assembly **400** described above with reference to FIG. **4**. More specifically, each of the interlayer assemblies **600** includes a polymer-nanoparticle-enhanced interlayer **310** (identified individually as a first interlayer **310**a and a second interlayer **310**b) melt-bonded or otherwise attached to a corresponding fiber layer **302** (identified individually as a first fiber layer **302**a and a second fiber layer **302**b). The interlayer assemblies **600** are stacked so that they form an alternating fiber layer/interlayer/fiber layer arrangement. A third fiber layer **602** can be placed over the second interlayer assembly **600**b.

Although three fiber layers and two interlayers are shown in FIG. **6**A for purposes of illustration, any number of interlayers and fiber layers in various orientations (e.g., a +**45/0/-45/90** orientation) can be used in accordance with the disclosure. For example various implementations can include three or more fiber layers with a corresponding polymer-nanoparticle-enhanced interlayer between each fiber layer and/or on the outside of the lay-up. In addition, the various interlayers and fiber layers can have different thicknesses, different material compositions, etc.

Once the desired number of the interlayer assemblies **600** and the fiber layer **602**a has been assembled on the mold surface **640** in the desired orientations, the first composite laminate **630**a can be formed into a finished composite part using a variety of liquid-molding processes known in the art. Such methods include, for example, vacuum-assisted resin transfer molding (VARTM). In VARTM, a vacuum bag is placed over the preform, and resin is infused into the preform using a vacuum-generated pressure differential. The laminate can then be placed in an autoclave, oven, etc. and heated to cure the resin. Other liquid-molding processes include resin transfer molding (RTM) and resin film infusion (RFI). In RTM, resin is infused under pressure into the preform in a closed mold. In RFI, a semi-solid resin is placed underneath or on top of the preform, and a tool is positioned on top of the laminate. The laminate assembly is then vacuum-bagged and placed in an autoclave to melt the semi-solid resin, causing it to infuse into the preform.

In another implementation, the interlayer assemblies **600** and/or the third fiber layer **602** can be impregnated with resin (i.e., "prepreg") before being placed on the mold surface **640**. The part can then be cured by placing the laminate under a vacuum-bag and curing the matrix material at an elevated temperature and/or pressure. As the foregoing examples illustrate, implementations are not limited to a particular liquid-molding process, or to liquid-molding, for that matter.

Referring next to FIG. **6**B, the second composite laminate **630**b includes a plurality of interlayer assemblies **650** (identified individually as a first interlayer assembly **650**a and a second interlayer assembly **650**b) in a stacked arrangement on the mold surface **640**. In the illustrated implementation, the interlayer assemblies **650** are at least generally similar in structure and function to the polymer-nanoparticle-enhanced interlayer assembly **300** described above with reference to FIGS. **3**A and **3**B. For example, each of the interlayer assemblies **650** includes a polymer-nanoparticle-enhanced interlayer **310** (identified individually as a first interlayer **310**a and a second interlayer **310**b) stitched or otherwise fastened to a corresponding fiber layer **302** (identified individually as a first fiber layer assembly **302**a and a second fiber layer **302**b) with the thread **520**. The interlayer assemblies **650** are stacked so that they form an alternating fiber layer/interlayer/fiber layer arrangement. A third fiber layer **602** can be placed over the second interlayer assembly **650**b. Although three fiber layers and two interlayers are shown in FIG. 6B for purposes of illustration, any number of interlayers and fiber layers can be used in various orientations (e.g., a **0/90/0** orientation) in accordance with the present disclosure. In addition, the various interlayers and fiber layers can have different thicknesses, different material compositions, etc.

Once the desired number of the interlayer assemblies **650** and the fiber layer **602**b has been assembled on the mold surface **640**, the second composite laminate **630**b can be formed into a finished part using a variety of liquid-molding processes known in the art. As described above with reference to FIG. **6**B, such methods can include, for example, vacuum-assisted resin transfer molding (VARTM), resin transfer molding (RTM), and resin film infusion (RFI). In another implementation, the interlayer assemblies **650** and/or the third fiber layer **602**b can be infused with resin in prepreg form before being placed on the mold surface **640**. Whether liquid-molding or prepreg methods are used, the second composite laminate **630**b can be compacted (debulked) using vacuum pressure and then hardened by elevating the temperature and curing the matrix material.

FIG. **7** illustrates an enlarged, cross-sectional isometric view of a portion of the composite laminates of FIG. **6**A and FIG. **6**B. In these composite laminates, the polymer-nanoparticle-enhanced interlayer **310** may be positioned between the two of the fiber layers **302**. As shown in FIG. **7**, the first interlayer **310**a is positioned between the first fiber layer **302**a and the second fiber layer **302**b. This configuration can enhance the strength of the interface between the two fiber layers **302**a and **302**b, and can thereby increase the fracture toughness and impact resistance of the finished composite part.

FIG. **8** is a flow diagram illustrating a method **800** for manufacturing composite part with a polymer-nanoparticle-enhanced interlayer in accordance with an implementation of the disclosure. At block **802**, a polymer-nanoparticle-enhanced interlayer is produced according to implementations described herein. At block **806**, the polymer-nanoparticle-enhanced interlayer is bonded (e.g., by melt-bonding) to a fiber layer to form an interlayer assembly. After block **806**, the method proceeds to decision block **808**.

Returning to block **802**, other methods may be used to attach the polymer-nanoparticle-enhanced interlayer to the fiber layer. In some implementations, the method may proceed to block **808** where the polymer-nanoparticle-enhanced interlayer is mechanically fastened (e.g., by stitching with a thread or other suitable material) to a fiber layer to form an interlayer assembly. After block **808**, the method proceeds to decision block **810**.

In decision block **810**, the decision is made whether to pre-impregnate the interlayer assembly with matrix (e.g., epoxy resin) and store the prepreg assembly for later use, or use the dry interlayer assembly in a preform. If the decision is made to pre-impregnate the interlayer assembly, the method proceeds to block **818** and infuses the interlayer assembly with matrix material (e.g., epoxy resin). Here, the interlayer assembly can be infused with uncured matrix material using any suitable method known in the art for preparing prepreg fiber layers. In block **820**, the prepreg interlayer assembly can be stored, if desired, for an extended period of time prior to use. When the prepreg interlayer assembly is ready for use, the method proceeds to block **822** and combines the prepreg interlayer assembly with one or more prepreg fiber layers and/or one or more additional prepreg interlayer assemblies on a mold surface in a desired orientation. In block **824**, the method vacuum-bags the prepreg assembly to compact the lay-up, and cures the assembly with the application of heat and/or pressure to harden composite part.

Returning to decision block **810**, if the decision is made to assemble the dry interlayer assembly into a preform, the method proceeds to block **812** and combines the interlayer assembly with one or more fiber layers and/or one or more additional interlayer assemblies on the mold surface. In block **814**, the method infuses the preform with matrix material using any suitable liquid-molding process known in the art. In block **816**, the method evacuates the resin-infused assembly to remove air bubbles, and then cures the assembly with the application of heat and/or pressure to form the finished composite part.

FIG. **9** is a flow diagram illustrating a method **900** for manufacturing a composite structure in accordance with another implementation of the disclosure. In block **910**, the method includes producing a polymer-nanoparticle-enhanced interlayer. In block **920**, the method involves attaching the polymer-nanoparticle-enhanced interlayer to a first fiber layer. In block **930**, a second fiber layer is positioned adjacent to the first fiber layer so that the polymer-nanoparticle-enhanced interlayer is positioned between the first and second fiber layers. In block **940**, the first and second fiber layers are infused with resin, and the resin is cured in block **950**.

The methods described above can be used to manufacture composite parts for a wide variety of different structures, including aircraft structures. For example, these methods can be used to form aircraft skins, frames, stiffeners, and/or various portions thereof. The composite parts can be assembled together to form aircraft structures (e.g., fuselages, wings, tail surfaces, etc.) using adhesives, fasteners, and/or other suitable attachment methods known in the art.

The implementations described herein provide for a polymer-nanoparticle enhanced interlayer or “toughening veil” with improved stiffness, strength, and ability to retain compression and shear strength at elevated temperatures and methods of manufacturing the same. The polymer-nanoparticle enhanced interlayer may be created from a mixture of one or more monomers with functionalized nanoparticles. The nanoparticles in the polymer-nanoparticle enhanced interlayer are typically attached directly to the polymer as opposed to bonding by weaker Van der Waals forces. Another important benefit is that the viscosity of the mixture of the one or more monomers with the functionalized nanoparticles is typically low enough to enable spinning using available methods.

While the foregoing is directed to implementations of the present disclosure, other and further implementations of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

EMBODIMENTS IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of manufacturing a composite structure, the method comprising:

positioning a polymer-nanoparticle-enhanced interlayer adjacent to a first fiber layer, wherein the polymer-nanoparticle-enhanced interlayer comprises:

at least one polymer having a molecular backbone; and

derivatized nanoparticles incorporated into the molecular backbone, wherein the derivatized nanoparticles are derivatized to include one or more functional groups and wherein the derivatized nanoparticles are selected from a group consisting of: nanographite, nanographene, graphene fibers, carbon black, carbon nanofibers and combinations thereof; and

positioning a second fiber layer adjacent to the polymer-nanoparticle-enhanced interlayer.

2. The method of claim **1**, further comprising:

infusing the first fiber layer and the second fiber layer with resin; and

curing the resin to harden the composite structure.

3. The method of claim **2**, wherein the at least one polymer comprises thermoplastic fibers.

4. The method of claim **2** or **3**, wherein the one or more functional groups form bonds with the resin.

5. The method of any one of claims **2** to **4**, further comprising infusing the polymer-nanoparticle-enhanced interlayer with the resin and wherein infusing the first and second fiber layers and the polymer-nanoparticle-enhanced interlayer with the resin includes preimpregnating the polymer-nanoparticle-enhanced interlayer and the first fiber layer with a first portion of the resin, and preimpregnating the second fiber layer with a second portion of the resin, before positioning the second fiber layer adjacent the polymer-nanoparticle-enhanced interlayer.

6. The method of any one of claims **1** to **5**, wherein the nanoparticles are single-walled or multiwalled.

7. The method of claim **6**, wherein the nanoparticles are single or multi-walled nanoparticles having amine or carboxy functional groups.

8. The method of any one of claims **1** to **6**, wherein the one or more functional groups comprises at least one functional group consisting of at least one of: amine, carboxy, hydroxy, epoxy, ether, ketone, alkoxy, aryl, aralkyl, lactone, functionalized polymeric groups, functionalized oligomeric groups.

9. The method of any one of claims **1** to **8**, wherein positioning the polymer-nanoparticle-enhanced interlayer adjacent to the first fiber layer comprises heating the polymer-nanoparticle-enhanced interlayer and the first fiber layer to melt-bond the polymer-nanoparticle-enhanced interlayer to the first fiber layer.

10. The method of any one of claims **1** to **8**, wherein positioning the polymer-nanoparticle-enhanced interlayer adjacent to the first fiber layer comprises stitching the polymer-nanoparticle-enhanced interlayer to the first fiber layer.

11. The method of any one of claims **1** to **10**, wherein the composite structure comprises a composite aircraft structure and wherein the method further comprises assembling the composite aircraft structure into a portion of the aircraft.

12. The method of any one of claims **1** to **11**, wherein the polymer-nanoparticle-enhanced interlayer is produced by:

mixing at least one monomer with the derivatized nanoparticles; and

melt spinning the polymer and the derivatized nanoparticles to form the polymer-nanoparticle-enhanced interlayer.

13. A laminate composite structure, comprising:

a first fiber layer;

a second fiber layer; and

a polymer-nanoparticle-enhanced interlayer positioned between the first fiber layer and the second fiber layer, wherein the polymer-nanoparticle-enhanced interlayer includes:

at least one polymer having a molecular backbone; and derivatized nanoparticles incorporated into the molecular backbone, wherein the derivatized nanoparticles are derivatized to include one or more functional groups and wherein the derivatized nanoparticles are selected from a group consisting of: nanographite, nanographene, graphene fibers, carbon nanofibers and combinations thereof;

resin infused into the first and second fiber layers.

14. The composite structure of claim **13**, wherein the at least one polymer comprises thermoplastic fibers.

15. The composite structure of claim **13** or **14**, wherein the one or more functional groups form bonds with the resin.

16. The composite structure of any one of claims **13** to **15**, wherein the nanoparticles are single-walled or multiwalled.

17. The composite structure of any one of claims **13** to **16**, wherein the one or more functional groups comprises at least one functional group consisting of at least one of: amine, carboxy, hydroxy, epoxy, ether, ketone, alkoxy, aryl, aralkyl, lactone, functionalized polymeric groups,functionalized oligomeric groups and combinations thereof.

18. The composite structure of any one of claims **13** to **17**, wherein the polymer-nanoparticle-enhanced interlayer is melt-bonded to the first fiber layer.

19. The composite structure of any one of claims **13** to **17**, wherein the polymer-nanoparticle-enhanced interlayer is mechanically fastened to the first fiber layer.

20. The composite structure of any one of claims **13** to **19**, wherein the first fiber layer and the second fiber layer are nonwoven fiber layers and wherein the polymer-nanoparticle-enhanced interlayer is a nonwoven synthetic polymer fabric.

21. The composite structure of any one of claims **13** to **19**, wherein the first fiber layer and the second fiber layer each include carbon fibers in a bi-directional weave.

22. The composite structure of any one of claims **13** to **19**, wherein the first fiber layer and the second fiber layer each include carbon fibers in a unidirectional weave.

23. The composite structure of any one of claims **13** to **22**, wherein the nanoparticles are present in the amount of about **0**.**001** wt. % to about **10** wt. % based on the total weight of the polymer-nanoparticle-enhanced interlayer.

24. The composite structure of any one of claims **13** to **23**, further comprising a bond layer positioned between the first fiber layer and the polymer-nanoparticle-enhanced interlayer, wherein the bond layer comprises a melt-bondable adhesive.

25. The composite structure of any one of claims **13** to **19**, further comprising:

a third fiber layer; and

a second polymer-nanoparticle-enhanced interlayer positioned between the second fiber layer and the third fiber layer, wherein the second polymer-nanoparticle-enhanced interlayer includes:

the at least one polymer having the molecular backbone; and

the derivatized nanoparticles incorporated into the molecular backbone.

26. The composite structure of claim **25**, further comprising resin infused into the third fiber layer.

27. The composite structure of claim **26**, wherein the second polymer-nanoparticle-enhanced interlayer is melt-bonded to the third fiber layer.

28. The composite structure of any one of claims **25** to **27**, wherein the first fiber layer, the second fiber layer, and the third fiber layer each include carbon fibers in a bi-directional weave.

29. The composite structure of any one of claims **25** to **27**, wherein the first fiber layer, the second fiber layer, and the third fiber layer each include carbon fibers in a unidirectional weave.

30. The composite structure of any one of claims **13** to **29**, wherein the composite structure is a composite aircraft structure.

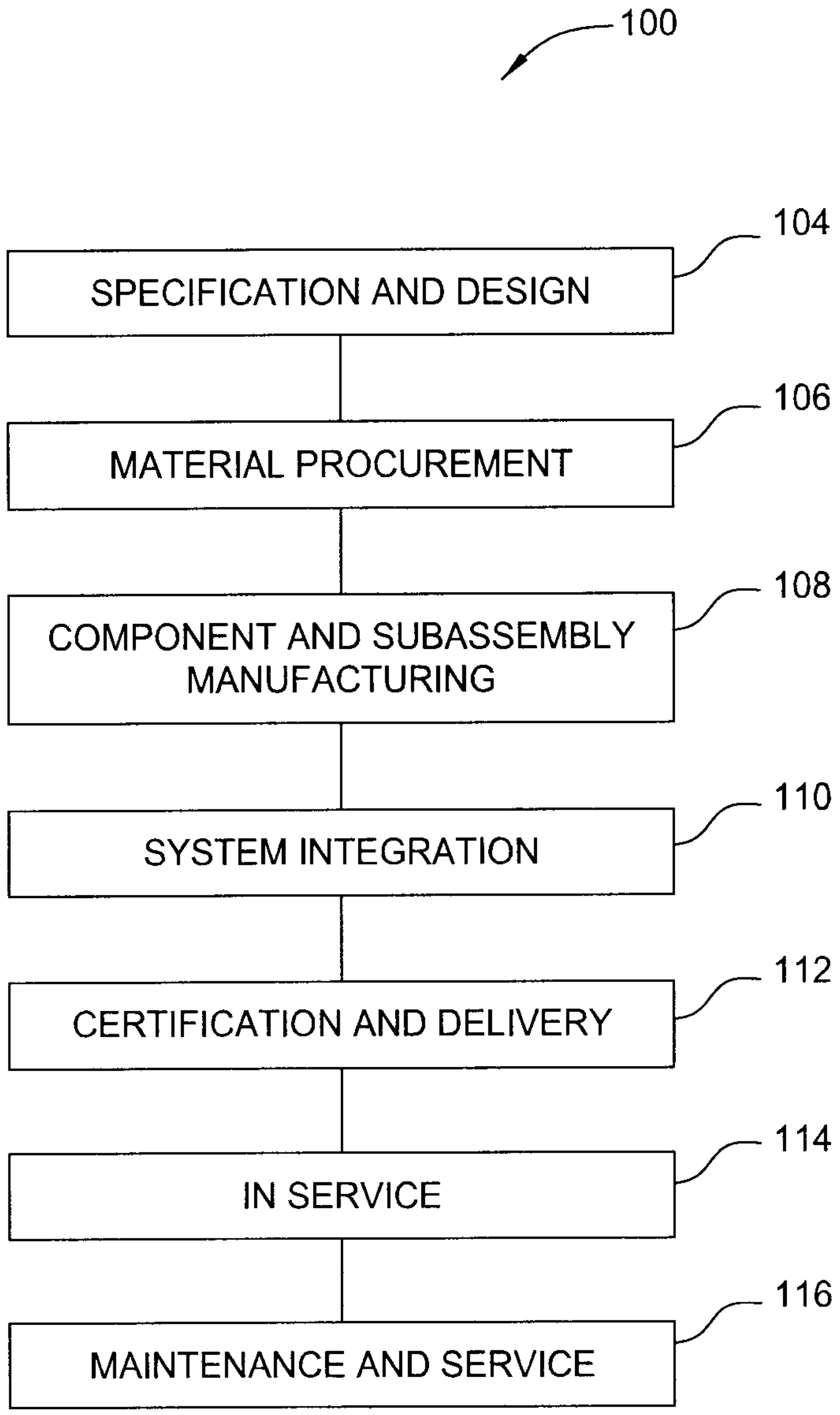

100
104
SPECIFICATION AND DESIGN
106
MATERIAL PROCUREMENT
108
COMPONENT AND SUBASSEMBLY MANUFACTURING
110
SYSTEM INTEGRATION
112
CERTIFICATION AND DELIVERY
114
IN SERVICE
116
MAINTENANCE AND SERVICE

FIG. 1

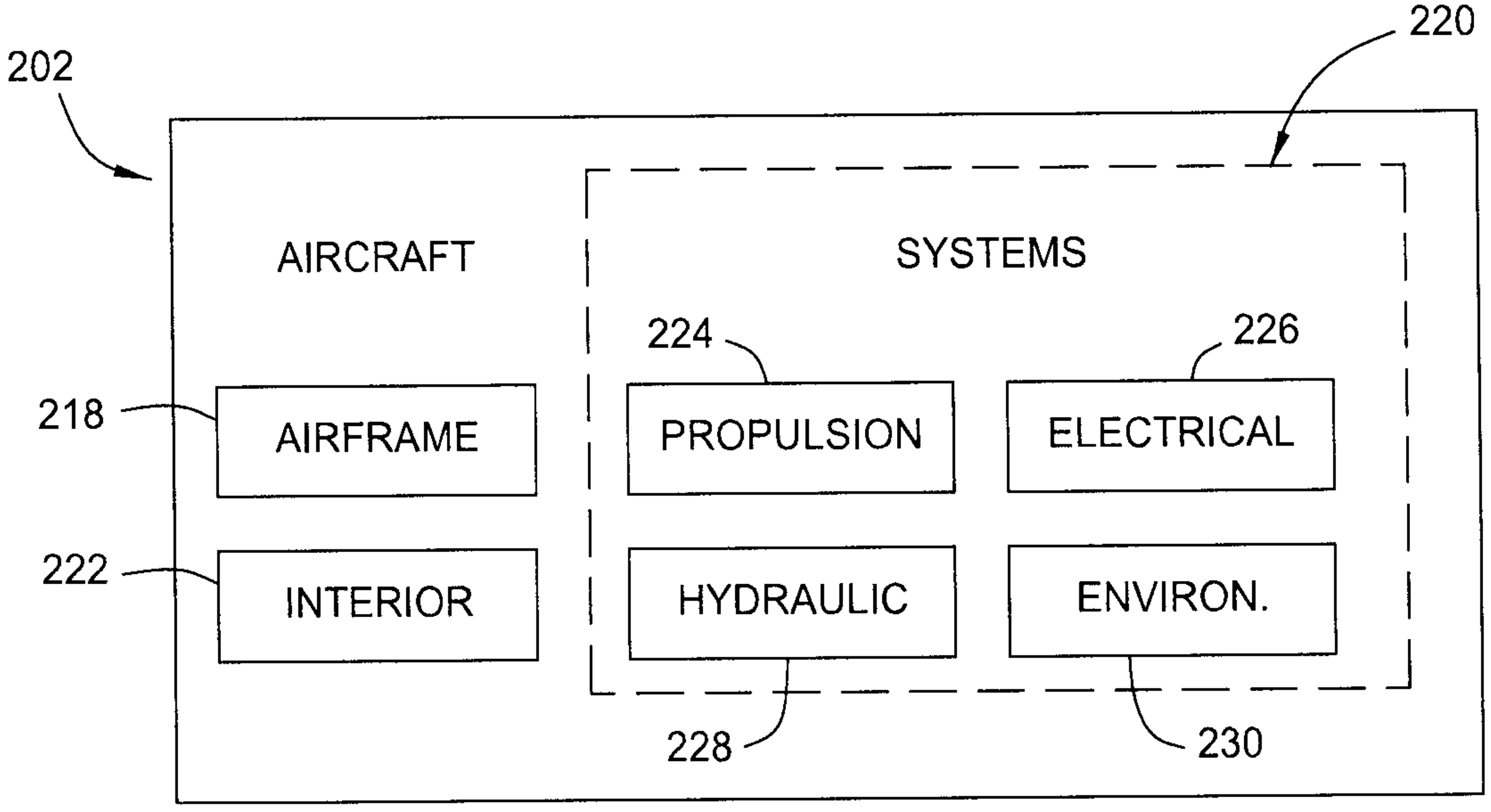

202
AIRCRAFT
218
AIRFRAME
222
INTERIOR
220
SYSTEMS
224
PROPULSION
226
ELECTRICAL
HYDRAULIC
ENVIRON.
228
230

FIG. 2

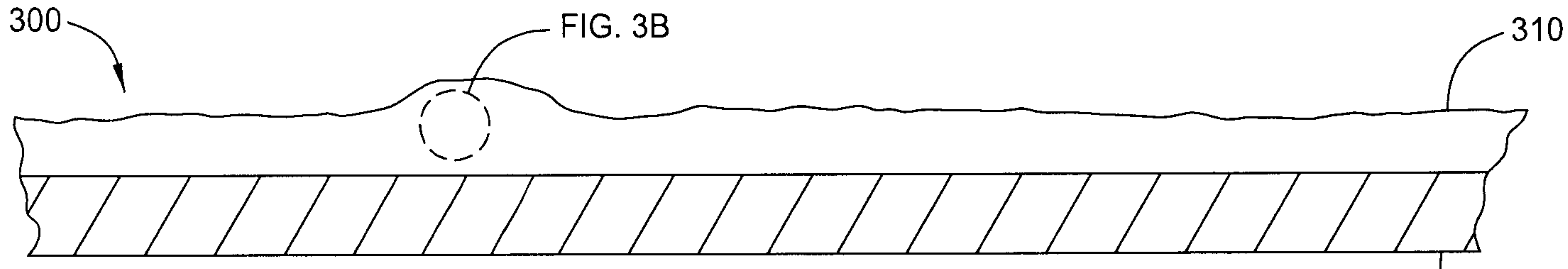


FIG. 3A

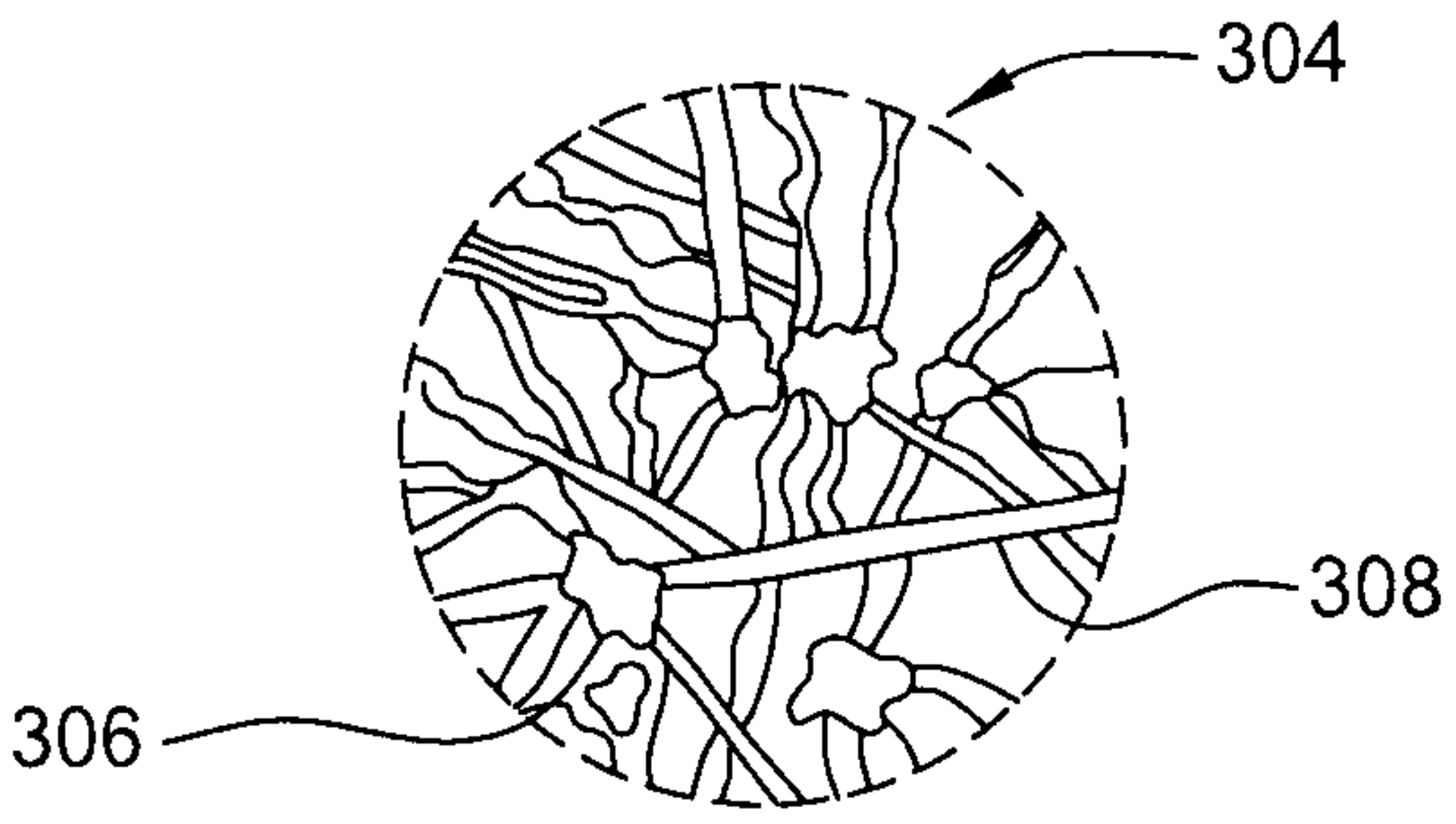


FIG. 3B

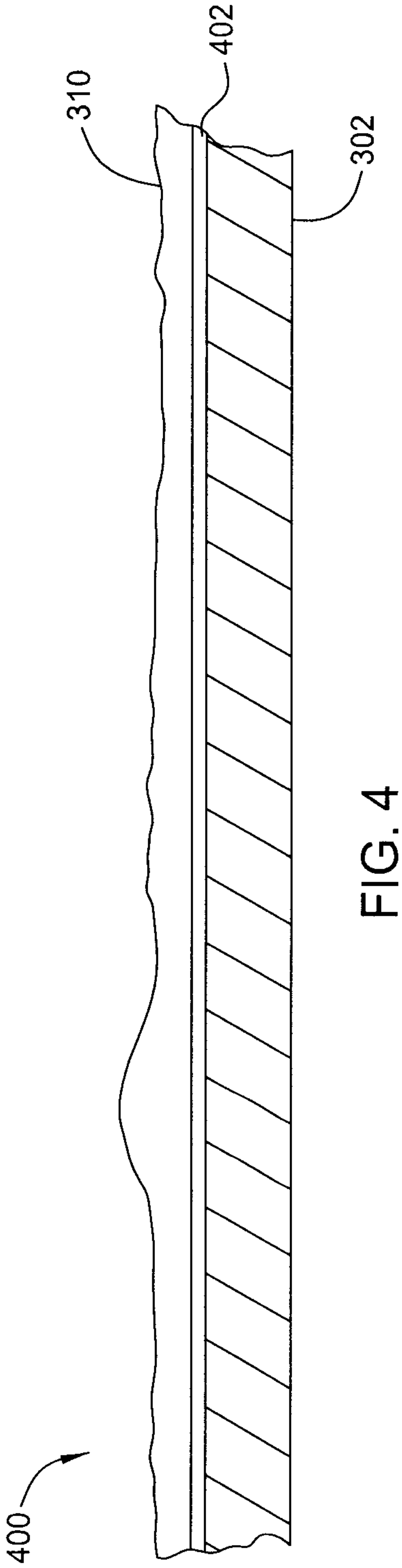


FIG. 4

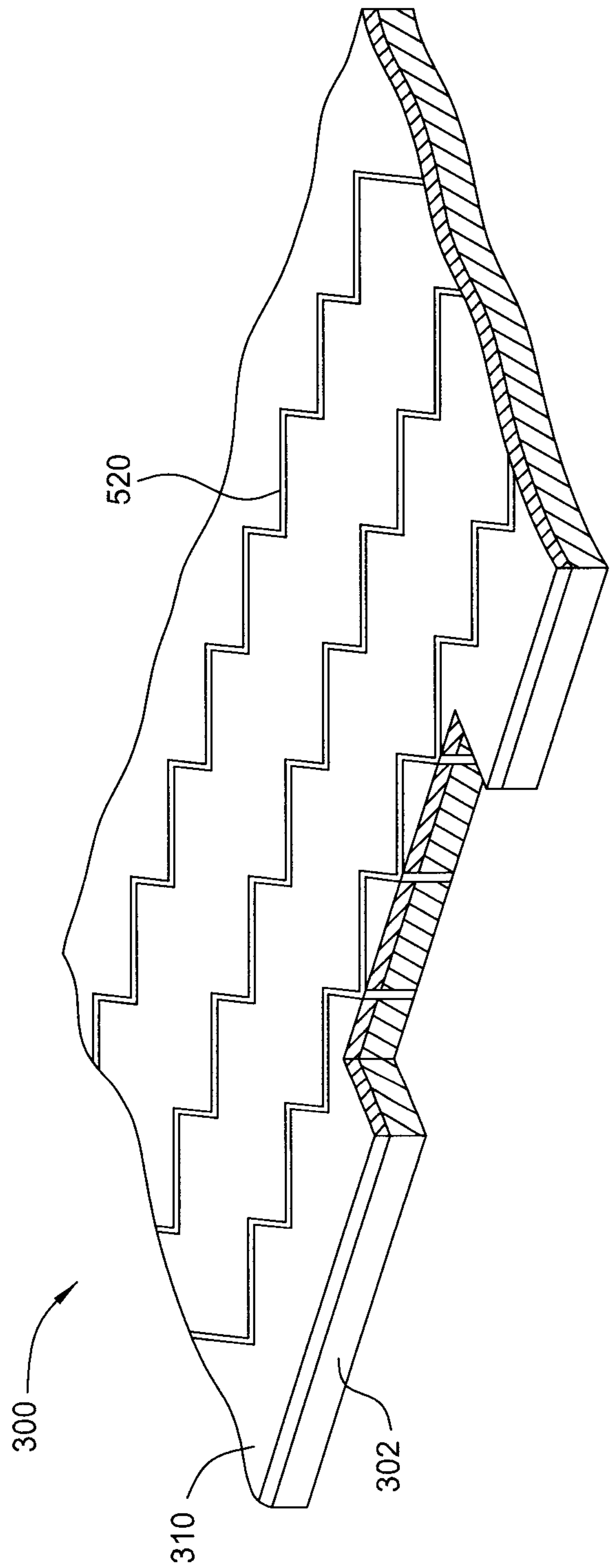


FIG. 5

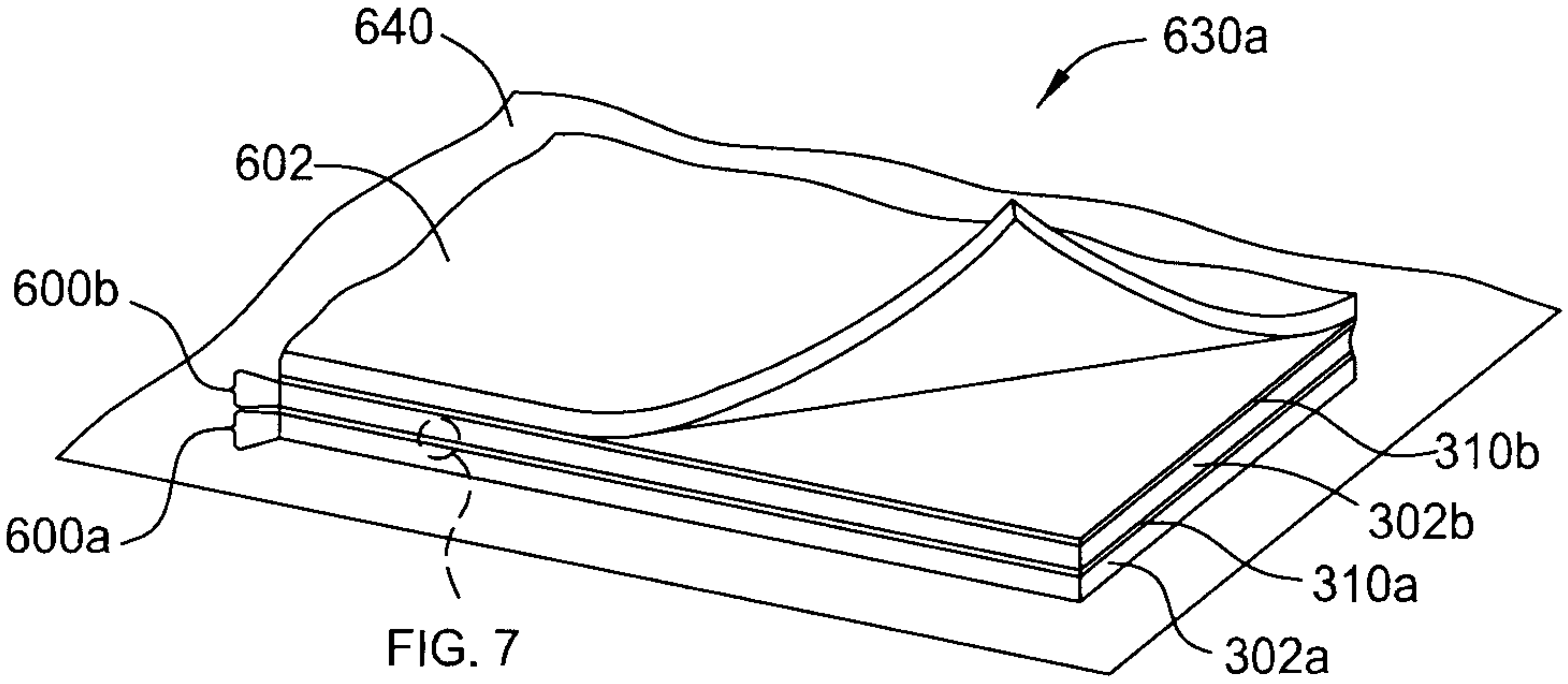

640
630a
602
600b
310b
302b
600a
310a
FIG. 7
302a

FIG. 6A

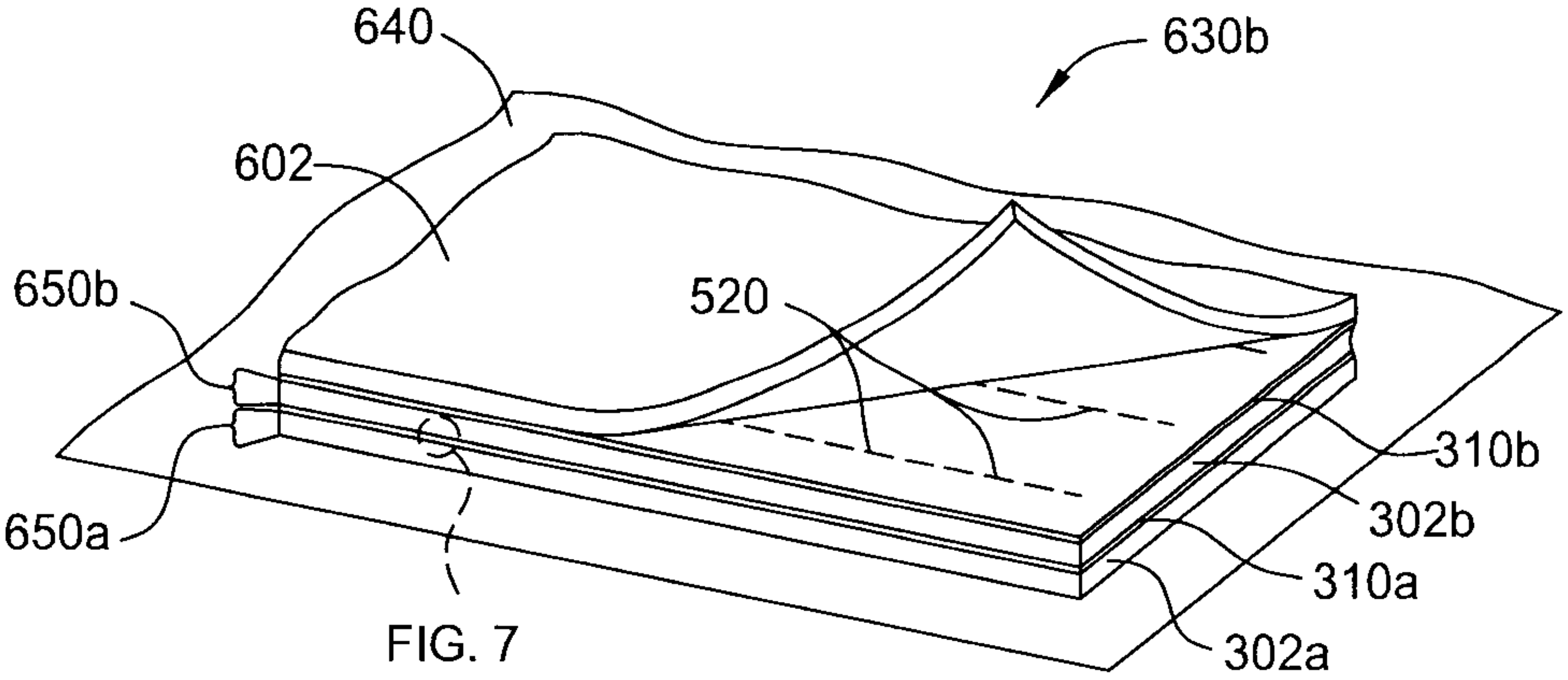

640
630b
602
650b
520
310b
302b
650a
310a
FIG. 7
302a

FIG. 6B

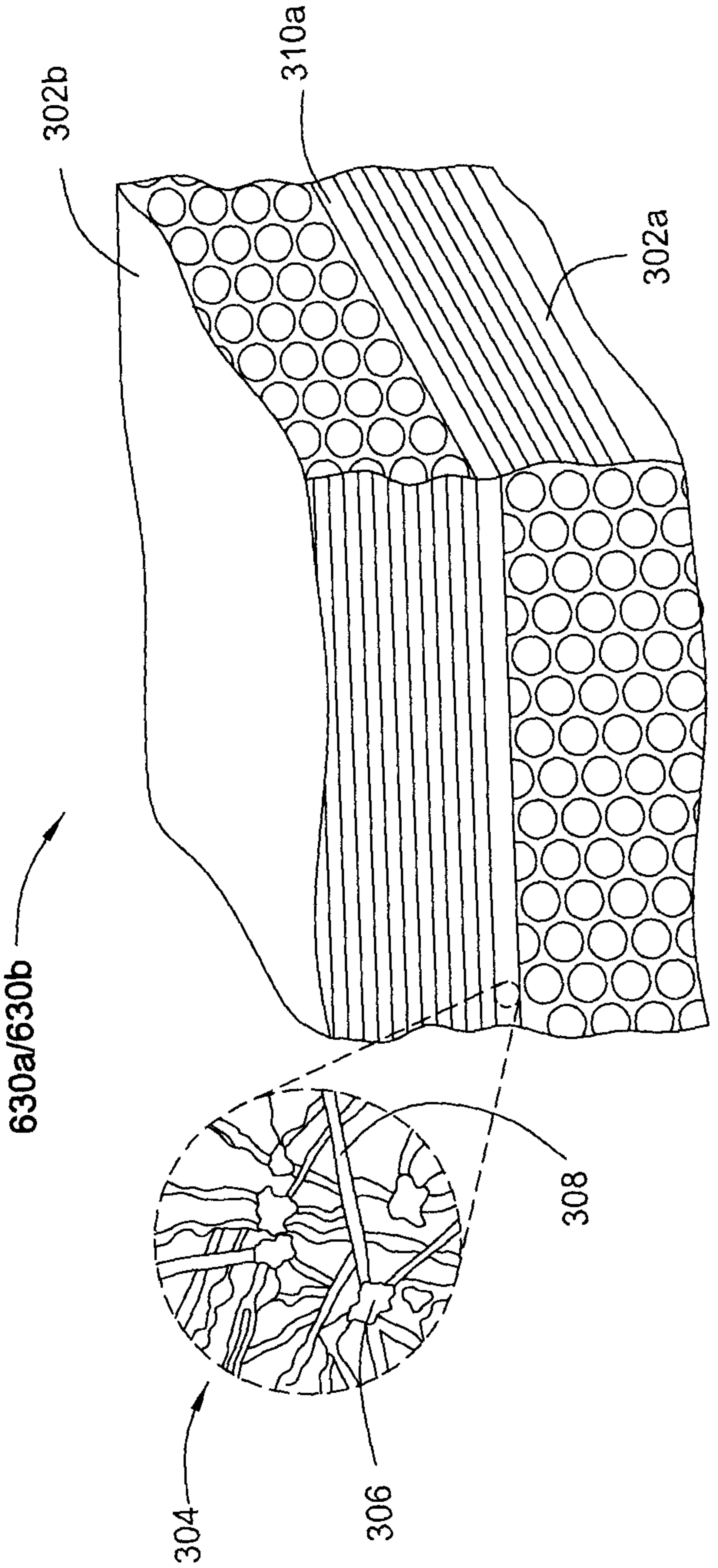


FIG. 7

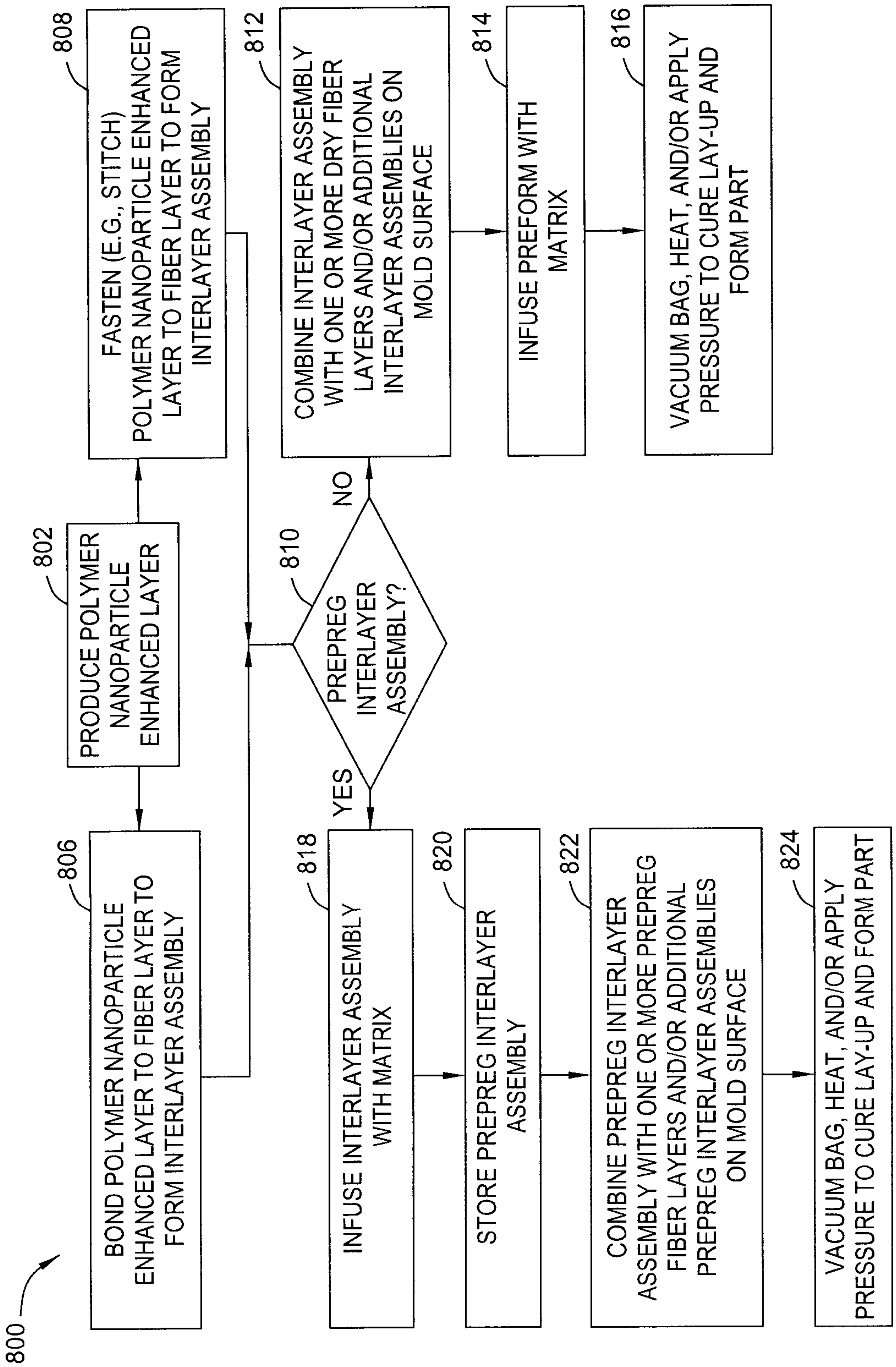

800
802
PRODUCE POLYMER NANOPARTICLE ENHANCED LAYER
806
BOND POLYMER NANOPARTICLE ENHANCED LAYER TO FIBER LAYER TO FORM INTERLAYER ASSEMBLY
808
FASTEN (E.G., STITCH) POLYMER NANOPARTICLE ENHANCED LAYER TO FIBER LAYER TO FORM INTERLAYER ASSEMBLY
810
PREPREG INTERLAYER ASSEMBLY?
NO
YES
812
COMBINE INTERLAYER ASSEMBLY WITH ONE OR MORE DRY FIBER LAYERS AND/OR ADDITIONAL INTERLAYER ASSEMBLIES ON MOLD SURFACE
814
INFUSE PREFORM WITH MATRIX
816
VACUUM BAG, HEAT, AND/OR APPLY PRESSURE TO CURE LAY-UP AND FORM PART
818
INFUSE INTERLAYER ASSEMBLY WITH MATRIX
820
STORE PREPREG INTERLAYER ASSEMBLY
822
COMBINE PREPREG INTERLAYER ASSEMBLY WITH ONE OR MORE PREPREG FIBER LAYERS AND/OR ADDITIONAL PREPREG INTERLAYER ASSEMBLIES ON MOLD SURFACE
824
VACUUM BAG, HEAT, AND/OR APPLY PRESSURE TO CURE LAY-UP AND FORM PART

FIG. 8

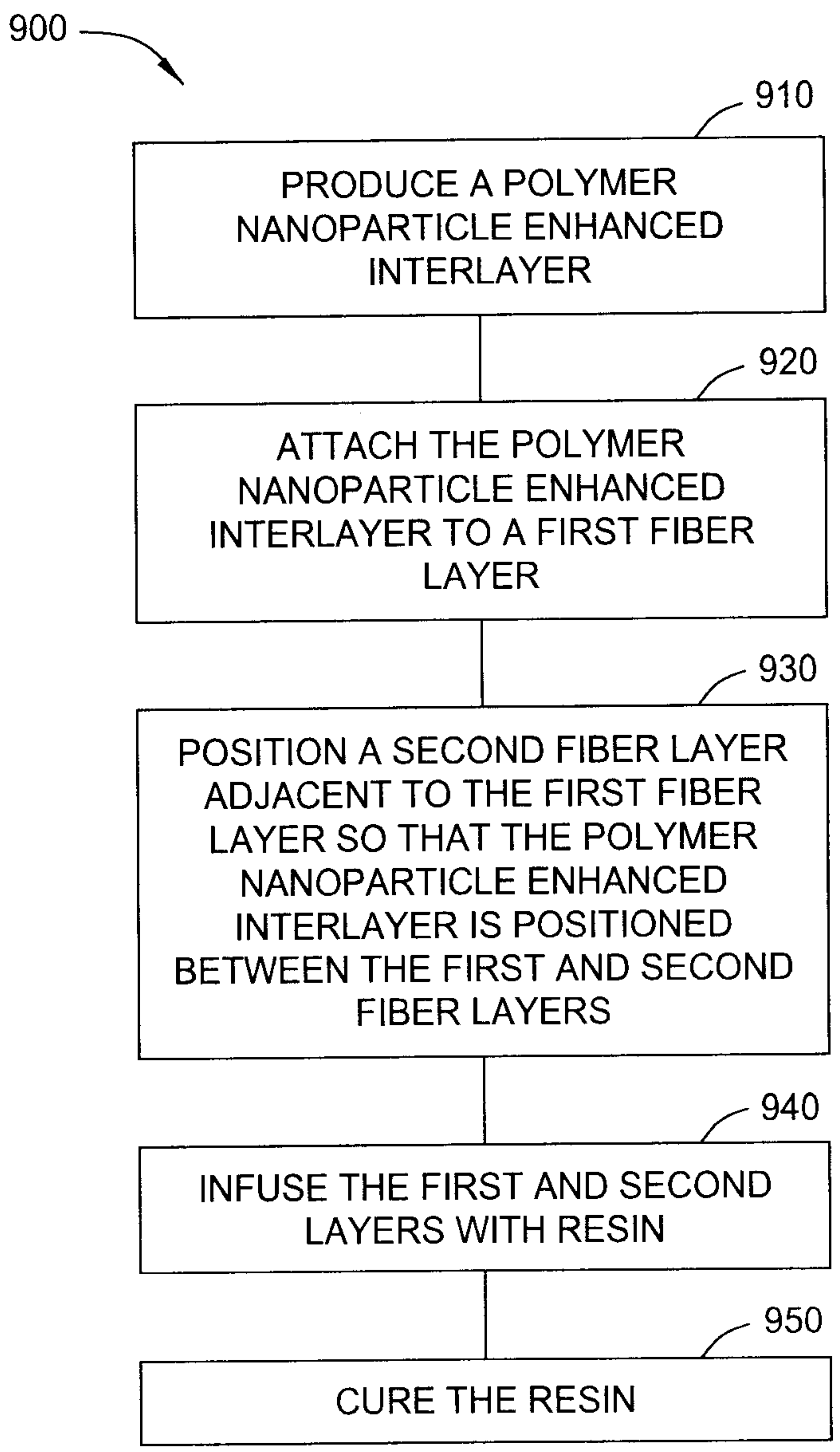
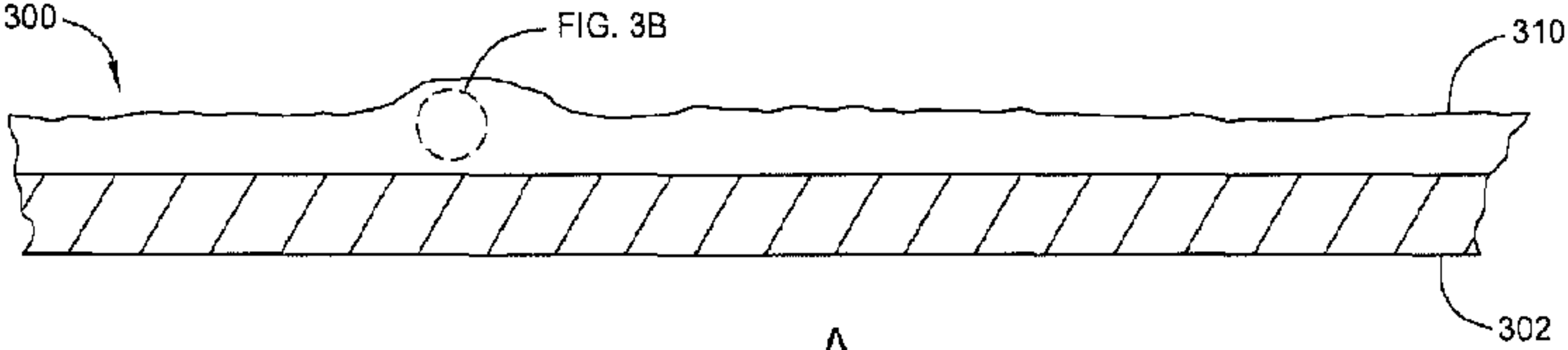
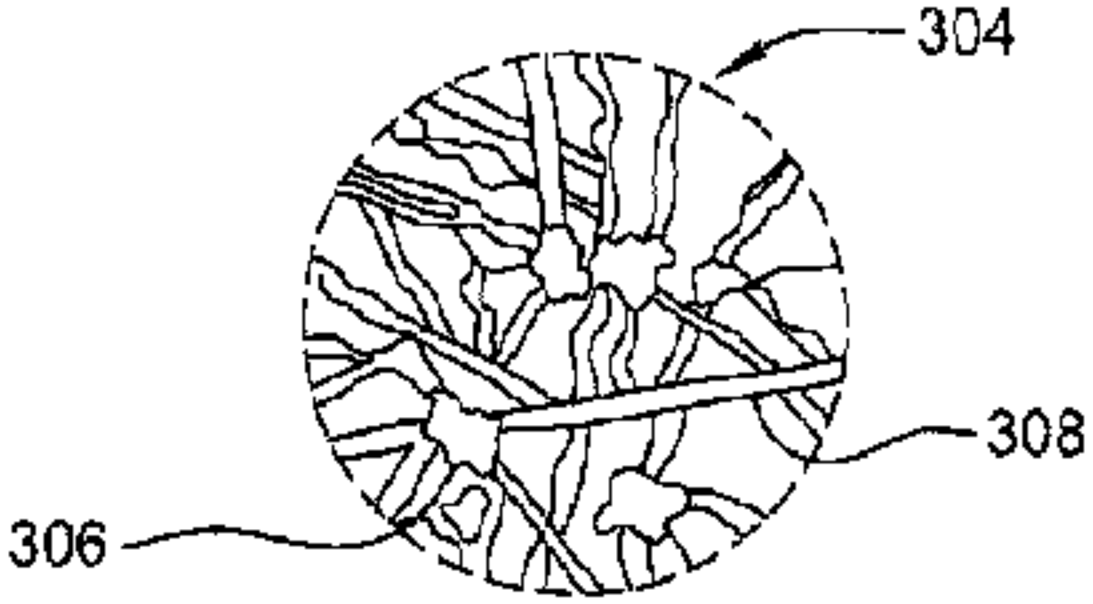

900
910
PRODUCE A POLYMER NANOPARTICLE ENHANCED INTERLAYER
920
ATTACH THE POLYMER NANOPARTICLE ENHANCED INTERLAYER TO A FIRST FIBER LAYER
930
POSITION A SECOND FIBER LAYER ADJACENT TO THE FIRST FIBER LAYER SO THAT THE POLYMER NANOPARTICLE ENHANCED INTERLAYER IS POSITIONED BETWEEN THE FIRST AND SECOND FIBER LAYERS
940
INFUSE THE FIRST AND SECOND LAYERS WITH RESIN
950
CURE THE RESIN

FIG. 9



A



B