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(54) **Title**: APPARATUS AND METHOD FOR MAKING REACTIVE POLYMER PRE-PREGS

(57) **Abstract**: A method and apparatus for making a reactive polymer pre- impregnated reinforcement material, comprising applying a substantially non-volatile composition of substantially solid particles of a reactive thermoset resin to a porous substrate at ambient temperature, initially by melting a first portion of the particles of the reactive thermoset resin. The first portion of the particles of the reactive thermoset resin flows into interstices of at least one layer of the porous substrate and a remaining portion of the particles of the substantially non-volatile composition remains solid. An apparatus for forming a drapable polymer pre-impregnated reinforcement material, comprising: a feeder roll of reinforcement material, a receiver roll of drapable polymer pre-impregnated reinforcement material and a conveyor belt having the reinforcement material from the feeder roll thereon, and a particle deposition hopper adapted to deposit between 20 g/(meter squared) and about 2,000 g/(meter squared) of the substantially non-volatile composition.

APPARATUS AND METHOD FOR MAKING REACTIVE POLYMER PRE-PREGS

1. FIELD OF THE INVENTION

[001] The present invention relates generally to an apparatus and method for making reactive polymer pre-impregnated reinforcement materials (pre-pregs). More specifically, the present invention relates to an apparatus and method for impregnating reinforcing materials, such as fabrics or assemblages of reinforcing fibers, with heat curable thermoset resins.

2. BACKGROUND

[002] There is a growing demand by industry, governmental regulatory agencies and consumers for durable and inexpensive products that are functional comparable or superior to metal products. This is particularly true in the automotive industry. Developers and manufacturers of these products are concerned with the strength parameters, such as impact, bending, stretching, and twisting resilience. To meet these demands, a number of reactive thermoplastic composite pre-pregs and thermoplastic based fully polymerized sheets have been engineered.

[003] Therefore there is a need for an improved apparatus and method for making reactive polymer pre-impregnated reinforcement materials (pre-pregs).

SUMMARY OF THE INVENTION

[004] A first aspect of the present invention provides a method for

making a reactive polymer pre-impregnated reinforcement material, comprising: providing a substantially non-volatile composition, comprising substantially completely solid particles of at least one heat curable thermoset resin, wherein the only volatile components of the substantially non-volatile composition are residual water or residual solvent; depositing a layer of the substantially non-volatile composition on a fabric or assemblage of reinforcing fiber to be impregnated, wherein the particles of the substantially non-volatile composition are solid at ambient temperature and are applied to the fabric or assemblage of reinforcing fiber to be impregnated at ambient temperature; forming a pre-preg by heating the substantially completely solid particles of the substantially non-volatile composition, so that the substantially completely solid particles partially melt, wherein the fabric or assemblage is impregnated by the partially melted composition, and the partially melted solid particles of the composition adhere to the fabric or assemblage of reinforcing fiber.

[005] A second aspect of the present invention provides a drapable polymer pre-impregnated reinforcement material, comprising: a porous substrate having at least one layer; randomly spaced particles of a substantially non-volatile composition, comprising at least one reactive thermoset resin(s), thereon, wherein the only volatile components of the substantially non-volatile composition are residual water or residual solvent; wherein a portion of each of the randomly spaced particles is impregnated into interstices of the first surface of the porous substrate, therein, and wherein a space, therebetween, separates adjacent randomly spaced particles.

[006] A third aspect of the present invention provides a method for forming a drapable polymer pre-impregnated reinforcement material, comprising: providing a the porous substrate having having at least one layer; and forming an array of a substantially non-volatile composition, comprising substantially uniformly spaced and substantially completely solid reactive thermoset particles, and covering a portion of the at least one layer, thereon, wherein the only volatile components of the composition are residual water or solvent: partially melting the array of substantially completely solid reactive thermoset particles; and fixing the partially melted array by impregnating the melt into interstices of a portion of the at least one layer of the porous substrate, therein, wherein a remaining portion of the at least one layer remains uncovered by the array.

[007] A fourth aspect of the present invention provides an apparatus for forming a drapable polymer pre-impregnated reinforcement material, comprising: a feeder roll of reinforcement material; a receiver roll of drapable polymer pre-impregnated reinforcement material; and a conveyor belt having the reinforcement material from the feeder roll thereon; a particle deposition hopper charged with a substantially non-volatile composition, comprising substantially completely solid reactive thermoset particles, wherein the only volatile components of the substantially non-volatile composition are residual water or solvent: a heating unit adapted to substantially uniformly maintain a temperature of the substantially non-volatile composition on at least one layer of the reinforcement material for a residence time, during which the particles of the composition on the at least one layer of the reinforcement material reside in the

oven; a conveyor belt, wherein residence time that the particles of the composition reside on the at least one layer of the reinforcement material is based on the conveyor belt's rate.

[008] A fifth aspect of the present invention provides a method for forming a thermoset composite sheet, comprising: providing at least one feeder roll, wherein one of the feeder rolls provides reinforcement material, a receiver roll of drapable polymer pre-impregnated reinforcement material and a conveyor belt having the reinforcement material from the feeder roll thereon, wherein the reinforcement material has a fiber content based on total weight of the thermoset composite sheet; providing a particle deposition hopper charged with reactive thermoset particles of a substantially non-volatile composition, wherein the only volatile components of the substantially non-volatile composition are residual water or solvent, and adapted to deposit between 20 g/m^2 and about 2,000 g/m^2 of the reactive thermoset particles of the substantially non-volatile composition, based on the surface area (m^2) of the reinforcement material; providing a heating unit adapted to substantially uniformly maintain the reactive thermoset particles of the substantially non-volatile composition on a first surface of the reinforcement material between about 40°C and about 230°C during a residence time that the reactive thermoset particles of the substantially non-volatile composition on at least one layer of the reinforcement material reside in the oven; providing a conveyor belt wherein residence time that the reactive thermoset particles of the substantially non-volatile composition on the at least one layer of the reinforcement material is based on the conveyor belt's rate; and providing a belt press after the heating unit, wherein the belt press has a hot zone and a cold zone, wherein the hot zone is adapted to receive drapable polymer pre-impregnated reinforcement material and to heat said pre-impregnated reinforcement material to less than or equal to about 260°C and greater than or equal to about 0.01 bar pressure, and wherein the cold zone is adapted to receive a fully impregnated and cured thermoset composite sheet and to cool said fully impregnated and cured thermoset composite sheet to about 25°C.

[009] A sixth aspect of the present invention provides a method for making a reactive polymer pre-impregnated reinforcement material, comprising: providing a layer of substantially completely solid particles of a heat curable thermoset resin on a liner, wherein the particles of heat curable thermoset resin are solid at ambient temperature and are applied to the liner at ambient temperature; heating the curable thermoset resin, so that the solid particles partially melt; and applying a layer of fabric or assemblage of reinforcing fiber to be impregnated to the partially melted layer of particles of the heat curable thermoset resin on the liner, wherein the fabric or assemblage of reinforcing fiber is impregnated by the partially melted particles of thermoset resin, and the solid particles adhere to the fabric or assemblage of reinforcing fiber.

[0010] A seventh aspect of the present invention provides A method for making a reactive polymer pre-impregnated reinforcement material, comprising: providing a substantially non-volatile mixture, comprising substantially completely solid particles of a heat curable thermoset resin and substantially completely solid particles of a heat curable thermoplastic resin, wherein the only volatile components of the substantially non-volatile mixture are residual water or solvent: depositing a layer of the mixture on a fabric or assemblage of reinforcing fiber to be impregnated, wherein the particles of the substantially non-volatile mixture are solid at ambient temperature and are deposited onto the fabric or assemblage of reinforcing fiber to be impregnated at ambient temperature; and forming a pre-preg by heating the particles of the substantially non-volatile mixture, so that the solid particles partially melt, wherein the fabric or assemblage is impregnated by the partially melted thermoset resin, and the partially melted solid particles adhere to the fabric or assemblage of reinforcing fiber

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The features of the invention are set forth in the appended claims. The invention itself, however, will be best understood by reference to the following detailed description of an illustrative embodiment when read in conjunction with the accompanying drawings, wherein:

[0012] **Fig. 1** depicts a longitudinal cross-sectional view of an apparatus for making a heat curable polymer pre-impregnated reinforcement material, according to embodiments of the present invention;

[0013] **Fig. 2** depicts a longitudinal cross-sectional view of the apparatus taken along an axis **2-2** of **Fig. 1**, according to embodiments of the present invention;

[0014] **Fig. 3A** depicts a longitudinal cross-sectional view of the apparatus taken along an axis **3A-3A** of **Fig. 1**, according to embodiments of the present invention;

[0015] **Fig. 3B** depicts a longitudinal cross-sectional view of the apparatus taken along an axis **3B-3B** of **Fig. 1**, according to embodiments of the present invention;

[0016] **Fig. 4** depicts a longitudinal cross-sectional view of an apparatus for pre-heating a first surface of a substrate of a prepreg, prior to thermally fixing particles of a reactive thermoplastic or thermoset resin on the first surface of the prepreg, according to embodiments of the present invention;

[0017] **Fig. 5** depicts a longitudinal cross-sectional view of the apparatus taken along an axis **5-5** of **Fig. 4**, according to embodiments of the present invention;

[0018] **Fig. 6A** depicts a longitudinal cross-sectional view of the particle prepreg retrieval stage **237** of the apparatus **253** taken along an axis **6A-6A** of **Fig. 4**;

[0019] **Fig. 6B** depicts a longitudinal cross-sectional view of the particle prepreg retrieval stage **237** of the apparatus **253** taken along an axis **6B-6B** of **Fig. 4**; and

[0020] **Fig. 7** is a flow diagram of a method for making a drapable or non-drapapable pre-preg, according to embodiments of the present invention;

[0021] **Figs. 8-9** is a flow diagram of a method for making a drapable or non-drapapable pre-preg, according to embodiments of the present invention;

[0022] **Fig. 10** depicts a longitudinal cross-sectional view of an apparatus for making a heat curable polymer pre-impregnated reinforcement material, according to embodiments of the present invention;

[0023] **Fig. 11** depicts a longitudinal cross-sectional view of an apparatus for making a free-form heat curable polymer pre-impregnated reinforcement material, according to embodiments of the present invention; and

[0024] **Figs. 12-13**depicts a longitudinal cross-sectional view of an apparatus for making a heat curable polymer pre-impregnated reinforcement material, according to embodiments of the present invention;.

DESCRIPTION OF THE INVENTION

[0025] **FIG.1** is a schematic diagram illustrating a longitudinal cross-sectional view of an apparatus **200** for manufacturing a polymer pre-impregnated reinforcement material (prepreg) **28**. The apparatus **200** comprises: a particle deposition stage **30**, a thermal fixing stage **40**, an optional belt press **407**, and a prepreg retrieval stage **50**.

[0026] The particle deposition stage **30** comprises: a first steel-net conveyor belt **14**; at least one supply roll(s) **20** for supplying a porous substrate **8**; at least one hopper(s) **10** being charged with particles **4** of reactive (polymerizable) thermoplastic or thermoset resin; an array of particles **4** of reactive thermoplastic or thermoset resin deposited onto a first surface **17** of the porous substrate **8**. The at least one supply roll(s) **20** may unroll by rotating in a direction of the arrow **1** about an axis orthogonal to a plane of the first surface **17** of the porous substrate **8**. **Figs. 1-2** depict the particles **4** of reactive (polymerizable) thermoplastic or thermoset resin may advantageously be deposited onto the first surface **17** of the porous substrate **8**, wherein both the particles **4** and the porous surface of the porous substrate **8** are advantageously at ambient temperature.

[0027] **Figs. 4-6** depict an alternative embodiment, in which the particles **205** of reactive (polymerizable) thermoplastic or thermoset resin may advantageously be deposited onto the first surface **234** of the porous substrate **233**, wherein only the particles **205** are advantageously at ambient temperature, but the first surface **234** of the porous substrate **203** has been "pre-warmed", to enable the particles **205** of the reactive thermoplastic or thermoset resin to adhere "immediately" to the first surface **234** of the porous substrate **233**. In the embodiment depicted in **Figs. 4-6**, and described in associated text, *infra*, the inventors report prevention of "rolling away", or "blowing away" of the particles **205** when they are deposited onto the first surface **234** of the porous substrate **233** by pre-warming the first surface **234** of the porous substrate **233**.

[0028] A range of particle size distribution of the particles **8**, **205** of reactive (polymerizable) thermoplastic or thermoset resin may advantageously be greater than the range of particle size distribution of powders used in certain powder impregnation methods for infusing reactive thermoplastic powders into the interstices **93** between fibers **95**, or fiber bundles, of the porous substrate **8**, **205**. In one embodiment the particles **8** of the reactive (polymerizable) thermoplastic or thermoset resin may advantageously be greater than between 150 to 1000 µm. In one embodiment the particles **8** of the reactive (polymerizable) thermoplastic or thermoset resin may advantageously have a diameter ranging from between 2 to 5 mm.

[0029] The thermal fixing stage **40** comprises: a second steel-net conveyor belt **15** for picking up the porous substrate **8** having the particles **4** of reactive (polymerizable) thermoplastic or thermoset resin, thereon, from the first steel-net conveyor belt **14** to convey the particles **4** into oven **5**. The oven **5** may provide hot air laminar flow **16**, warming the porous substrate **8** having the particles **4** of the reactive (polymerizable) thermoplastic or thermoset resin thereon and the second steel net conveyor **15**. The oven **5** may be any appropriate heating device capable of raising the temperature of the substrate **8** between about 190°C and 220°C in a residence time between 1 and 5 minutes. In one embodiment, the porous substrate **8** may be a fiber reinforcement fabric, a glass mat, or a fiber bed.

[0030] The apparatus **200** may optionally be equipped with a belt press **407** after the heating unit **5**, **209**, wherein the belt press **407** has a hot zone **405** and a cold zone **403**, wherein the hot zone **405** is adapted to receive drapable polymer pre-impregnated reinforcement material **28B**, **285B** and to heat said pre-impregnated reinforcement material **28B**, **285B** to less than or equal to 250°C and greater than or equal to 0.01 bar pressure, and wherein the cold zone **403** is adapted to receive a fully impregnated and cured thermoplastic composite sheet and to cool said fully impregnated and cured thermoplastic composite sheet to 25°C.

[0031] The first and second steel-net conveyor belts **14**, **15** may be supported by legs **243** that rest on manufacturing floor **241**. The first and second steel-net conveyor belts **14**, **15** may rotate in a direction of the arrow **6** to carry the porous substrate **8** having the particles **4** of reactive (polymerizable) thermoplastic or thermoset resin, thereon, from the first steel-net conveyor belt **14** to convey the particles **4** into oven **5**.

[0032] The prepreg retrieval stage **50** comprises: at least one retrieving roll(s) **25** for retrieving the prepreg **28**; a prepreg **28**, wherein the prepreg **28** comprises the porous substrate **8** from supply roll **20**, and an array **9** of thermally fixed particles, thereon. The at least one retrieving roll(s) **25** may retrieve the prepreg **28** by rotating in a direction of the arrow **7** about an axis orthogonal to a plane of the first surface **17** of the porous substrate **8**.

[0033] **Fig. 2** depicts a longitudinal cross-sectional view of the particle distribution stage **30** of the apparatus **200** taken along an axis **2-2** of **Fig. 1**. **Fig. 2** depicts first surface **17** of the porous substrate **8**, on which the particles **4** of reactive (polymerizable) thermoplastic or thermoset resin have been deposited, thereon. The porous substrate **8** comprises a first surface **17**, having particles **4**, thereon, and spaces **11**, therebetween. In one embodiment, the porous substrate **8** is a fiber reinforced fabric, or a fiber bed, and the particles **4** of the reactive (polymerizable) thermoplastic or thermoset resin, thereon, are granules. A particle size distribution of the particles **8** of reactive (polymerizable) thermoplastic or thermoset resin may advantageously be greater than the range of particle size distribution of powders used in certain powder impregnation methods for infusing reactive (polymerizable) thermoplastic powders into the interstices **93** between fibers **95** or fiber bundles of the porous substrate **8**. In one embodiment the particles **4** of the reactive (polymerizable) thermoplastic or thermoset resin may advantageously be greater than between 150 to 1000 μm. In one embodiment the particles **4** of the reactive (polymerizable) thermoplastic or thermoset resin may advantageously have a diameter ranging from between 2 to 5 mm. In one embodiment, a shape of the particles **4** of the thermoplastic or thermoset resin may be a granule, pellet, flake, pastille, needle, chunks, or a chip.

[0034] Hereinafter, a “granule” is defined as a particle larger than a sand grain and smaller than a pebble, between 2 mm and 4 mm in diameter.Hereinafter a “pellet” is defined as a small rounded, spherical, or cylindrical body, having a diameter between about 2 mm and 5 mm.

[0035] Hereinafter a “flake” is defined as a particle having a surface area greater than 2 mm^2 and a thickness between 0.02 mm and 0.1 mm.

[0036] Hereinafter, a “pastille” is an enrobed active catalytic thermoplastic orthermoset resin material with a protective coating. The pastille may be prepared using a low-shear jacketed blender and a pastillator. The resultant pastille varies in shape and has a diameter of from about 2 mm to about 100 mm and a thickness of 1 mm to 10 mm.

[0037] Hereinafter a “needle” is defined as narrow and long and pointed; as pine leaves.

[0038] Hereinafter a “chunk” is defined as a short, thick piece or lump.

[0039] Hereinafter a “chip” is defined as a small fragment of reactive (polymerizable) thermoplastic or thermoset resin broken off from the whole.

[0040] **Fig. 3A** depicts a longitudinal cross-sectional view of the particle prepreg retrieval stage **50** of the apparatus **200** taken along an axis **3A-3A** of **Fig. 1**. **Fig. 3A** depicts a drapable prepreg **28**. The prepreg **28** is drapable because an array **9** of thermally fixed particles **265** are thermally fixed by partially melting the particles **4** of reactive (polymerizable) thermoplastic or thermoset resin shown in **Fig. 2**. The partially melted reactive (polymerizable) thermoplastic or thermoset resin particles **265**, shown in **Fig. 3A**, may flow into the interstices **93** between the fibers **95** or fiber bundles of the porous substrate **8**, resulting in the particles **265** becoming thermally fixed to the fibers or fiber bundles of the porous substrate **8** when the reactive (polymerizable) thermoplastic or thermoset resin crystallizes or resolidifies when the prepreg **28** cools below the melting point of the reactive (polymerizable) thermoplastic or thermoset resin after coming out of oven **5** on cooling in the prepreg **28** retrieval stage **50**. The prepreg **28** is drapable because an array **9** of thermally fixed particles **265** are thermally fixed to the first surface **17**, thereon, and separated by spaces **18**. Alternatively, a non-drapable prepreg **28** may be formed by completely melting the low melt viscosity reactive (polymerizable) thermoplastic or thermoset resin particles **4** in oven **5** to form particles **265**.

[0041] **Fig. 3B** depicts a longitudinal cross-sectional view of the particle prepreg retrieval stage **50** of the apparatus **200** taken along an axis **3B-3B** of **Fig. 1**. The prepreg **28A**, shown in **Fig. 3B**, may be non-drapable because an at least one layer(s) **97**, **19** of reactive (polymerizable) thermoplastic or thermoset resin has been formed that does not have voids. In one embodiment, the reactive (polymerizable) particles **4**, shown in **Figs. 1-2**, have been completely melted to form a layer **97** of reactive (polymerizable) thermoplastic or thermoset resin. A first portion **99** of the layer **97** may be impregnated or impressed into the interstices **93** between fibers **95** or fiber bundles of the porous substrate **8**, shown in **Figs. 2**, **3A**. The impressed or impregnated first portion **99** of the layer **97** may form a layer **19**, in which the reactive (polymerizable) thermoplastic or thermoset resin has been thermally fixed onto the fibers **93** or fiber bundles. The completely melted layer **97** may have flowed into the spaces **18** between the particles **265** of the array **9**, shown in **Fig. 3A**, to become the layers **97** and/or **19**. In another embodiment, the completely melted reactive (polymerizable) thermoplastic or thermoset resin layer **97** has melted and extends essentially completely into the substrate **8**, forming the layers **19** and **13** in the substrate **8**. Hereinafter, "thermally fixed" means reactive functionalities of the reactive (polymerizable) thermoplastic or thermoset resin particles **265** have become chemically bonded or attracted by Van der Wahls forces or other attractive intermolecular forces to the fibers **95** or fiber bundles of the substrate **8** during the melting process.

[0042] **Fig. 3B** depicts a prepreg **28B** that is non-drapable because a first portion **97** of the completely melted reactive (polymerizable) thermoplastic or thermoset resin **265** has flowed into interstices **93** between fibers **95** or fiber bundles of the porous substrate **8**, so that some of the melt impregnates or impresses between and among the fibers **95** or fiber bundles of the porous substrate **8**, forming at least one layer **13**, **19** of reactive (polymerizable) thermoplastic or thermoset resin in the porous substrate **8**. A remaining portion **99** of the completely melted reactive (polymerizable) thermoplastic or thermoset resin **265** that doesn't flow into the interstices between fibers or fiber bundles of he porous substrate **8** forms the layer **23A** which lies upon the first surface **17** of the porous substrate **8**.

[0043] Void free laminates or composite structures may be made from drapableor non-drapable reactive (polymerizable) polymer pre-impregnated reinforcement materials (prepregs) **28**. The non-drapable reactive (polymerizable) polymer pre-impregnated reinforcement materials (prepregs) **28** may be at least one layer **13**, **19** or **23A** of low melt viscosity reactive (polymerizable) thermoplastic or thermoset resin, having been completely melted when thermally fixed or compression molded. The combination of heat and pressure may force the low viscosity reactive (polymerizable) thermoplastic or thermoset resin to penetrate the fibers **95** or fiber bundles of the porous substrate **8** to form at least one layer **13**, **19**.

[0044] In one embodiment, the particles **265** of the reactive (polymerizable) thermoplastic or thermoset resin on the first surface **17** of the porous substrate **8** are reactive (polymerizable) thermoplastic or thermoset resin granules placed on top of a fiber bed and partly fused into fiber bundles of the fiber bed by impregnating particles **4** of a reactive (polymerizable) thermoplastic or thermoset resin into interstices **93** between fibers **95** in the fiber bundles of the fiber bed. Hereinafter, reactive (polymerizable) thermoplastic or thermoset resin is defined as the particles **4** of the reactive (polymerizable) thermoplastic or thermoset resin on the first surface **17** of the porous substrate **8**, which can subsequently be partially polymerized or fully polymerized.

[0045] **Fig. 4** depicts a longitudinal cross-sectional view of an apparatus **253** for manufacturing a polymer pre-impregnated reinforcement material (prepreg) **287**. Specifically, the apparatus **253** may be for pre-heating a first surface **233** of a porous substrate **234** of a prepreg **287**, prior to thermally fixing particles **205** of a reactive thermoplastic or thermoset resin on the first surface **233** of the prepreg **285**.

[0046] The apparatus **253** comprises: a combined particle deposition and a thermal fixing stage **227**, a prepreg finishing stage **229**, and a prepreg retrieval stage **237**. The at least one supply roll(s) **200** of the combined particle deposition and a thermal fixing stage **227** may unroll by rotating in a direction of the arrow **100** about an axis orthogonal to a plane of the first surface **233** of the porous substrate **234**.

[0047] **Fig. 5** depicts a longitudinal cross-sectional view of the apparatus taken along an axis **5-5** of **Fig. 4**. **Figs. 4-5** depict the particles **205** of reactive (polymerizable) thermoplastic or thermoset resin may advantageously be deposited onto the first surface **234** of the porous substrate **233**, wherein the first surface **233** of the porous substrate **234** has been advantageously heated to at least 90°C before the particles **205** being at ambient temperature have been deposited thereon.

[0048] **Fig. 4** depicts an embodiment, in which the particles **205** of reactive (polymerizable) thermoplastic or thermoset resin may advantageously be deposited onto the first surface **233** of the porous substrate **234**, wherein only the particles **205** are advantageously at ambient temperature, but the first surface **233** of the porous substrate **204** has been "pre-warmed", to enable the particles **205** of the reactive (polymerizable) thermoplastic or thermoset resin to adhere "immediately" to the first surface **233** of the porous substrate **234**. In the embodiments depicted in **Figs. 4-5**, and described in associated text, *infra*, the inventors report prevention of "rolling away", or "blowing away" of the particles **205** when they are deposited onto the first surface **233** of the porous substrate **234** by pre-warming the first surface **233** of the porous substrate **234**.

[0049] The combined particle deposition and a thermal fixing stage **227** comprises: a first steel-net conveyor belt **217**; at least one supply roll(s) **200** for supplying a porous substrate **234**; at least one hopper(s) **225** being charged with particles **205** of reactive (polymerizable) thermoplastic or thermoset resin; a thermally fixed array of particles **235** of reactive (polymerizable) thermoplastic or thermoset resin deposited onto a first surface **233** of the porous substrate **234**. The combined particle deposition and a thermal fixing stage **227** includes a pre-warming oven **207** for pre-warming the first surface **233** of the porous substrate **234**, so a first portion the particles **205** may be thermally fixed to the first surface **233** of the porous substrate **234** when the particles **205** are randomly deposited on the first surface **233** of the porous substrate **234**, so that the particles **205** may be thermally fixed as the array of particles **235**. In this embodiment of the invention "rolling away", or "blowing away" of the particles **205** is prevented when the particles **205** are deposited onto the first surface **233** of the porous substrate **234** by pre-warming the first surface **233** of the porous substrate **234**.

[0050] A range of particle size distribution of the particles **205** of reactive (polymerizable) thermoplastic or thermoset resin may advantageously be greater than the range of particle size distribution of powders used in certain powder impregnation methods for infusing reactive (polymerizable) thermoplastic powders into the interstices **295** between fibers **221** or fiber bundles of the porous substrate

234, as depicted in **Figs. 5**, **6A**, and **6B** and described in associated text herein. In one embodiment, the particles **205** of the reactive (polymerizable) thermoplastic or thermoset resin may advantageously be greater than between 150 to 1000 μm. In one embodiment the particles **205** of the reactive (polymerizable) thermoplastic or thermoset resin may advantageously have a diameter ranging from between 2 to 5 mm.

[0051] The prepreg finishing stage **229** comprises: a second steel-net conveyor belt **223** for picking up the porous substrate **234** having the thermally fixed array of particles **235** of reactive (polymerizable) thermoplastic or thermoset resin, thereon, from the first steel-net conveyor belt **217** to convey the thermally fixed array of particles **235** into oven **209**. The oven **209** may provide hot air laminar flow **213** to the porous substrate **234** having the thermally fixed array of particles **235** of the reactive (polymerizable) thermoplastic or thermoset resin thereon and to the second steel net conveyor **223**. The oven **209** may be any appropriate heating device capbable of raising the temperature of the porous substrate **234** between about 190°C and 220°C in a residence time between about 1 and about 5 minutes. In one embodiment, the porous substrate **234** is a fiber reinforcement fabric, a glass mat, or a fiber bed.

[0052] The first and second steel-net conveyor belts **217**, **223** may be supported by legs **245** that rest on manufacturing floor **239**. The first and second steel-net conveyor belts **217**, **223** may rotate in a direction of the arrow **60** to carry the porous substrate **234** having the thermally fixed array of particles **235** of reactive (polymerizable) thermoplastic or thermoset resin, thereon, from the first steel-net conveyor belt **217** to convey the thermally fixed array of particles **235** into oven **209**.

[0053] The prepreg retrieval stage **237** comprises: a retrieving roll **215** for retrieving the prepreg **285**; a prepreg **285**, wherein the prepreg **285** comprises the porous substrate **234** from supply roll **200**, and a thermally fixed particle array **231**, thereon. The at least one retrieving roll(s) **215** may retrieve the prepreg **285** by rotating in a direction of the arrow **65** about an axis orthogonal to a plane of the first surface **233** of the porous substrate **234**.

[0054] **Figs. 5** depicts a longitudinal cross-sectional view of the combined particle deposition and a thermal fixing stage **227** of the apparatus **253** taken along an axis **5-5** of **Fig. 4**. **Fig. 5** depicts a thermally fixed particle array **235**. The prepreg **285** is drapable because the array **235** of thermally fixed particles **205** may be thermally fixed by partially melting the particles **205** of reactive (polymerizable) thermoplastic or thermoset resin which partially melt when the particles **205** touch or undergo heat transfer from the pre-warmed first surface **233** of the porous substrate **234**. The melt from the partially melted reactive (polymerizable) thermoplastic or thermoset resin particles **205**, shown in **Fig. 5**, may flow into the interstices **295** between the fibers **221** or fiber bundles of the porous substrate **234**, resulting in the particles **205** becoming thermally fixed to the fibers **221** or fiber bundles in the first surface **233** of the porous substrate **234** when the reactive (polymerizable) thermoplastic or thermoset resin crystallizes or resolidifies when the thermally fixed particle array **235** cools below the melting point of the reactive (polymerizable) thermoplastic or thermoset resin after coming out of oven **207** of the combined particle deposition and thermally fixing stage **227**. The prepreg **285** may be drapable because the array **235** of thermally fixed particles **205** are thermally fixed to the first surface **233**, thereon, and separated by spaces **250**.

[0055] **Fig. 6A** depicts a longitudinal cross-sectional view of the particle prepreg retrieval stage **237** of the apparatus **253** taken along an axis **6A-6A** of **Fig. 4**. **Fig. 6A** depicts a drapable prepreg **285**, having a thermally fixed particle array **235**. The prepreg **285A** is drapable because the array **235** of thermally fixed particles **205** may be thermally fixed by partially melting the particles **205** of reactive (polymerizable) thermoplastic or thermoset resin which partially melt when the particles **205** touch or undergo heat transfer from the pre-warmed first surface **233** of the porous substrate **234**. The melt from the partially melted reactive (polymerizable) thermoplastic or thermoset resin particles **205**, shown in **Fig. 5**, may flow into the interstices **295** between the fibers **221** or fiber bundles of the porous substrate **234**, resulting in the particles **205** becoming thermally fixed to the fibers **221** or fiber bundles in the first surface **233** of the porous substrate **234** when the reactive (polymerizable) thermoplastic or thermoset resin crystallizes or resolidifies when the thermally fixed particle array **235** cools below the melting point of the reactive (polymerizable) thermoplastic or thermoset resin after coming out of oven **207** of the combined particle deposition and thermally fixing stage **227**. The prepreg **285** may be drapable because the array **235** of thermally fixed particles **205** are thermally fixed to the first surface **233**, thereon, and separated by spaces **250**.

[0056] **Fig. 6B** depicts a longitudinal cross-sectional view of the particle prepreg retrieval stage **237** of the apparatus **253** taken along an axis **6B-6B** of **Fig. 4**. The prepreg **285B**, shown in **Fig. 6B**, may be non-drapable because an at least one layer(s) **397**, **360** of reactive (polymerizable) thermoplastic or thermoset resin have been formed that do not have voids. In one embodiment, the reactive (polymerizable) particles **205**, shown in **Figs. 4-5**, have been completely melted to form a layer **397** of reactive (polymerizable) thermoplastic or thermoset resin. A portion **399** of the layer **397** may be impregnated or impressed into the interstices **295** between fibers **221** or fiber bundles of the porous substrate **234**, shown in **Figs. 4**, **6A** may form a layer **360**, in which the reactive (polymerizable) thermoplastic or thermoset resin has been thermally fixed onto the fibers **221** or fiber bundles and filled into the spaces **255** between the particles **365** of the array **235**, shown in **Fig. 6A**, have flowed together to become the layer **360**. In another embodiment, the completely melted reactive (polymerizable) thermoplastic or thermoset resin layer **97** has melted and extends essentially completely into the substrate **234**, forming the layer **360** and **367** in the substrate **234**. Hereinafter, "thermally fixed" means reactive functionalities of the reactive (polymerizable) thermoplastic or thermoset resin particles **205** have become chemically bonded or attracted by Van der Wahls forces or other attractive intermolecular forces to the fibers **221** or fiber bundles of the substrate **234** during the melting process. **Fig. 6B** depicts a prepreg **285B** that is non-drapable because a first portion **399** of the completely melted reactive (polymerizable) thermoplastic or thermoset resin **397** has flowed into interstices **295** between fibers **221** or fiber bundles of the porous substrate **234**, so that some of the melt impregnates or impresses between and among the fibers **221** or fiber bundles of the porous substrate **234**, forming at least one layer **360**, **367** of reactive (polymerizable) thermoplastic or thermoset resin in the porous substrate **234**. A remaining portion **395** of the completely melted reactive (polymerizable) thermoplastic or thermoset resin that doesn't flow into the interstices between fibers or fiber bundles of the porous substrate **234** forms the layer **397** which lies upon the first surface **233** of the porous substrate **234**.

[0057] Void free laminates or composite structures may be made from drapable or non-drapable reactive (polymerizable) polymer pre-impregnated reinforcement materials (prepregs) **285A**, **B**. The non-drapable reactive (polymerizable) polymer pre-impregnated reinforcement materials (prepregs) **285A** may be an at least one layer(s) **97**, **19**, and/or **13**, as in **Fig. 3B** or **397**, **360**, and/or **367**, as in **Fig. 6B**, of low melt viscosity reactive (polymerizable) thermoplastic or thermoset resin particles **4**, **205**, having been completely melted when thermally fixed or compression molded. The combination of heat and pressure may force the low viscosity reactive (polymerizable) thermoplastic or thermoset resin to penetrate the fibers **95**, **221** through the porous substrate **8**, **234**.

[0058] Reactive (polymerizable) thermoplastic composite pre-pregs **28A**, **B**, **285A**, **B** and thermoplastic based fully polymerized sheets may be manufactured from powdered macrocyclic polyester oligomers using powder impregnation, or solvent or slurry based impregnation, or hot melt impregnation technologies. However, powder impregnation, or solvent or slurry based impregnation, or hot melt impregnation technologies are undesirable for the following reasons.

[0059] Using powders as precursor material is expensive, since grinding of typically available granules is an additional production step, which in the case of polyesters and polyamides has to happen under cryogenic temperatures. Also, powder impregnation followed by melting the powder forms a continuous thermoplastic layer that is not drapable.

[0060] Using solvent or slurry based methods have issues with evaporating the slurry carrier or solvent during the process, making these methods highly complicated and expensive.

[0061] Using hot melt technologies requires the use of complex melting, dosing and delivering systems such as extruders and rotoformers and also have the problem of having to initiate an advanced polymerization inside the delivery equipment before impregnating the fiber bed.

[0062] Therefore, there has been a long felt need for a process for making the pre-pregs **28A**, **B**, **285A**, **B** and thermoplastic based fully polymerized sheets that do not require powder impregnation, or solvent or slurry based impregnation, or hot melt impregnation technologies, in which low melt viscosity reactive (polymerizable) thermoplastic or thermoset resins particles **4**, **205** are directly deposited onto a first surface **17**, **233** of a porous substrate **8**, **234** of the -pregs **28A**, **B**, **285A**, **B** and thermoplastic based fully polymerized sheets, thereon. In this process, which is an alternative to powder impregnation, or solvent or slurry based impregnation, or hot melt impregnation technologies, direct deposition of the low melt viscosity reactive (polymerizable) thermoplastic or thermoset resin particles **4**, **205** onto the first surface **17**, **233** of the porous substrate **8**, **234** thereon, is followed by impregnating or impressing a portion or all of the low melt viscosity particles **4**, **205** into the fibers or fiber bundles **95**, **221** of the porous substrate **8**, **234** by melting the reactive (polymerizable) thermoplastic or thermoset resin particles **4**, **205** and optionally applying pressure. A process requiring that only ambient temperature resin particles **4**, **205** be directly deposited onto the first surface **17**, **233** of the porous substrate **8**, **234** is preferred over processes requiring the reactive (polymerizable) thermoplastic or thermoset resin particles **4**, **205** to be melted, slurried, commingled, or diluted with solvents, fillers, or plasticizers, before being deposited, because it is less expensive by avoiding these steps. Reactive (polymerizable) thermoplastic or thermoset resin particles **4**, **205** having melt viscosities between about 5 cp and about 5,000 cp before being cured (polymerized) are commercially available from the Cyclics Corporation, Schenectady, NY 12308, USA. CBT® 100 and CBT® 200 melt to water-like viscosity when heated, then polymerize into engineering thermoplastic PBT when catalyzed. CBT 100 features processing temperature between 190-240°C, while CBT 200 ranges from 170-240°C. Melting the particles **4**, **205** before depositing the reactive (polymerizable) thermoplastic or thermoset resin particles **4** onto the first surface **17**, **233** of the porous substrate **8**, **234** has been used when it is necessary to melt thermoplastic or thermoset resins having higher melt viscosities than 5,000 cp in order to ensure the higher melt viscosity thermoplastic or thermoset resins come in close contact with the first surface **17**, **233** of the porous substrate **8**, **234** and the fibers and fiber bundles **95**, **221** therein, such as a fiber bed before consolidation.

[0063] **Fig. 7** depicts a flow sheet for a method **100** for making a reactive (polymerizable) polymer pre-impregnated reinforcement material. In a step **115** of the method **100** a reactive (polymerizable) thermoplastic or thermoset resin having a melt viscosity between about 5 cp and about 5,000 cp is applied to a first surface **117** of a porous substrate **8** to be pre-impregnated.

[0064] In one embodiment of the step **115** of the method **100**, particles **4** of the heat curable thermoplastic or thermoset resin may be deposited onto the first surface **117** of the porous substrate **8** at ambient temperature from a hopper **10**, such as a solid particle feeder.

[0065] In a step **120** of the method **100**, the reactive (polymerizable) thermoplastic or thermoset resin is thermally fixed into interstices of the first surface of the porous substrate by partially melting a first portion of the curable thermoplastic or thermoset resin by heating to a first temperature T_1 over a first period of time t_1 so that the first portion of the reactive (polymerizable) thermoplastic flows into interstices of the porous substrate and a remaining portion of the curable thermoplastic or thermoset resin remains solid.

[0066] Fiber-reinforced plastic materials such as fiber-reinforced composites or fiber-reinforced laminates may be manufactured by first forming a reactive (polymerizable) polymer pre-impregnated reinforcement material (a “prepreg”), as in the method **100**. In the method **100**, the prepreg is formed by impregnating a fiber reinforcement material with a reactive (polymerizable) thermoplastic or thermoset resin.

[0067] In one embodiment, the method **100** may comprise a consolidating step **115**, in which a plurality of prepregs are consolidated into a laminate, such as a reactive (polymerizable) thermoplastic or thermoset resin composite sheet. Fiber-reinforced plastic materials based on polyesters and nylon materials may be manufactured by first impregnating the fiber reinforcement with the thermoplastic or thermoset resin to form a prepreg, then consolidating one, two or more of the same into a laminate, like a thermoplastic composite sheet. In the consolidating step, consolidating may be necessary to fully impregnate the fiber reinforcement material, which may be laid out as a multi-layered bed before impregnation.

[0068] In one embodiment of the consolidating step of the method **100**, the prepregs may be consolidated by applying heat and pressure. Higher temperatures and pressures are required to achieve substantially void free laminates by consolidation if the melt viscosity of the reactive (polymerizable) thermoplastic or thermoset resin is greater than between about 5 cp to about 5,000 cps.

[0069] Reactive (polymerizable) thermoplastic or thermoset resins having melt viscosities between about 5 cp and about 5,000 cp before being cured are commercially available from the Cyclics Corporation, Schenectady, NY USA. Having a very low melt viscosity during processing, enables the reactive (polymerizable) thermoplastic or thermoset resins to impregnate a dense fibrous preform or bed more easily. Upon melting and in the presence of an appropriate catalyst, polymerisation occurs and the reactive (polymerizable) thermoplastic cures to form the laminate.

[0070] In one embodiment of the method **100**, the reactive (polymerizable) thermoplastic or thermoset resin may be a blend of a polymerization catalyst and a linear polyester or a linear polyamide, wherein the polymerization catalyst is chosen so that the melt viscosity of the thermoplastic or thermoset resin characterizes its viscosity during the heating and impregnation steps **117**, **120** of the method **100** to impregnate the reactive (polymerizable) thermoplastic or thermoset resin into the fiber reinforcement material.

[0071] In one embodiment of the method **100**, the reactive (polymerizable) thermoplastic or thermoset resin may be a blend of a polymerization catalyst and a linear poly alkylene terephthalate (where the alkylene has between about 2 and about 8 carbon atoms) or a linear poly alkylene amide (where the alkylene has between about 4 and about 12 carbon atoms).

[0072] In one embodiment of the method **100**, the reactive (polymerizable) thermoset resin may be an epoxy resin system such as a bifunctional epoxy (diglycidyl ether of bisphenol-A) matrix system.

[0073] In one embodiment of the method **100**, the reactive (polymerizable) thermoset resin may be a reactive (polymerizable) unsaturated polyester resin or epoxy resin. Unsaturated polyester resins (USR) are the third-largest class of thermoset molding resins. The polyesters are low molecular weight viscous liquids dissolved in vinyl monomers like styrene to facilitate molding or shaping of the resin into a desired form before curing to rigid solids. Typical applications are in fiberglass-reinforced shower stalls, boat hulls, truck caps and airfoils, construction panels, and autobody parts and trim. Mineral-filled UPRs are used in synthetic marble countertops and autobody putty. Unfilled UPRs are used in gel coats and maintenance coatings. Adipic acid improves tensile and flexural strength in these resins and, at high levels, can give soft, pliable products for specialty applications. 1-Alkyd resins, a common type of unsaturated polyester resin, utilize adipic acid where low viscosity and high flexibility are valued in plasticizer applications. UPR resins are mainly aromatic polyesters. Flexibility of UPR is increased by replacing a portion of aromatic acid with adipic acid. A cure site monomer, like maleic anhydride, is incorporated to provide unsaturation within the polymer backbone. Crosslinking is by free radical addition polymerization of styrene monomer/diluent.

[0074] In one embodiment of the method **100**, the reactive (polymerizable)thermoplastic or thermoset resin may be reactive macrocyclic oligomeric polyester, reactive macrocyclic oligomeric polybutyleneterephthalate, reactive macrocyclic oligomeric polyethyleneterephthalate, reactive macrocyclic oligomeric polycarbonate, and reactive lactam monomers.

[0075] In one embodiment of the method **100**, the fiber reinforcement material may be carbon fiber, glass fiber, basalt fiber, aramid fiber, steel fiber, natural fiber, polymer fiber, and combinations thereof.

[0076] In a step **120** of the method **100**, the reactive thermoplastic or thermoset resin is thermally fixed into interstices of the first surface of the porous substrate.

[0077] In the step **120**, a first portion of the curable thermoplastic or thermoset resin is partially melted by heating to a first temperature T_1 over a first period of time t_1 so that the first portion of the reactive thermoplastic flows into interstices of the porous substrate and a remaining portion of the curable thermoplastic or thermoset resin remains solid.

[0078] In one embodiment of the method **100**, a shape of the thermoplastic or thermoset resin is selected from the group consisting of a granule, pellet, flake, pastille, needle, chunks, and a chip.

[0079] In one embodiment of the method **100**, the porous substrate is a reinforcement material selected from the group consisting of carbon fiber, glass fiber, basalt fiber, aramid fiber, steel fiber, natural fiber, polymer fiber and combinations thereof.

[0080] In one embodiment of the method **100**, the reinforcement material is in a form selected from the group consisting of roving, tape, web, weave, bi- or -multi-axial fabrics, knit, braid, random mat, and fleece.

[0081] In the step **120**, in one embodiment, the first temperature is between about 190°C and about 220°C and the first period of time is between about 1 and 5 minutes.

[0082] In one embodiment of the method **100**, a weight of the reinforcement material per surface area of the reinforcement material is between about 200 g/m^2 and about 4,000 g/m^2 and a weight percent of the reactive thermoplastic is between about 30% to about 80%, based on a weight of the reactive polymer pre-impregnated reinforcement material.

[0083] Hereinafter a reactive (polymerizable) thermoplastic or thermoset resin particle loading of 100 g/mm^2 equals 70wt% on a 460 g/mm^2 GF fabric (the granule size needs to become smaller and smaller). 1000 g/mm^2 equals 30wt% on a 810 g/mm² GF Fabric, respectively 38wt% on a 810 g/mm² CF fabrc. This is always meant to be for "one layer per substrate". 1700 g/m² for 4x layers of 810 g/m² GF; considering even fiber volume fraction as low as 30% up to 4000 g/m² resin have to be deposited.

[0084] In the step **120**, in one embodiment, the first temperature is 190°C and the first time period is less than or equal to 1 minute.

[0085] In one embodiment of the method **100**, a weight of the reinforcement material persurface area of the reinforcement material is about 460 g/m^2 and a weight percent of the reactive thermoplastic is between about 34% to about 35%, based on a weight of the reactive polymer pre-impregnated reinforcement material.

[0086] In one embodiment of the method **100**, a weight of the reinforcement material per surface area of the reinforcement material is about 620 g/m^2 and a weight percent of the reactive thermoplastic is between about 33% to about 36%, based on a weight of the reactive polymer pre-impregnated reinforcement materials.

[0087] In one embodiment of the method **100**, a weight of the reinforcement material per surface area of the reinforcement material is about 810 g/m^2 and a weight percent of the reactive thermoplastic is between about 34% to about 36%, based on a weight of the reactive polymer pre-impregnated reinforcement material.

[0088] In one embodiment, the drapable polymer pre-impregnated reinforcement material pre-preg **28A**, **285A** comprises: a porous substrate **8**, **234** having a first surface **17**, **231**; randomly spaced particles **4**, **205** of a reactive thermoplastic, thereon, wherein a portion **99**, **399** of each of the randomly spaced particles **4**, **205**

is impregnated into interstices **93**, **295** of the first surface **17**, **231**of the reinforcement material, therein, and wherein a space **11**, **50** therebetween, separates adjacent randomly spaced particles **4**, **205**.

[0089] In one embodiment of the drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **285A**, the reactive thermoplastic particles have a melt viscosity between about 5 cp and about 5,000 cp.

[0090] In one embodiment of the drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **285A**, an area of the space between each particle is between about 2 mm^2 and about 200 mm^2.

[0091] In one embodiment of the drapable polymer pre-impregnated Reinforcement material (pre-preg) **28A**, **285A** the particles have a diameter between about 1 mm to about 5 mm and a length between about 1 mm and about 8 mm.

[0092] In one embodiment of the drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **285A** the particles have a thickness between 0.5 mm and 3 mm and a diameter between 1 mm and about 8 mm.

[0093] In one embodiment of the drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **285A** the particles have a diameter between about 1 mm to about 8 mm and a length between about 1 mm and about 8 mm.

[0094] In one embodiment of the drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **285A** the particles are made from macrocyclic oligomeric butyleneterephthalate.

[0095] In one embodiment of the drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **285A** the particles have a diameter between about 1 mm and about 5 mm and a length between about 1 mm and about 8 mm.

[0096] In one embodiment, a method for forming a drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **285A**, comprises: providing a porous substrate **8**, **234** having a first surface **17**, **231**; and thermal fixing an array **9**, **235** of essentially randomly spaced particles **4**, **205** of a reactive thermoplastic having a melt viscosity between about 5 cp and about 5,000 cp., thereon.

[0097] An apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg), comprising: at least one feeder device **20**, **200** of reinforcement material **8**, **234**; at least one receiver device **25**, **215** of polymer pre-impregnated reinforcement material **8**, **234**; and at least one conveyor belt(s) **14**, **15**, **217**, **223** having the reinforcement material **8**, **234** from the at least one feeder device(s) **20**, **200** thereon; a particle deposition hopper **10**, **225** charged with reactive thermoplastic particles **4**, **205** and adapted to deposit between 100 g/m^2 and about 1000 g/m^2 of the reactive thermoplastic particles **4**, **205**, based on the surface area (m^2) of the reinforcement material **8**, **234**; at least one heating unit oven **5**, **209** adapted to substantially uniformly maintain a temperature of the reactive thermoplastic particles **4**, **205** on a first surface **17**, **231** of the reinforcement material **8**, **234** for a residence time, during which the reactive thermoplastic particles **4**, **205** on a first surface **17**, **231** of the reinforcement material **8**, **234** reside in the oven **5**, **209**; and at least one conveyor belt(s) **14**, **15**, **217**, **223** wherein residence time that the reactive thermoplastic particles **4**, **205** on the first surface **17**,

231 of the reinforcement material **8**, **234** is based on the conveyor belt's **14**, **15**, **217**, **223** rate.

[0098] In one embodiment of the apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, the conveyor belt's **14**, **15**, **217**, **223** rate is between about 1 meters per minute and about 4 meters per minute.

[0099] In one embodiment of the apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, the residence time that the reactive thermoplastic particles **4**, **205** on a first surface **17**, **231** of the reinforcement material **8**, **234** reside in the oven**5**, **209** is between about 1 min. and about 5 min.

[00100] In one embodiment of the apparatus **200**, **253** for forming a drapable ornon drapable polymer pre-impregnated reinforcement material (pre-preg), the reactive thermoplastic material is selected from the group consisting of reactive macrocyclic oligomeric polyester, reactive macrocyclic oligomeric polybutyleneterephthalate, reactive macrocyclic oligomeric polyethyleneterephthalate, reactive macrocyclic oligomeric polycarbonate, and reactive lactam monomers.

[00101] In one embodiment of the apparatus **200**, **253** for forming a drapable ornon drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, a shape of the thermoplastic or thermoset resin is selected from the group consisting of a granule, pellet, flake, pastille, needle, chunks, and a chip.

[00102] In one embodiment of the apparatus **200**, **253** for forming a drapable ornon drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, the porous substrate is a reinforcement material selected from the group consisting of carbon fiber, glass fiber, basalt fiber, aramid fiber, steel fiber, natural fiber, polymer fiber, and combinations thereof.

[00103] In one embodiment of the apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, the reinforcement material **8**, **234** is in a form selected from the group consisting of roving, tape, web, weave, bi- or -multi-axial fabrics, knit, braid, random mat, and fleece.

[00104] In one embodiment of the apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, the temperature is between about 190°C and about 220°C and the residence time is between about 1 and 5 minutes.

[00105] In one embodiment of the apparatus **200**, **253** for forming a drapable ornon drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, a weight of the reinforcement material per surface area of the reinforcement material is between about 200 g/m^2 and about 2,000 g/m^2 and a weight percent of the reactive thermoplastic is between about 30% to about 80%, based on a weight of the reactive polymer pre-impregnated reinforcement material.

[00106] In one embodiment of the apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, the temperature is 190°C and the residence time is less than or equal to 1 minute.

[00107] In one embodiment of the apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, a weight of the reinforcement material per surface area of the reinforcement material is about 460 g/m^2 and a weight percent of the reactive thermoplastic is between about 34% to about 35%, based on a weight of the reactive polymer pre-impregnated reinforcement material.

[00108] In one embodiment of the apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, a weight of the reinforcement material per surface area of the reinforcement material is about 620 g/m^2 and a weight percent of the reactive thermoplastic is between about 33% to about 36%, based on a weight of the reactive polymer pre-impregnated reinforcement materials.

[00109] In one embodiment of the apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, a weight of the reinforcement material per surface area of the reinforcement material is about 810 g/m^2 and a weight percent of the reactive thermoplastic is between about 34% to about 36%, based on a weight of the reactive polymer pre-impregnated reinforcement material.

[00110] In one embodiment of the apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, the reactive thermoplastic particles **4**, **205** have a thickness between 0.5 mm and 3 mm and a diameter between 1 mm and about 8 mm.

[00111] In one embodiment of the apparatus **200**, **253** for forming a drapable

ornon drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, the reactive thermoplastic particles **4**, **205** have a diameter between about 1 mm to about 8 mm and a length between about 1 mm and about 8 mm.

[00112] In one embodiment of the apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, the reactive thermoplastic particles **4**, **205** are made from macrocyclic oligomeric butyleneterephthalate.

[00113] In one embodiment of the apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, the reactive thermoplastic particles **4**, **205** have a diameter between about 1 mm and about 5 mm and a length between about 1 mm and about 8 mm.

[00114] In one embodiment of the apparatus **200**, **253** for forming a drapable or non drapable polymer pre-impregnated reinforcement material (pre-preg) **28A**, **B**, **285A**, **B**, comprises: a belt press **407** after the heating unit oven **5**, **209**, wherein the belt press **407** has a hot zone and a cold zone, wherein the hot zone is adapted to receive drapable polymer pre-impregnated reinforcement material and to heat said pre-impregnated reinforcement material to less than or equal to 250°C and greater than or equal to 0.01 bar pressure, and wherein the cold zone is adapted to receive a fully impregnated and cured thermoplastic composite sheet and to cool said fully impregnated and cured thermoplastic composite sheet to 25°C.

[00115] In one embodiment, a method for forming a thermoplastic composite sheet**28B**, **285B**, comprises: providing a feeder roll **20**, **200** of reinforcement material **8**, **234**, a receiver roll **25**, **215** of drapable polymer pre-impregnated reinforcement material **8**, **234** and a conveyor belt **14**, **217** having the reinforcement material **8**, **234** from the feeder roll **20**, **200** thereon, wherein the reinforcement material **8**, **234** has a fiber content based on total weight of the thermoplastic composite sheet; providing a particle deposition unit **10**, **225** charged with reactive thermoplastic particles **4**, **205** and adapted to deposit between 240 g/m^2 and about 470 g/m^2 of the reactive thermoplastic particles **4**, **205**, based on the surface area (m^2) of the reinforcement material **8**, **234**;

[00116] In one embodiment, a method for forming a thermoplastic composite sheet **28B**, **285B**, comprises: providing a heating unit **5**, **209** adapted to substantially uniformly maintain the reactive thermoplastic particles **4**, **205** on a first surface **17**, **231** of the reinforcement material **8**, **234** between about 190°C and about 220°C during a residence time that the reactive thermoplastic particles **4**, **205** on a first surface **17**, **231** of the reinforcement material **8**, **234** reside in the oven **5**, **209**.

[00117] In one embodiment, a method for forming a thermoplastic composite sheet**28B**, **285B**, comprises: providing a conveyor belt **14**, **217** wherein residence time that the reactive thermoplastic particles **4**, **205** on the first surface **17**, **231** of the reinforcement material **8**, **234** is based on the conveyor belt's **14**, **217** rate; and providing a belt press **407** after the heating unit **5**, **209**, wherein the belt press **407** has a hot zone and a cold zone, wherein the hot zone is adapted to receive drapable polymer pre-impregnated reinforcement material **28B**, **285B** and to heat said pre-impregnated reinforcement material **28B**, **285B** to less than or equal to 250°C and greater than or equal to 0.01 bar pressure, and wherein the cold zone is adapted to receive a fully impregnated and cured thermoplastic composite sheet and to cool said fully impregnated and cured thermoplastic composite sheet to 25°C.

[00118] In one embodiment of the method for forming a thermoplastic composite sheet **28B, 285B**, the fiber content of the reinforcement material **8, 234** is between about 50% and about 70% by weight, based on a weight of the drapable polymer pre-impregnated reinforcement material **28B, 285B**.

[00119] **Figs. 8-9** depict a flow sheet diagram of a method **10** for manufacturing "pre-pregs". Hereinafter, a "pre-preg" is defined as fiber reinforced sheets impregnated with a thermosetting resin which may be subsequently cured to form a thermoset composite sheet. A pre-preg is also defined as a reactive polymer pre-impregnated reinforcement material from thermosets. The fibers could be, but are not exclusively, glass fiber, carbon fiber, steel fibers, aramid fibers, basalt fiber, polymer fiber, natural fibers, or combinations thereof.

[00120] Thermoset resins and thermoplastic resins suited for preparing pre-pregs from the substantially non-volatile composition **4** may have a melt viscosity between about 5 cps and about 5,000 cps such as: epoxy resins, unsaturated polyester resins, vinyl ester resins, thermoset polyurethane resins, phenol-formaldehyde resins (phenolic resins), polyimide resins, silicone resins, crosslinkable thermoplastic resins, e.g., crosslinkable polyethylene resins, crosslinkable polypropylene resins, crosslinkable polymers, crosslinkable polymers, and crosslinkable polyvinyl chloride resins. The substantially non-volatile composition **4** comprises thermoset resins that are substantially completely solid at ambient temperature, i.e. 40 °C. The only volatile components in the substantially non-volatile composition **4** are residual solvents or water. A comprehensive listing of thermoset resins may be found in "Handbook of Thermoset Resins," 2nd Edition, by Sidney H. Goodman, Noyes Publications, Westwood, NJ, ISBN: 0-8155-1421-2 (1998), which is hereby incorporated by reference

[00121] This list is not meant to be limiting or exhaustive but merely illustrates the wide range of polymeric materials which may be employed in the present invention. Thermoset resins of the present invention may be epoxy based or unsaturated polyester based that are also solid at room temperature. The resins are substantially completely solid at room temperature and are deposited in their solid form on the fibers. The resins are generally particles having powder, granules, pellets, pastilles, flakes, chips, or any other suitable solid form. Depositing the thermoset resins in their solid form, instead of their molten liquid form is advantageous because solids are easier to deposit on the fiber mat than molten liquids. FREOPOX resin, available from Freilacke and RESICOAT resin available from AKZO NOBEL are examples of suitable resins.

[00122] The method **10** comprises the following steps. In a step **12**, a thermosetting resin, substantially completely in its solid form, e.g. as a powder, is deposited on a fabric or assemblage of reinforcing fiber. The thermoset resin is in its solid form at ambient temperature. The resin may be dried to remove moisture or solvent prior to depositing the resin on the fabric or assemblage of reinforcing fiber to avoid voids in the formed pre-preg.

[00123] In one embodiment of the step **12** of the method **10**, the resin can be pre-catalyzed and have a long shelf life because it is solid at room temperature.

[00124] In one embodiment of the step **12** of the method **10**, solid resins can be in the form of powders, granules, pellets, pastilles, flakes, chips, or any other suitable solid form.

[00125] In one embodiment of the step **12** of the method **10**, the resin can be uniformly deposited with a particle deposition unit **10**, **225**, e.g., a powder sprinkling device. Schott & Meissner powder sprinkler from textile industry is an example of an appropriate powder sprinkling device which typically costs approximately 50-80,000 euro for a 3m wide sprinkler. In one embodiment, the particle deposition unit is a powder sprinkling device and a field of deposition of the sprinkling device is from about 0 to about 4.0 m wide

[00126] In a step **14**, a "pre-preg" is formed by heating the fabric or assemblage of reinforcing fiber, melting the resin so that it adheres to the fabric or assemblage of reinforcing fiber, and possibly impregnates the fiber or assemblage of reinforcing fiber with the heat curable thermoset resin. The pre-preg may then be stored for later use.

[00127] In a step **16**, applying heat and pressure or vacuum to the pre-preg essentially completely melts the solid particles and essentially completely impregnates the fabric or assemblage of reinforcing fiber with the heat curable thermoset resin and may cure the resin if it was pre-catalyzed.

[00128] In the steps **14-16** of the method **10**, processing is faster than thermoplastic processing because the melt viscosity of the thermoset resin is lower viscosity than the melt viscosity of a thermoplastic when melted and can wet fibers quickly.

[00129] In one embodiment, the step **16** includes curing in a low pressure double belt press **407**.

[00130] In one embodiment, the step **16** includes curing in a vacuum bagging process.

[00131] In one embodiment, the step **16** includes curing in a heated press.

[00132] In one embodiment, the step **16** includes curing in a vacuum bagging process.

[00133] Being able to use a thermoset resin in its solid form enables advantageously using a particle deposition unit **10**, **225**, e.g. a powder sprinkling device in the step **12-14** of the method **10**.

[00134] Being able to use a thermoset resin in its solid form offers several advantages. First, thermoset resins typically have a lower melt viscosity than alternative thermoplastic resins which are also used to make pre-pregs and cured composite sheets. Lower temperatures and pressures are required to impregnate a fiber mat with the thermoset resin because thermoset resins typically melt at a lower temperature than thermoplastics and have a lower melt viscosity. Therefore a belt press **407**, such as a double belt press used for impregnating the resin into the fiber mat in the step **16** of the method **10** may operate at a lower temperature and pressure when the resin is a thermoset rather than a thermoplastic.

[00135] Being able to use a thermoset resin in its solid form enables using equipment developed to make fiber reinforced thermoplastic sheets, consisting of a particle deposition unit **10**, **225**, e.g. a powder sprinkling device and a belt press **407**, such as a double belt press. The double belt press can have a much lower operating pressure, and hence lower cost, than those developed for thermoplastics. In particular, the belt can be made of fiber reinforced plastic in place of steel.

[00136] **FIG. 10** is a schematic diagram illustrating a longitudinal cross-sectional view of an apparatus **200** for manufacturing a polymer pre-impregnated reinforcement material (prepreg) **28**. The apparatus **200** comprises: a particle deposition stage **30**, a belt press **407**, such as a double belt press, and a prepreg retrieval stage **50**.

[00137] The particle deposition stage **30** comprises: at least one supply roll(s) **20** for supplying a porous substrate **8**; at least one hopper(s) **10** being charged with particles **4** of reactive (polymerizable) thermoset resin; an array of particles **4** of reactive thermoset resin deposited onto a first surface **17** of the porous substrate **8**. The at least one supply roll(s) **20** may unroll by rotating in a direction of the arrow **1** and the receiving roll 25 may receive by rotating in a direction of the arrow **7** about an axis orthogonal to a plane of the at least one layer **17** of the porous substrate **8**. The particles **4** of reactive (polymerizable) thermoset resin may advantageously be deposited onto the first surface **17** of the porous substrate **8**, wherein both the particles **4** and the porous surface of the porous substrate **8** are advantageously at ambient temperature.

[00138] Referring first to **FIG. 10**, it can be seen that a belt press **407**, such as a double belt press comprises a pair of belts **21** and **22** which are displaceable on rollers **23**. The belts **21** and **22** define a pressing gap **24** between two arrays of support rolls **25** and **26**.

[00139] **Fig. 11** depicts a cross-sectional view of an apparatus **50** for making a free form thermoset apparatus **10**. The apparatus **50** comprises: a vacuum bag **45**, an apparatus **10** in the vacuum bag **45**, and a mold **51**, having a first surface **46**. The vacuum bag **45** comprises a plurality of vacuum bag sheets **53**, **55**. In one embodiment, the apparatus **50** for free-forming a shape of the apparatus **10**, such as a composite assembly, comprises: a mold **51** having a first surface **46** and a vacuum bag **45** thereon, wherein the vacuum bag **45** comprises a plurality of vacuum bag sheet(s) **53**, **55**, and the apparatus **10** therein.

[00140] **Figs. 12-13** depict a schematic diagram illustrating a longitudinal cross-sectional view of an apparatus **200** for forming a thermoset composite sheet, comprises: at least one feeder roll **20**, **400**, wherein one of the feeder rolls **400** provides reinforcement material **510**, a receiver roll **25** of drapable polymer pre-impregnated reinforcement material **500** and a conveyor belt **14** having the reinforcement material **510** from the feeder roll **20** thereon. The reinforcement material **510** has a fiber content based on total weight of the thermoset composite sheet made from curing the polymer pre-impregnated reinforcement material (prepreg) **500**. The apparatus **200** for forming a thermoset composite sheet, comprises: a particle deposition hopper **10** charged with a substantially non-volatile composition **4**, comprising a substantially completely solid reactive thermoset particles.

[00141] The substantially non-volatile composition **4** may also include non-volatile inorganic or thermoplastic fillers. The non-volatile inorganic fillers may be calcium carbonate, fumed silica, mined quartz, graphite, and the like. Thermoplastic fillers are selected from the group consisting of crosslinkable polyethylene resins, crosslinkable polypropylene resins, crosslinkable polyvinyl chloride resins, crosslinkable polymers, and combinations thereof. Thermoplastic fillers may be reactive macrocyclic oligomeric polyester, reactive macrocyclic oligomeric polybutyleneterephthalate, reactive macrocyclic oligomeric polyethyleneterephthalate, reactive macrocyclic oligomeric polycarbonate, and reactive lactam monomers.

[00142] **Fig. 12** depicts the apparatus **200** for forming a thermoset composite sheet, comprises: at least one heating unit **470**, **480**, e.g. thermal convection oven, an infrared oven, a hot plate or other heating element, a heat exchanger for heating or cooling the particles of the substantially non-volatile composition **4** for a residence time for which the reactive thermoset particles reside on at least one layer **520** of the reinforcement material **510** in the heating unit **470**, **480**. The apparatus **200** for forming a thermoset composite sheet, comprises: a conveyor belt **14** wherein residence time that the particles of the substantially non-volatile composition **4** reside on the at least one layer **520** of the reinforcement material **510** is based on the conveyor belt's rate. The conveyor belt 14 rotates in a direction shown by the arrow **430** about an axis orthogonal to a plane of the at least one layer **520** of the reinforcement material **510**.

[00143] In one embodiment, the particle deposition hopper **10** is adapted to deposit between 20 g/m^2 and about 2,000 g/m^2 of the particles of the substantially non-volatile composition **4**, based on the surface area (m^2) of the reinforcement material **510**.

[00144] In one embodiment, **Fig. 13** depicts apparatus **200** for forming a thermoset composite sheet, comprises: the belt press **407**, at thermal fixing stage **40**, is adapted to melt the substantially completely solid particles of the substantially non-volatile composition **4** on the at least one layer **520** of the reinforcement material **530** in a temperature range between about 40°C and about 230°C.

[00145] In one embodiment, the hot zone, optionally **407a** or **407b**, of the belt press **407**, depicted in **Figs. 1**, **10**, and **13**, and described herein, is adapted to receive the reinforcement material **510** having at least one layer **520** and the deposited substantially completely solid particles of the substantially non-volatile composition **4**, thereon. The hot zone, optionally **407a** or **407b**, of the belt press **407**, is adapted to heat said substantially completely solid particles of the substantially non-volatile composition **4** on the at least one layer **520** of the reinforcement material **510** to less than or equal to about 260°C at greater than or equal to 0.01 bar pressure. The zones **407a** or **407b** may be hot or cold temperature exchangers, that provide either heat or cold to the reactive drapable pre-preg **500**.

[00146] In one embodiment, the cold zone, optionally **407a** or **407b**, of the belt press **407**, depicted in **Figs. 1**, **10**, and **13**, and described herein, is adapted to receive a fully impregnated and cured thermoset composite sheet from the hot zone of the belt press **407**, and to cool said fully impregnated and cured thermoset composite sheet to 25°C.

[00147] In one embodiment, **Fig. 13** depicts particles of the substantially non-volatile composition **4** are deposited on a releasable surface **540** of the film **530**. The releasable surface **540** of the film **530** may be releasable because it has a release agent on the releasable surface **540**, e.g., a releasable coating between the composition **4** and the film. The film **530** may be paper and the releasable coating may be a silicone agent. The particles of the composition **4** may be releasably fixed on the releasable surface **540** of the film **530** by passing the combination of film **530** and composition **4** through the press **450**, e.g. a cylindrical press having a heating element.

[00148] In this embodiment, as in **Fig. 13**, the reinforcement material **510** may be overlaid on the releasable surface **540** of the film **530** so that the substantially non-volatile composition **4** is sandwiched between the at least one layer **520** of the reinforcement material **510** and the releasable surface **540** of the film **530**. The film is then released, leaving the composition **4** as a deposit on the at least one layer **520** of the reinforcement material **510**. In this embodiment, the film **530** is releasably coupled to composition **4**. The film **530** is made from a material selected from the group consisting of paper coated with silicone release agent. Alternatively, the film **530** may be polytetrafluoroethylene (PTFE), perfluoroalkoxy polymer resin, PFA, polyfluoroalkanes, or polyethylene film, and polypropylene film.

[00149] The foregoing description of the embodiments of this invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously, many modifications and variations are possible.

I claim:

1. A method for making a reactive polymer pre-impregnated reinforcement material, comprising:

providing a substantially non-volatile composition, comprising substantially completely solid particles of at least one heat curable thermoset resin, wherein the only volatile components of the composition are residual water or residual solvent:

depositing a layer of the substantially non-volatile composition on a fabric or assemblage of reinforcing fiber to be impregnated,

wherein the particles of the substantially non-volatile composition are solid at ambient temperature and are applied to the fabric or assemblage of reinforcing fiber to be impregnated at ambient temperature; and

forming a pre-preg by heating the substantially completely solid particles of the substantially non-volatile composition, so that the substantially completely solid particles partially melt, wherein the fabric or assemblage is impregnated by the partially melted composition, and the partially melted solid particles of the substantially non-volatile composition adhere to the fabric or assemblage of reinforcing fiber.

2. The method of claim 1, comprising:

applying heat and pressure or vacuum to the pre-preg;

essentially completely melting the partially melted particles of the composition; and

substantially completely impregnating the fabric or assemblage of reinforcing fiber with the melted composition.

3. The method of claim 1, wherein the substantially completely solid particles of the composition are selected from the group consisting of epoxy resins, unsaturated polyester resins, vinyl ester resins, thermoset polyurethane resins, phenol-formaldehyde resins (phenolic resins), polyimide resins, silicone resins, crosslinkable thermoset resins, and combinations thereof.

4. The method of claim 1, wherein the substantially completely solid particles of the composition are pre-catalyzed and the particles of the composition are substantially completely solid at room temperature.

5. The method of claim 1, wherein the fabric or assemblage of reinforcing fiber is selected from the group consisting of carbon fiber, glass fiber, basalt fiber, polymer fiber, aramid fiber, steel fiber, natural fiber, and combinations thereof.

6. The method of claim 5, wherein the fabric or assemblage of reinforcing fiber is selected from the group consisting of roving, tape, web, weave, bi- or -multi-axial fabrics, knit, braid, random mat, fleece, and combinations thereof.

7. The method of claim 1, wherein the substantially completely solid particles of the composition are dried to remove moisture or solvent prior to depositing the substantially completely solid particles of the composition on the fabric or assemblage of reinforcing fiber to avoid voids in the formed pre-preg.

8. The method of claim 1, wherein the layer of the substantially completely solid particles of the non-volatile composition is formed by depositing the substantially completely solid particles of the non-volatile composition by a particle deposition unit.

9. The method of claim 8, wherein the particle deposition unit is a powder sprinkling device and a field of deposition of the sprinkling device is from about 0 to about 4.0 m wide.

10. The method of claim 2, wherein applying heat and pressure or vacuum to the pre-preg includes curing in a low pressure double belt press.

11. The method of claim 2, wherein applying heat and pressure or vacuum to the pre-preg includes curing in a vacuum bagging process.

12. A drapable polymer pre-impregnated reinforcement material, comprising:

a porous substrate having at least one layer; and randomly spaced particles of a substantially non-volatile composition, comprising at least one reactive thermoset resin, thereon,

wherein the only volatile components of the composition are residual water or solvent,

wherein a portion of each of the randomly spaced particles is impregnated into interstices of the at least one layer of the porous substrate, therein, and

wherein a space, therebetween, separates adjacent randomly spaced particles.

13. The drapable polymer pre-impregnated reinforcement material of claim 12, wherein the porous substrate having at least one layer comprises fiber reinforced sheets impregnated with the at least one reactive thermoset resin(s), which may be subsequently cured to form a thermoset composite sheet.

14. The drapable polymer pre-impregnated reinforcement material of claim 13, wherein the fibers of the fiber reinforced sheets are selected from the group consisting of carbon fiber, glass fiber, basalt fiber, polymer fiber, aramid fiber, steel fiber, natural fiber, and combinations thereof.

15. The drapable polymer pre-impregnated reinforcement material of claim 12, wherein the composition is selected from the group consisting of epoxy resins, unsaturated polyester resins, vinyl ester resins, thermoset polyurethane resins,

phenol-formaldehyde resins (phenolic resins), polyimide resins, silicone resins, crosslinkable thermoset resins, and combinations thereof.

16. The drapable polymer pre-impregnated reinforcement material of claim 15, wherein the crosslinkable thermoplastic resins are selected from the group consisting of crosslinkable polyethylene resins, crosslinkable polypropylene resins, crosslinkable polyvinyl chloride resins, crosslinkable polymers, and combinations thereof.

17. The drapable polymer pre-impregnated reinforcement material of claim 12, wherein the composition is epoxy based or unsaturated polyester based, and wherein the epoxy based or unsaturated polyester based thermoset resin(s) are solid at room temperature.

18. A method for forming a drapable polymer pre-impregnated reinforcement material, comprising:

providing a the porous substrate having having at least one layer; and

forming an array of a substantially non-volatile composition, comprising substantially uniformly spaced and substantially completely solid reactive thermoset particles, and covering a portion of the at least one layer, thereon,

wherein the only volatile components of the composition are residual water or solvent:

partially melting the array of substantially completely solid reactive thermoset particles; and

fixing the partially melted array by impregnating the melt into interstices of a portion of the at least one layer of the porous substrate, therein,

wherein a remaining portion of the at least one layer remains uncovered by the array.

19. The method of claim 18, wherein the substantially solid reactive thermoset particles of the array have a melt viscosity between about 5 cps and about 5,000 cps.

20. The method of claim 18, wherein the porous substrate having at least one layer comprises fiber reinforced sheets impregnated with the at least one reactive thermoset resin(s), which may be subsequently cured to form a thermoset composite sheet.

21. The method of claim 18, wherein the substantially solid reactive thermoset particles of the array are selected from the group consisting of epoxy resins, unsaturated polyester resins, vinyl ester resins, thermoset polyurethane resins, phenol-formaldehyde resins (phenolic resins), polyimide resins, silicone resins, crosslinkable thermoset resins, and combinations thereof.

22. The method of claim 21, wherein the substantially solid reactive thermoset particles of the array are pre-catalyzed and the reactive thermoset resin particles are solid at room temperature.

23. The method of claim 18, wherein fibers of the porous substrate having at least one layer is selected from the group consisting of carbon fiber, glass fiber, basalt fiber, polymer fiber, aramid fiber, steel fiber, natural fiber, and combinations thereof.

24. The method of claim 18, wherein fibers of the porous substrate having at least one layer is selected from the group consisting of roving, tape, web, weave, bi- or -multi-axial fabrics, knit, braid, random mat, fleece, and combinations thereof.

25. The method of claim 18, wherein the substantially solid reactive thermoset particles of the array are dried to remove moisture or solvent to avoid voids in the formed pre-preg or in a composite sheet formed from the pre-preg.

26. The method of claim 18, wherein the array of substantially uniformly spaced and substantially completely solid reactive thermoset particles is formed by depositing the substantially completely solid particles of the at least one heat curable thermoset resin by a particle deposition unit.

27. The method of claim 26, wherein the powder deposition unit is a powder sprinkling device and a field of deposition of the sprinkling device is at least 4.0 m wide.

28. An apparatus for forming a drapable polymer pre-impregnated reinforcement material, comprising:

a feeder roll of reinforcement material;

a receiver roll of drapable polymer pre-impregnated reinforcement material; and

a conveyor belt having the reinforcement material from the feeder roll thereon;

a particle deposition hopper charged with a substantially non-volatile composition, comprising substantially completely solid reactive thermoset particles,

wherein the only volatile components of the substantially non-volatile composition are residual water or solvent:

a heating device adapted to substantially uniformly maintain a temperature of the substantially non-volatile composition on at least one layer of the reinforcement material for a residence time, during which the particles of the composition on the at least one layer of the reinforcement material reside in the oven; and

a conveyor belt,

wherein residence time that the particles of the composition reside on the at least one layer of the reinforcement material is based on the conveyor belt's rate.

29. The apparatus of claim 28, wherein the particle deposition hopper is adapted to deposit between 20 g/m^2 and about 2,000 g/m^2 of the particles of the composition, based on the surface area (m^2) of the reinforcement material.

30. A method for forming a thermoset composite sheet, comprising:

providing at least one feeder roll, wherein one of the feeder rolls provides reinforcement material, a receiver roll of drapable polymer pre-impregnated reinforcement material and a conveyor belt having the reinforcement material from the feeder roll thereon,

wherein the reinforcement material has a fiber content based on total weight of the thermoset composite sheet;

providing a particle deposition hopper charged with a substantially non-volatile composition,

wherein the substantially non-volatile composition comprises substantially completely solid reactive thermoset particles, and

wherein the only volatile components of the substantially non-volatile composition are residual water or solvent;

depositing the particles of the substantially non-volatile composition on at least one layer of the reinforcement material;

providing a thermal heating unit for heating the substantially non-volatile composition for a residence time for which the substantially solid reactive thermoset particles of the substantially non-volatile composition reside on the at least one layer of the reinforcement material in the oven;

providing a conveyor belt wherein residence time that the particles of the substantially non-volatile composition reside on the at least one layer of the reinforcement material is based on the conveyor belt's rate; and

providing a belt press after the heating unit,

wherein the belt press has a hot zone and a cold zone.

31. The method of claim 30, wherein the particle deposition hopper is adapted to deposit between 20 g/m^2 and about 2,000 g/m^2 of the particles of the composition, based on the surface area (m^2) of the reinforcement material.

32. The method of claim 30, wherein the oven is adapted to melt the particles of the substantially non-volatile composition on the at least one layer of the reinforcement material in a temperature range between about 40°C and about 230°C.

33. The method of claim 30, wherein the hot zone is adapted to receive drapable polymer pre-impregnated reinforcement material and to heat said pre-impregnated reinforcement material to less than or equal to about 260°C at greater than or equal to 0.01 bar pressure.

34. The method of claim 30, wherein the cold zone is adapted to receive a fully impregnated and cured thermoset composite sheet and to cool said fully impregnated and cured thermoset composite sheet to 25°C.

35. The method of claim 30, comprising a second feeder roll, wherein the second feeder roll provides a carrier film, so that the composition is sandwiched between the reinforcement material and the releasable surface of the carrier film.

36. The method of claim 35, wherein the releasable film is either a film coated with a release agent, wherein the release agent is selected from the group consisting of silicone release agent or polytetrafluoroethylene (PTFE), perfluoroalkoxy polymer resin, PFA, polyfluoroalkanes, or polyethylene film, and polypropylene film.

37. A method for making a reactive polymer pre-impregnated reinforcement material, comprising:

providing a substantially non-volatile mixture, comprising substantially completely solid particles of a heat curable thermoset resin and substantially completely solid particles of a heat curable thermoplastic resin,

wherein the only volatile components of the substantially non-volatile mixture are residual water or solvent:

depositing a layer of the mixture on a fabric or assemblage of reinforcing fiber to be impregnated,

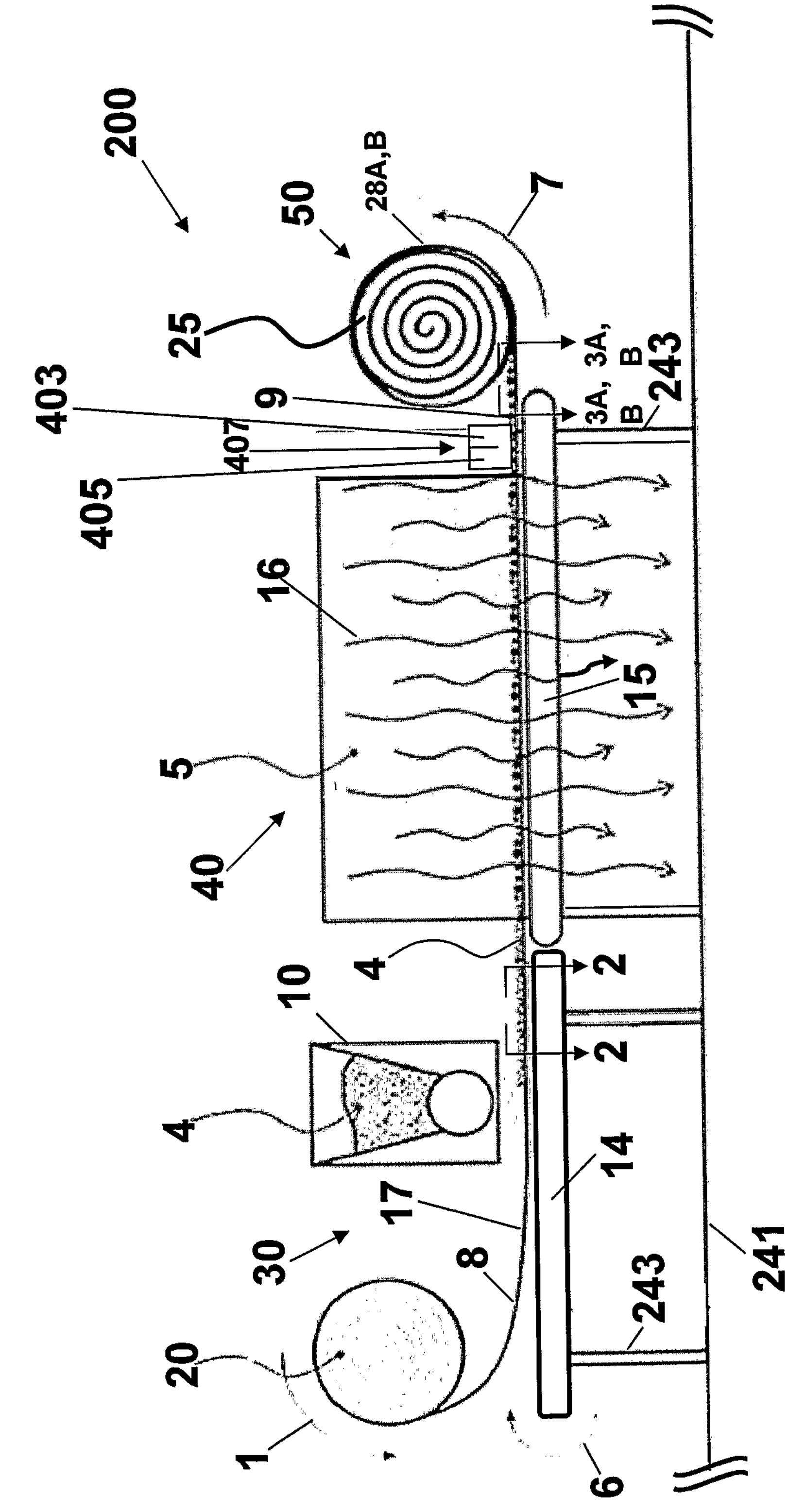
wherein the particles of the substantially non-volatile mixture are solid at ambient temperature and are deposited onto the fabric or assemblage of reinforcing fiber to be impregnated at ambient temperature; and

forming a pre-preg by heating the particles of the substantially non-volatile mixture, so that the solid particles partially melt, wherein the fabric or assemblage is impregnated by the partially melted thermoset resin, and the partially melted solid particles adhere to the fabric or assemblage of reinforcing fiber.

38. The method of claim 35, wherein the thermoplastic resin is from about 0 % to about 40% by weight of the composition and is not soluble in the melted composition.

39. The method of claim 36, wherein the substantially completely solid particles of thermoplastic resin are a different color than the particles of the substantially completely solid thermoset resin.

40. The method of claim 39, wherein the substantially completely solid particles of thermoplastic resin are a different viscosity than the particles of the substantially completely solid thermoset resin.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9
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16
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8
20
243
241
1
6

Fig. 1

Fig. 2

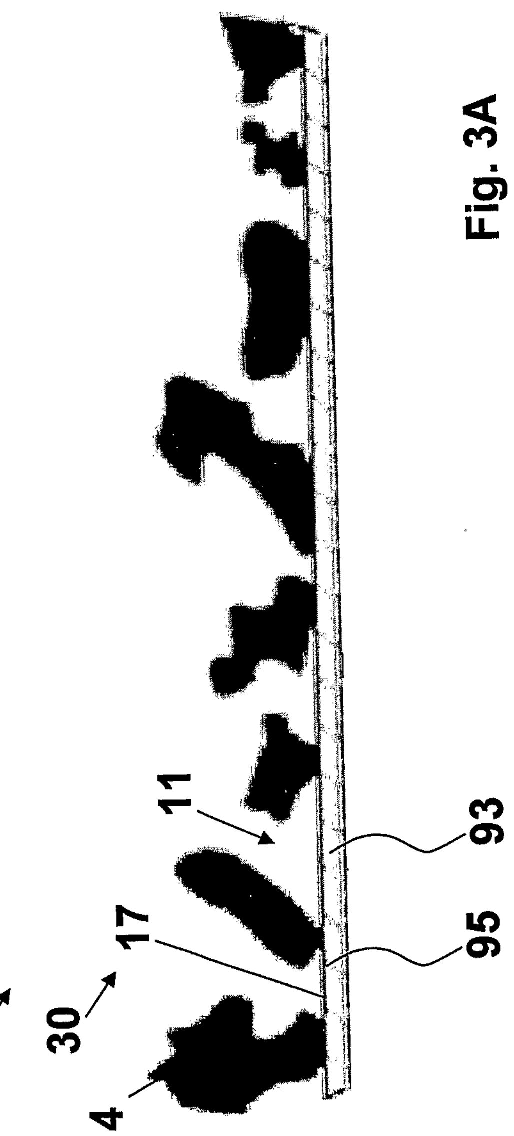
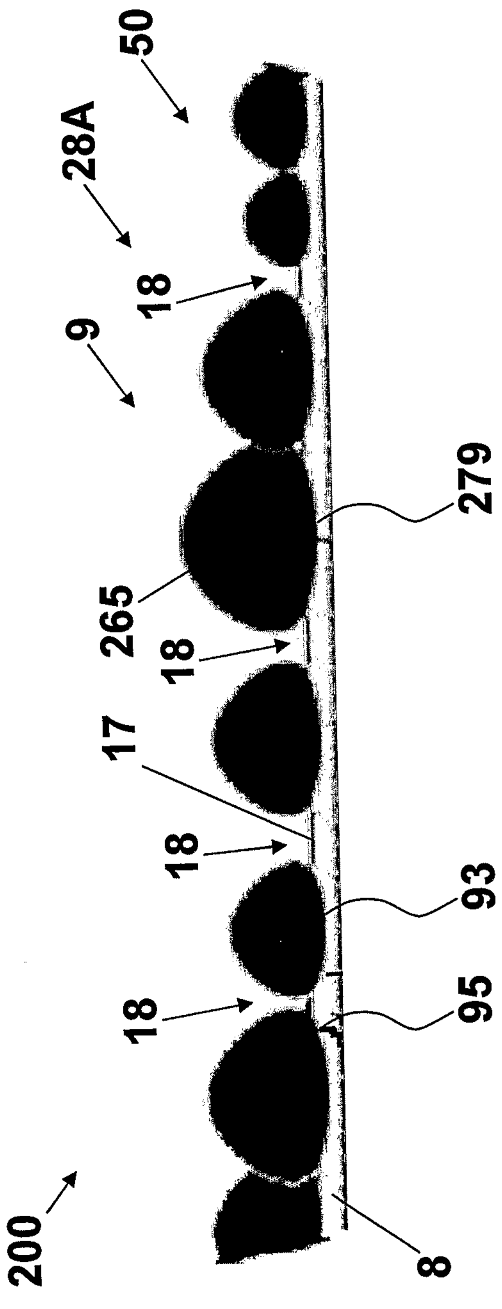


Fig. 3A



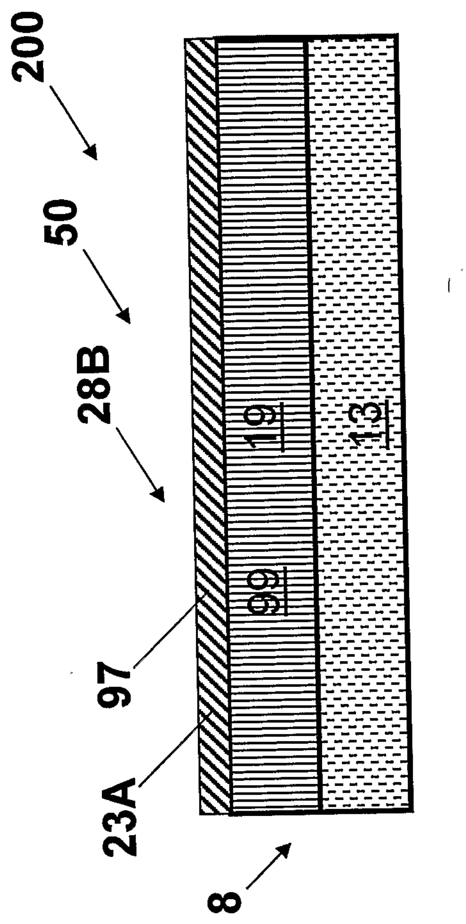
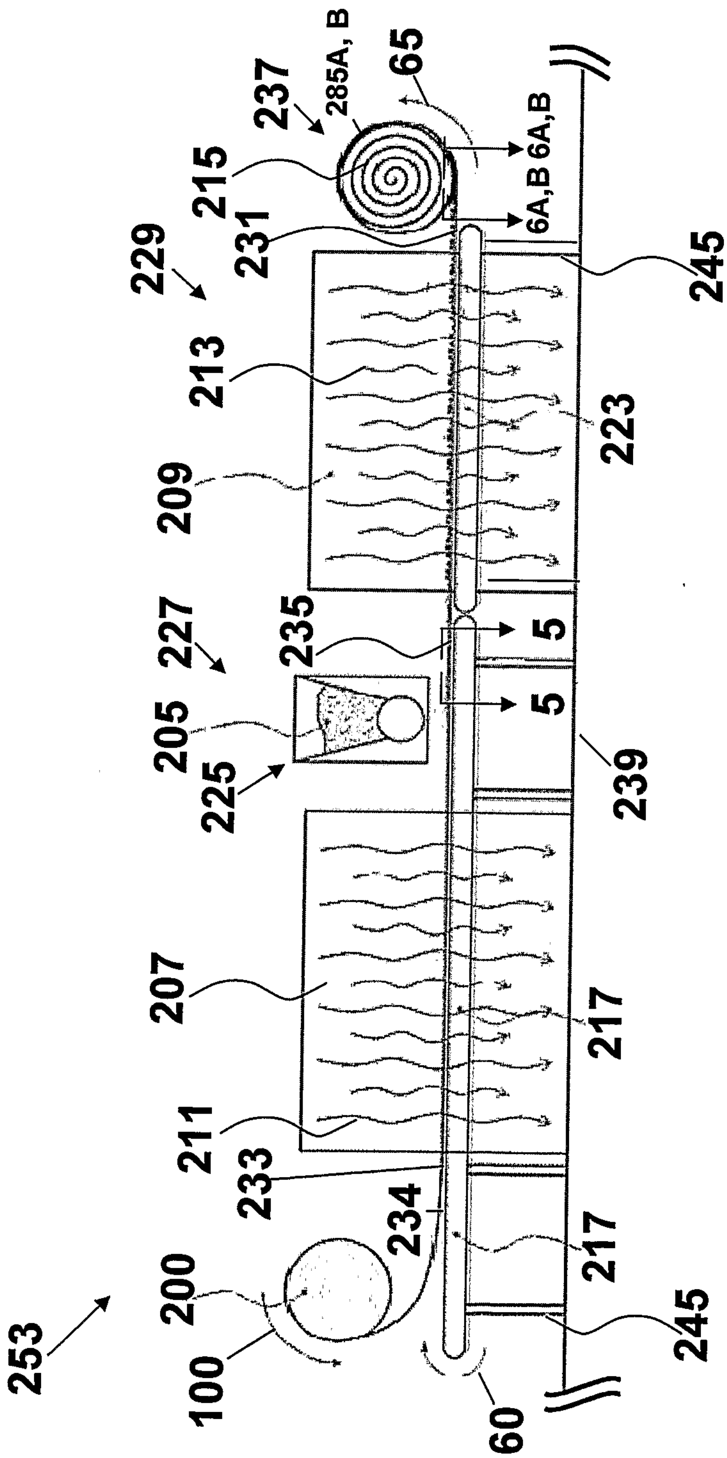


Fig. 3B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231
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6A,B
6A,B
245

Fig. 4

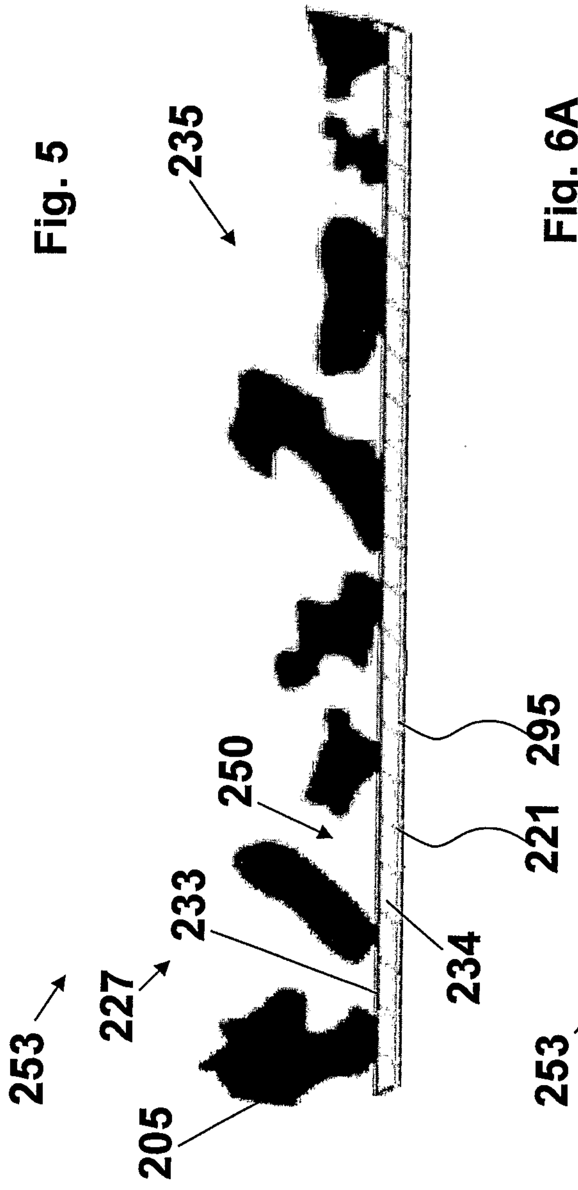
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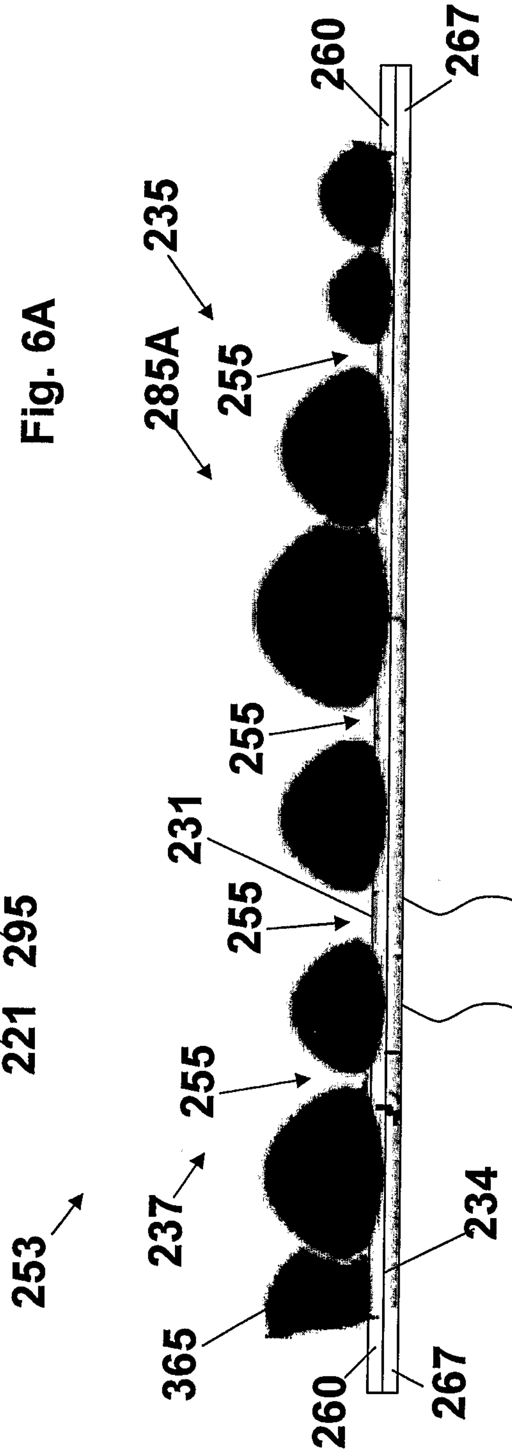
Fig. 5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234
221
295
260
267

Fig. 6A

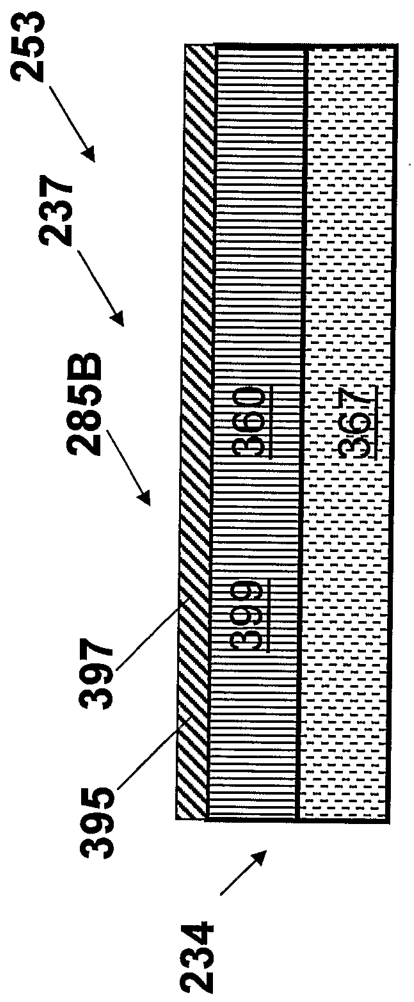
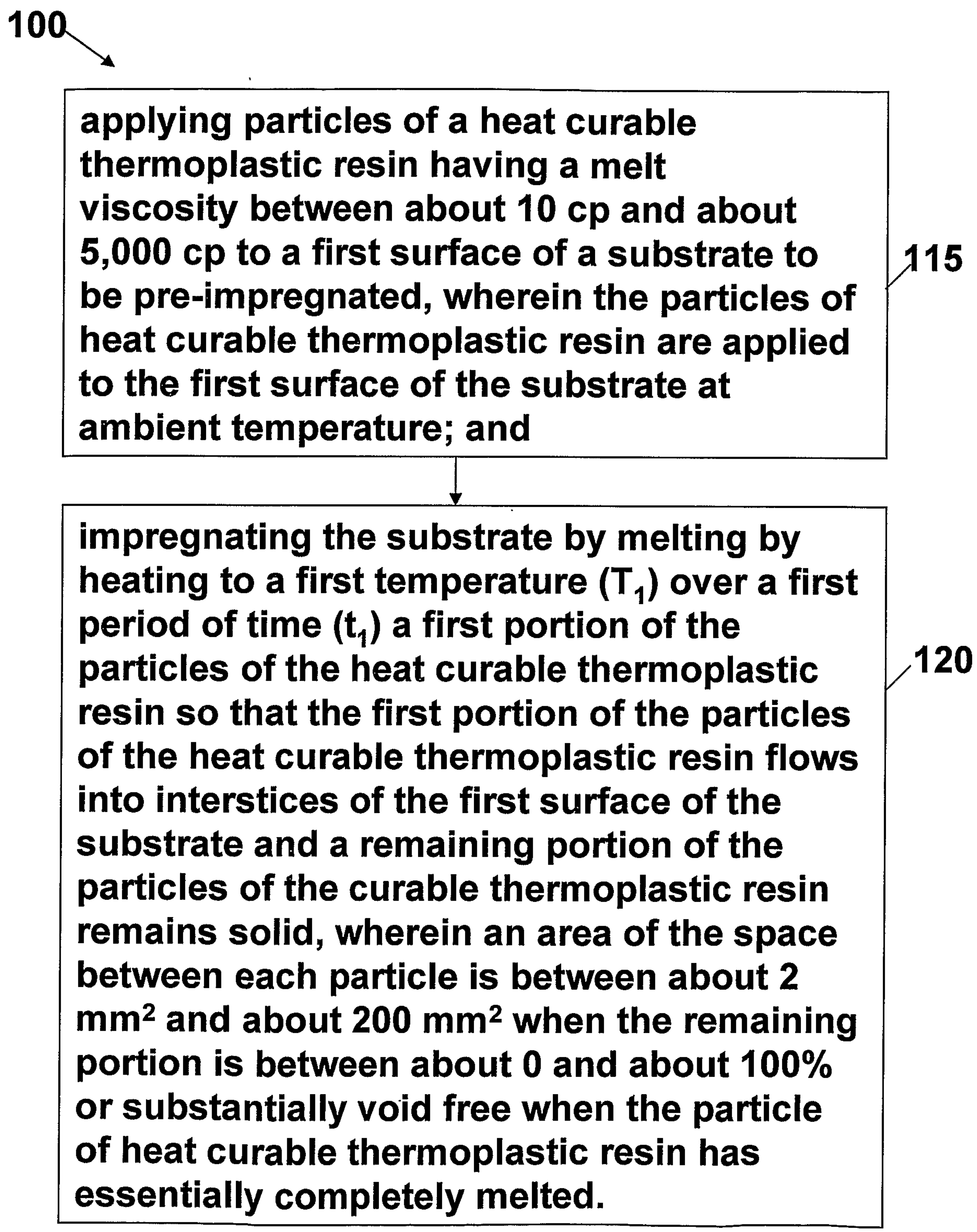


Fig. 6B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applying particles of a heat curable thermoplastic resin having a melt viscosity between about 10 cp and about 5,000 cp to a first surface of a substrate to be pre-impregnated, wherein the particles of heat curable thermoplastic resin are applied to the first surface of the substrate at ambient temperature; and
115
impregnating the substrate by melting by heating to a first temperature (T_1) over a first period of time (t_1) a first portion of the particles of the heat curable thermoplastic resin so that the first portion of the particles of the heat curable thermoplastic resin flows into interstices of the first surface of the substrate and a remaining portion of the particles of the curable thermoplastic resin remains solid, wherein an area of the space between each particle is between about 2 mm^2 and about 200 mm^2 when the remaining portion is between about 0 and about 100% or substantially void free when the particle of heat curable thermoplastic resin has essentially completely melted.
120

Fig. 7

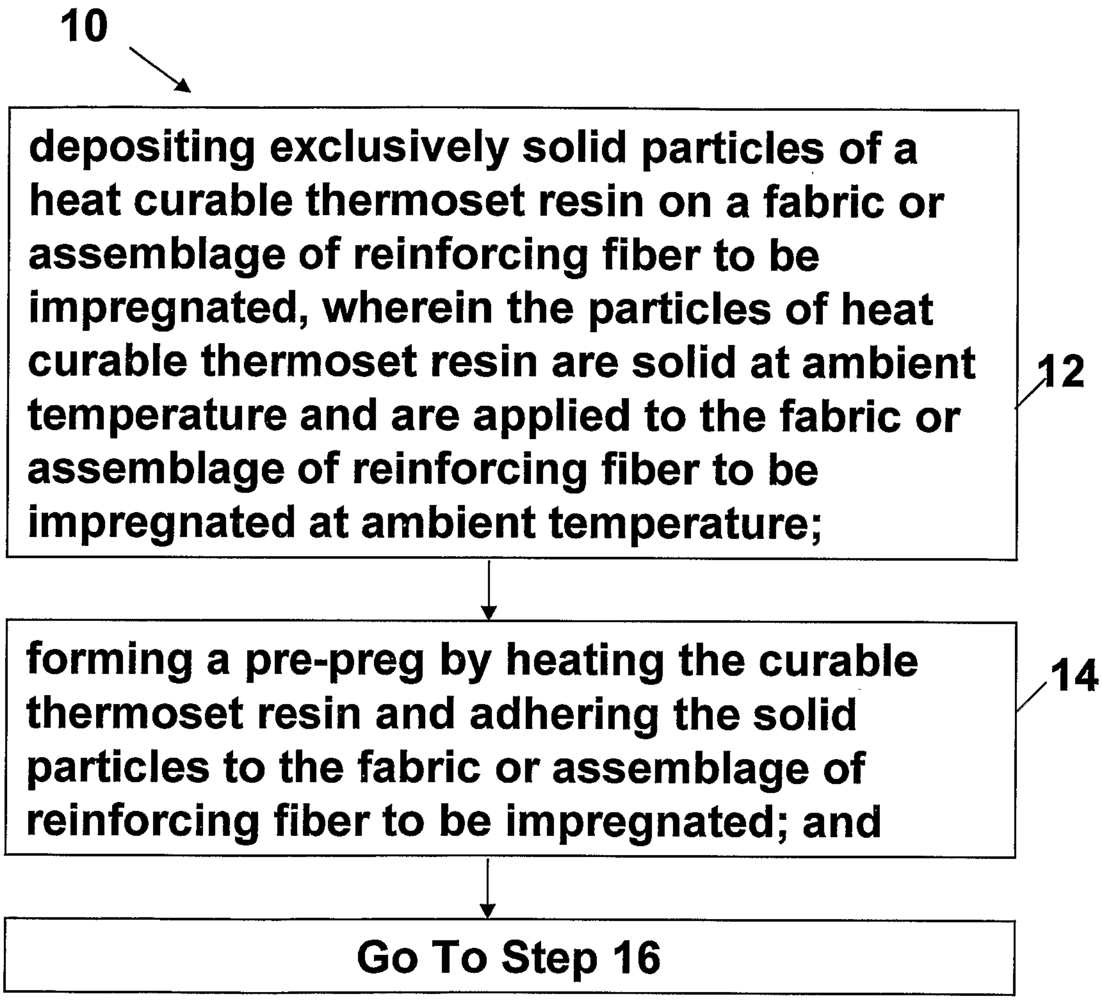
10
depositing exclusively solid particles of a heat curable thermoset resin on a fabric or assemblage of reinforcing fiber to be impregnated, wherein the particles of heat curable thermoset resin are solid at ambient temperature and are applied to the fabric or assemblage of reinforcing fiber to be impregnated at ambient temperature;
12
forming a pre-preg by heating the curable thermoset resin and adhering the solid particles to the fabric or assemblage of reinforcing fiber to be impregnated; and
14
Go To Step 16

Fig. 8

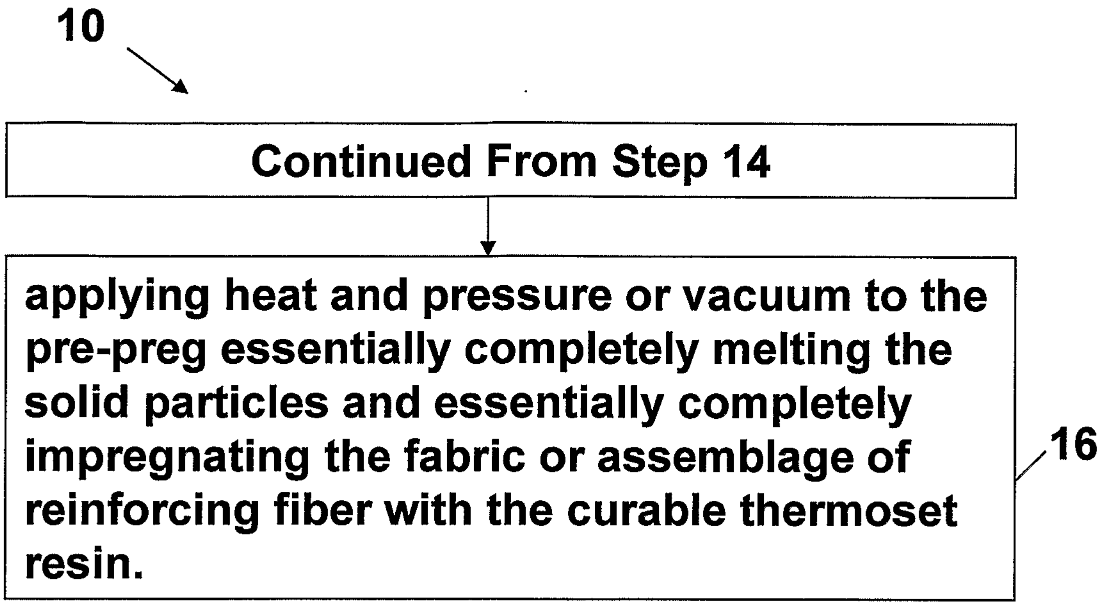
10
Continued From Step 14
applying heat and pressure or vacuum to the pre-preg essentially completely melting the solid particles and essentially completely impregnating the fabric or assemblage of reinforcing fiber with the curable thermoset resin.
16

Fig. 9

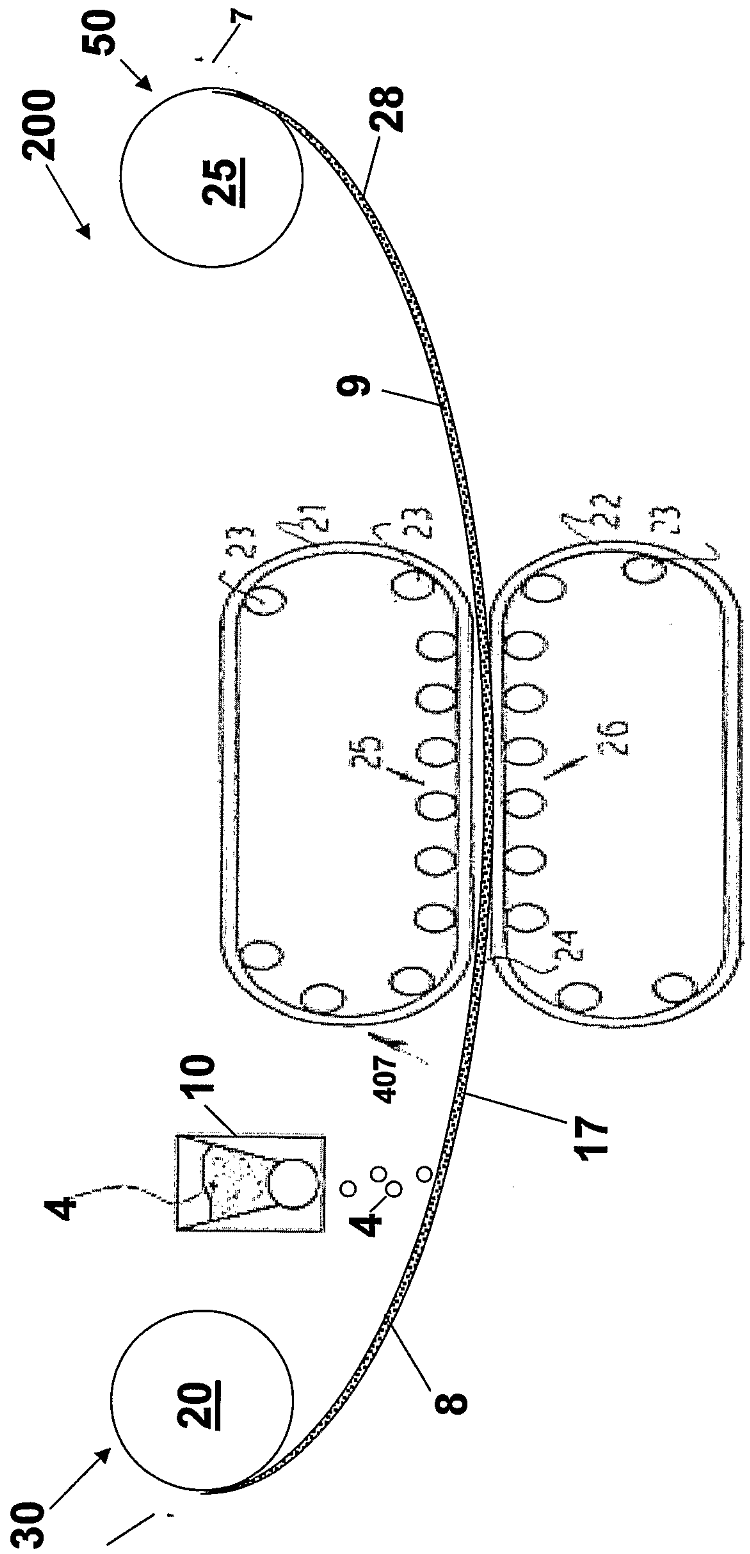

FIG. 10

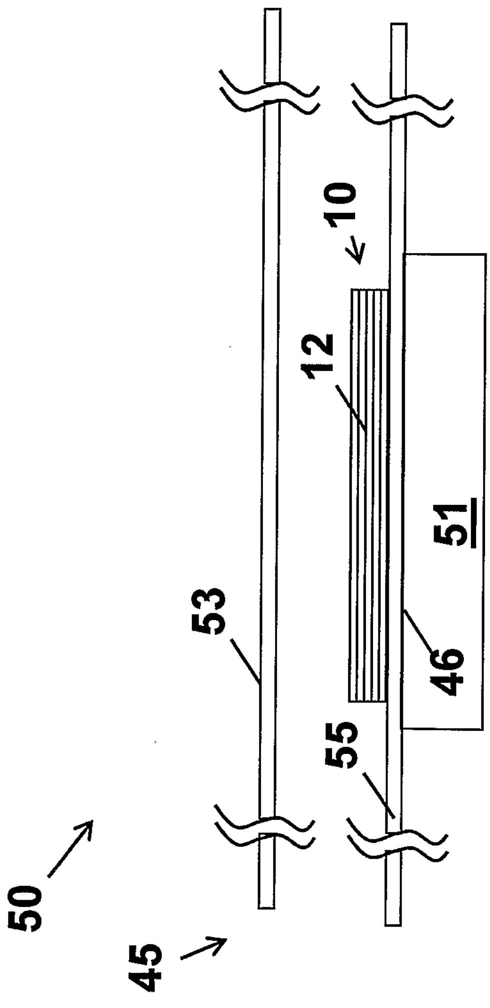

Fig. 11

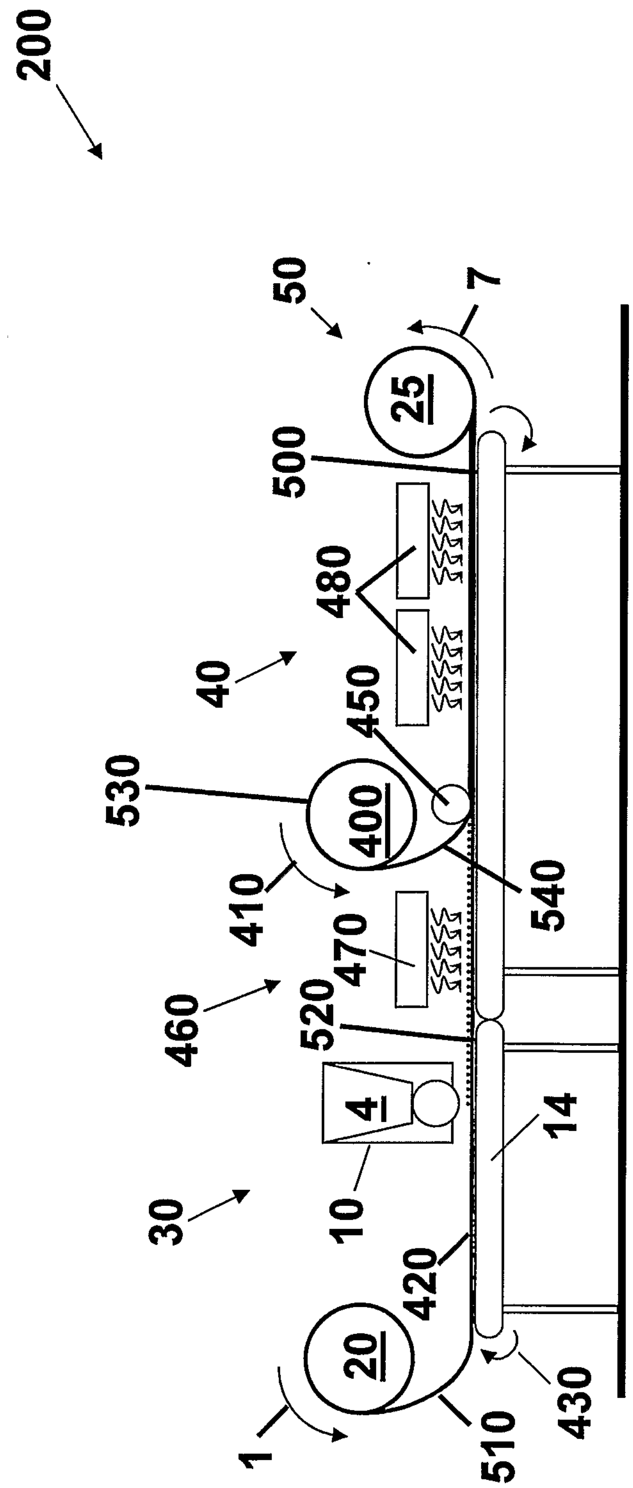
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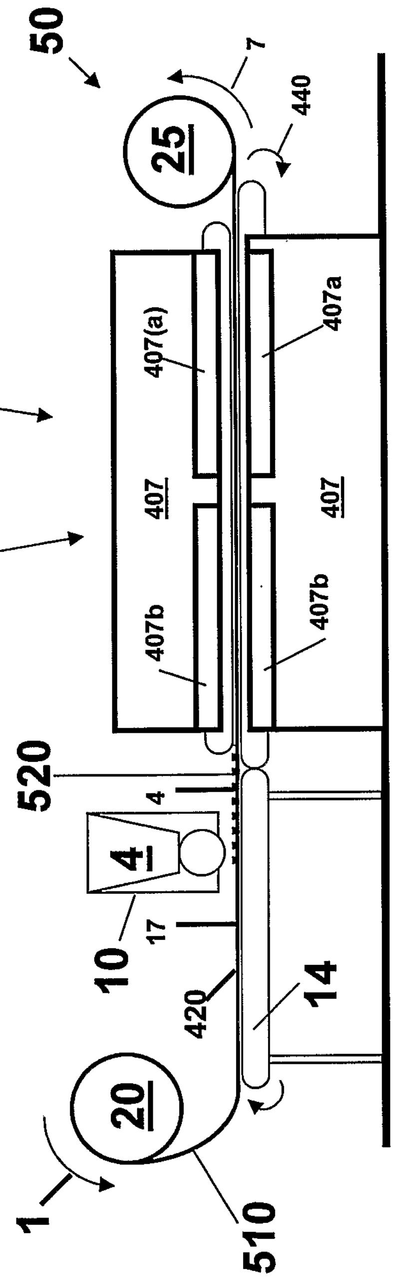
Fig. 12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407(a)
407a
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407
407b
407b
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17
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1
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FIG. 13

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2009/007212

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 2009/122259 A (IQ TEC SWITZERLAND GMBH [CH]; SCHUBIGER MARCEL J [CH]) 8 October 2009 (2009-10-08) claims 1-40; example 1	1-40
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X	US 2008/081170 A1 (TILBROOK DAVID [GB] ET AL) 3 April 2008 (2008-04-03) claims 1-20; example 1	1-40

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
19 January 2010	28/01/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Glomm, Bernhard

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2009/007212

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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