



(51) International Patent Classification:

*D04H 3/02* (2006.01)      *D04H 3/14* (2012.01)  
*D04H 3/07* (2012.01)      *D04H 3/16* (2006.01)

(21) International Application Number:

PCT/US2015/013429

(22) International Filing Date:

29 January 2015 (29.01.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

14/167,366      29 January 2014 (29.01.2014)      US

(71) Applicant: **BIAX-FIBERFILM** [US/US]; N1001 Tower View Drive, Greenville, Wisconsin 54942 (US).

(72) Inventors: **HASSAN, Mohammad**; 1584 Pond View Drive, Neenah, WI 54956 (US). **BROWN, Douglas**; N1160 Shaky Lake Road, Fremont, Wisconsin 54940 (US). **STARK, Jeffrey**; 1290 Glenview Drive, Neenah, Wisconsin 54956 (US).

(74) Agents: **CONNELLY, Thomas** et al.; Wilhelm Law Service, 100 W. Lawrence St., Third Floor, Appleton, WI 54911 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

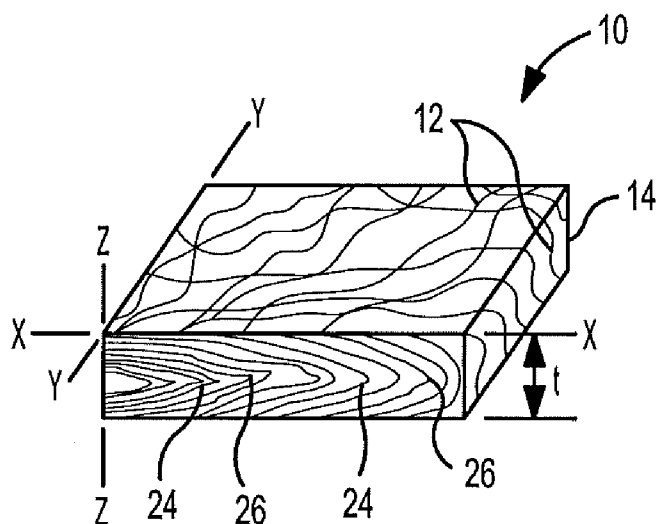
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: A HIGH LOFT, NONWOVEN WEB EXHIBITING EXCELLENT RECOVERY

(57) Abstract: A high loft, nonwoven web exhibiting excellent recovery.



**FIG. 1**

PCT PATENT APPLICATION

5      TITLE: A HIGH LOFT, NONWOVEN WEB EXHIBITING EXCELLENT RECOVERY

FIELD OF THE INVENTION

10

        This invention relates to a high loft, nonwoven web exhibiting excellent recovery.

## BACKGROUND OF THE INVENTION

Typically, polymeric fibers, formed by spunbonding, meltblowing or by some other extrusion process are collected downstream from an emitter, such as a die with a plurality of nozzles, on a horizontal oriented conveyor belt. Such processes tends to produce two-dimensional web where the fibers are oriented in the x and y directions since they are laid down in a horizontal plane. There are few if any fibers within the formed web that are oriented in the z-direction. Because of this, the finished web tends to lack recovery once it is compressed. This presents an issue when such finished webs need to be rolled up or stacked for transport by truck, or rail to a distant manufacturing, or distribution facility. If the webs are compacted or compressed during shipment, they lack the ability to recovery to their original thickness. In addition, once compacted or compressed, such webs tend to become hard and/or stiff and their pore structure may become less open. Furthermore, the drapeability of such webs can be diminished. Functionally, if a compacted or compressed web cannot recover to approximately its initial loft thickness after shipment, it can lose some of its thermal and/or acoustical insulation properties, thereby rendering the material less than desirable for this purpose.

Now, a high loft, nonwoven web, exhibiting excellent recovery, has been invented.

## SUMMARY OF THE INVENTION

Briefly, this invention relates to a high loft, nonwoven web exhibiting excellent recovery.

5       The high loft, nonwoven web is a three dimensional structure with fibers oriented in the x, y and z directions. The web can be constructed as a single layer or be formed with two or more layers. The web has a thickness of less than about 250 millimeters and a basis weight of from between about 50 g/m<sup>2</sup> to about 3,000 g/m<sup>2</sup>. The web can be bonded using a thermal bonder, a chemical bonder, a hydro-  
10       mechanical bonder, a mechanical bonder, or be left unbonded. A vertical cross-section of the web, when taken parallel to its machine direction, exhibits a plurality of snugly stacked, approximately V, U, or C-shaped structures, with each approximately V, U, or C-shaped structure having an apex facing in the machine direction. The web has a recovery value of from between about 20% to about 99% after being  
15       compressed under a pressure of 0.25 psi for a time period of 30 minutes according to the guidelines of the IST 120.2 (01).

      An apparatus for producing a high loft, nonwoven web having a three dimensional structure with fibers oriented in the x, y and z directions is also taught. The apparatus includes a die having a plurality of nozzles each emitting a filament,  
20       and each of the plurality of nozzles having a distal end. A pair of moving surfaces is located from between about 10 cm to about 150 cm of the distal end of each of the plurality of nozzles. The pair of moving surfaces forms a convergent passage having an entry and an exit. The apparatus also includes a mechanism for depositing the plurality of filaments onto and between the pair of moving surfaces. The plurality of  
25       filaments is routed through the convergent passage in descending travel from the entry to the exit to form a 3-dimensional structure. The apparatus further includes a bonder located downstream of it and in vertically alignment with the pair of moving surfaces for bonding the 3-dimensional structure to create a high loft, nonwoven web with the filaments transformed into fibers oriented in the x, y and z directions. The  
30       web has a thickness of less than about 250 mm and a basis weight ranging from between about 50 g/m<sup>2</sup> to about 3,000 g/m<sup>2</sup>. A vertical cross-section of the high loft, nonwoven web, when taken parallel to its machine direction, exhibits a plurality of snugly stacked, approximately V, U, or C-shaped structures, with each approximately V, U, or C-shaped structure having an apex facing in the machine direction. In other  
35       words, the approximately V or U shaped structure is rotated 90 degrees to a horizontal orientation with the apex of each facing to the right. The C-shaped structure is reversed in position so that the apex of each faces to the right. The high

loft, nonwoven web has a recovery value ranging from between about 20% to about 99% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes.

5 A process for forming a high loft, nonwoven web includes the steps of introducing a molten polymer to a die having a plurality of nozzles. Emitting, ejecting or extruding the molten polymer through the plurality of nozzles to form a plurality of filaments. Air or gas streams are then used to facilitate movement and drawing/accelerating of the plurality of filaments. The filaments are directed towards a pair of moving surfaces located at a distance of from between about 10 cm to about 10 150 cm from the plurality of nozzles. The pair of moving surfaces forms a convergent passage having an entry and an exit. The plurality of filaments is deposited into the entry of the convergent passage. The plurality of filaments is then routed through the convergent passage in descending travel from the entry to the exit and between the pair of moving surfaces in a machine direction to form a 3-dimensional structure with 15 the filaments transformed into fibers which are oriented in the x, y and z directions. Lastly, the 3-dimensional structure is bonded to form a high loft, nonwoven web having a thickness of less than about 250 millimeters and a basis weight ranging from between about 50 g/m<sup>2</sup> to about 3,000 g/m<sup>2</sup>. A vertical cross-section of the high loft, nonwoven web, when taken parallel to its machine direction, exhibits a plurality 20 of snugly stacked, approximately V, U, or C-shaped structures, with each approximately V, U, or C-shaped structure having an apex facing in the machine direction. The high loft, nonwoven web has a recovery value ranging from between about 20% to about 99% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes.

25 The general object of this invention is to provide high loft, nonwoven web exhibiting excellent recovery such that it can be compactly shipped without losing any material properties. A more specific object of this invention is to provide high loft, nonwoven web with good thermal insulation and/or acoustical insulation values.

30 Another object of this invention is to provide high loft, nonwoven web which can be used in the bedding, upholstery, filtration, foam replacement materials, and products utilizing cushioning materials.

A further object of this invention is to provide a high loft, nonwoven web exhibiting from between about 20% to about 99% recovery after compression, and such web exhibits a high porosity.

35 Still another object of this invention is to provide a high loft, nonwoven web exhibiting from between about 30% to about 95% recovery after compression.

Still further, an object of this invention is to provide a high loft, nonwoven web exhibiting from between about 40% to about 90% recovery after compression.

Other objects and advantages of the present invention will become more apparent to those skilled in the art in view of the following description and the  
5 accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view of a high loft, nonwoven web of this invention showing a plurality of snugly stacked, approximate V, U or C-shaped structures, with each uniquely shaped structure having an apex facing in the machine direction of the web.

Fig. 2 is a schematic of a vertical cross-section of a section of a high loft, nonwoven web showing a plurality of snugly stacked, approximate V, U or C-shaped structures, with each uniquely shaped structure having an apex facing in the machine direction of the web.

Fig. 3 is a cross-sectional view of a two layer web.

Fig. 4 is a cross-sectional view of a multi-layer web.

Fig. 5 is a perspective view of an alternative embodiment of a high loft, nonwoven web depicting textured upper and lower surfaces

Fig. 6 is a schematic of the textured upper surface of the high loft, nonwoven web shown in Fig. 4.

Fig. 7 is a schematic of an apparatus utilizing a pair of rotatable drums located immediately downstream of a die.

Fig. 8 is a schematic of an alternative apparatus utilizing a pair of angled conveyors located immediately downstream of a die.

Fig. 9 is a schematic of still another apparatus using a combination of a spunbond die positioned between first and second meltblown dies.

## DETAILED DESCRIPTION OF THE INVENTION

Referring to Figs. 1 and 2, a high loft, nonwoven web 10 is shown. The high loft, nonwoven web 10 is a 3-dimensional structure with a plurality of fibers 12 oriented in the x, y and z directions. In Fig. 1, X--X represents the longitudinal central axis, Y--Y represents the vertical central axis, and Z--Z represents the transverse central axis. By "web" it is meant a fabric or material manufactured in sheet form. By "high loft" it is meant a low density, fibrous web characterized by a high ratio of thickness to weight per unit area. The fibers in the web 10 may be continuous or discontinuous, bonded or unbounded. Desirably, the fibers 12 are continuous and some of the fibers 12 are bonded. A high loft web has from between about 5% to about 60% solids by volume. By "nonwoven" it is meant a web, sheet or batt of natural and/or man-made fibers or filaments (excluding paper) that have not been converted into yarns, and that are bonded to each other by thermal, chemical, mechanical, hydro-mechanical, or by some other means known to those skilled in the art.

The high loft, nonwoven web 10 can be formed from a variety of materials. The high loft, nonwoven web 10 can be formed from man-made fibers. The fibers can be staple fibers. Typically, the high loft, nonwoven web 10 is formed from a polymer. The polymer can be selected from the group consisting of: polyolefins, polyesters, polyethylene terephthalates, polybutylene terephthalates, polycyclohexylene dimethylene terephthalates, polytrimethylene terephthalates, polymethyl methacrylates, polyamides, nylons, polyacrylics, polystyrenes, polyvinyls, polytetrafluoroethylenes, ultrahigh molecular weight polyethylenes, very high molecular weight polyethylenes, high molecular weight polyethylenes, polyether ether ketones, non-fibrous plasticized celluloses, polyethylenes, polypropylenes, polybutylenes, polymethylpentenes, low-density polyethylenes, linear low-density polyethylenes, high-density polyethylenes, polystyrenes, acrylonitrile-butadiene-styrenes, styrene-acrylonitriles, styrene-butadienes, styrene-maleic anhydrides, ethylene vinyl acetates, ethylene vinyl alcohols, polyvinyl chlorides, cellulose acetates, cellulose acetate butyrates, plasticized celluloses, cellulose propionates, ethyl celluloses, natural fibers, any derivative thereof, any polymer blend thereof, any copolymer thereof or any combination thereof. Those skilled in the chemical arts may know of other polymers that can also be used to form the high loft, nonwoven web of this invention. It should be understood that the high loft, nonwoven web 10 of this invention is not limited to just those polymers identified above.



The high loft, nonwoven web 10 can be formed or manufactured using many different kinds and types of equipment and processes. Some commonly known technology which can be used to form the high loft, nonwoven web 10 include, but are not limited to: spinning processes such as meltblowing, spunbond, spunmelt, solution blowing, electrospinning. In addition, the high loft, nonwoven web 10 can be manufactured by a dry-laid process such as an air-lay process, a carding process or any combination of any two or more such processes where fibers are laid down at a nip between two moving surfaces. The manufactured high loft, nonwoven web 10 can be bonded or be unbounded. A bonding step adds strength and integrity to the finished web 10.

By "spunbond" it is meant a process for producing strong fibrous nonwovens webs directly from thermoplastic polymers by attenuating the spun filaments using low temperature, high speed air while quenching the fibers near the spinnerette face. Individual fibers are then laid down randomly on a collection belt and are then conveyed to a bonder. The bonder gives the web strength and integrity. Fiber size is usually below 250  $\mu\text{m}$ , the average fiber size is in the range of from between about 10 microns to about 50 microns and the fibers are very strong compared to meltblown fibers because of the molecular chain alignment that is achieved during the attenuating of the crystallized (solidified) filaments. A typical spunbond die has multiple rows of polymer nozzle holes. A typical melt flow rate is below about 500 grams/10 minutes.

By "spunmelt" it is meant a process where fibers are spun from molten polymers through a plurality of nozzles located in a die head connected to one or more extruders. A spunmelt process may include meltblowing and/or spunbonding.

By "meltblowing" it is meant a process where a plurality of molten polymer streams are attenuated using an elevated temperature, high speed gas stream. The gas can be air or other gases known to those skilled in the art. The attenuated fibers are then collected on a moving belt, conveyor or a dual drum collector. Typically, a meltblowing die has around 35 nozzles per inch, a row of spinnerettes and two inclined air or gas jets for attenuating the fiber streams. U.S. Patent 4,380,570 and WO 2005/106,085 A1 teach meltblowing processes where multiple rows of polymer nozzles are surrounded by air nozzles and the streams flowing therefrom are aligned parallel to one another.

Still referring to Figs. 1 and 2, the high loft, nonwoven web 10 can be constructed as a single layer 14 of material. The high loft, nonwoven web 10 can be formed using equipment where air or gas is used to facilitate movement and drawing

of the molten polymer through a plurality of nozzles into a plurality of filaments. Each of the plurality of filaments is emitted through a single nozzle.

Referring to Figs. 3 and 4, it should be understood that the high loft, nonwoven web 10' can also be formed of two separate and distinct layers, 14 and 16, see Fig. 3, or the web 10" can have multiple layers, see Fig. 4. By "multiple layers" it is meant 3, 4, 5, 6, 7 or more separate and distinct layers. Some of the layers can be similar and/or identical in composition and characteristics to another layer, while one or more layers can vary in composition and/or characteristics from one or more of the remaining layers. In Fig. 4, three separate and distinct layers 18, 20 and 22 are present. It should be understood that the web 10, consisting of a single layer 14, the web 10', consisting of two layers 14 and 16, or the web 10", consisting of three layers 18, 20 and 22, can be bonded to provide strength and integrity.

In Fig. 3, the web 10' is a two layer embodiment having an upper layer 14 and a lower layer 16. In Fig. 4, the web 10" is a three layer embodiment having an upper layer 18, a middle layer 20 and a lower layer 22. When two or more layers are present in the finished nonwoven web, it should be understood that each layer can vary in the type of polymer it is made from. In addition, the characteristics of a given layer can vary. For example, the characteristics of one layer can be different from another layer. The thickness of each layer in the web 10" can vary or be the same. The density of each layer in the web 10" can also vary or be the same. The basis weight of each layer in the web 10" can also vary or be the same.

Referring again to Figs. 1 and 2, the high loft, nonwoven web 10 is depicted as a single layer structure. The high loft, nonwoven web 10 has a thickness  $t$  which can vary in dimensions. Generally, the thickness  $t$  of the high loft, nonwoven web 10 can range from between about 5 millimeters (mm) to about 300 mm. Desirably, the thickness  $t$  of the high loft, nonwoven web is less than about 250 millimeters. More desirably, the thickness  $t$  of the high loft, nonwoven web 10 is less than about 200 mm. Even more desirably, the thickness  $t$  of the high loft, nonwoven web 10 is less than about 100 mm. Most desirably, the thickness  $t$  of the high loft, nonwoven web 10 is less than about 50 mm. When two or more layers are present in the finished web 10' or 10", the overall thickness of the web 10' or 10" can double, triple, etc. depending upon how many layers are present.

The high loft, nonwoven web 10 can be formed with different basis weights. Generally, the basis weight of the high loft, nonwoven web 10 ranges from between about 50 grams per square meter ( $\text{g/m}^2$ ) to about 3,000  $\text{g/m}^2$ . Desirably, the basis weight of the high loft, nonwoven web 10 ranges from between about 750 grams per square meter ( $\text{g/m}^2$ ) to about 2,500  $\text{g/m}^2$ . More desirably, the basis weight of the

high loft, nonwoven web 10 ranges from between about 100 grams per square meter ( $\text{g/m}^2$ ) to about 1,000  $\text{g/m}^2$ . Even more desirably, the basis weight of the high loft, nonwoven web 10 is less than about 600  $\text{g/m}^2$ .

The high loft, nonwoven web 10 can also vary in density. Generally, the high loft, nonwoven web 10 has a density ranging from between about 10 kilograms per cubic meters ( $\text{Kg/m}^3$ ) to about 250  $\text{Kg/m}^3$ . Desirably, the high loft, nonwoven web 10 has a density ranging from between about 20  $\text{Kg/m}^3$  to about 200  $\text{Kg/m}^3$ . More desirably, the high loft, nonwoven web 10 has a density ranging from between about 30  $\text{Kg/m}^3$  to about 150  $\text{Kg/m}^3$ . Even more desirably, the high loft, nonwoven web 10 has a density ranging from between about 40  $\text{Kg/m}^3$  to about 100  $\text{Kg/m}^3$ .

The high loft, nonwoven web 10 can be bonded or unbounded. Desirably, the high loft, nonwoven web 10 is bonded. Bonding generally imparts strength and integrity to the web 10. Bonding can be performed using different type of equipment and processes known to those skilled in the art. Various bonders include: mechanical bonders such as needle bonding, hydro-mechanical bonders, also known as wet bonding, thermal bonders, which include through air bonding and oven thermal bonding and chemical bonding. Whichever type of bonder is utilized, some of the fibers 12, 14, 16, 18, 20 and 22 are bonded together to make the high loft, nonwoven web 10, 10' and 10" stronger.

Furthermore, the high loft, nonwoven web 10 can be formed from polypropylene having a melt flow rate ranging from between about 4 g/10 min. to about 6,000 g/10min at a temperature of 230 °C and at a pressure of 2.16 kg according to the teachings of ASTM D 1238 testing method. Desirably, the high loft, nonwoven web 10 can be formed from polypropylene having a melt flow rate ranging from between about 35 g/10 min. to about 2,500 g/10min at a temperature of 230 °C and at a pressure of 2.16 kg. More desirably, the high loft, nonwoven web 10 can be formed from polypropylene having a melt flow rate ranging from between about 500 g/10 min. to about 2,000 g/10min at a temperature of 230 °C and at a pressure of 2.16 kg. Most desirably, the high loft, nonwoven web 10 can be formed from polypropylene having a melt flow rate ranging from between about 500 g/10 min. to about 1,500 g/10min at a temperature of 230 °C and at a pressure of 2.16 kg.

Referring again to Fig. 2, the schematic clearly shows a vertical cross-section of the high loft, nonwoven web 10 taken parallel to the machine direction (MD). During formation of the high loft, nonwoven web 10, the material advances from left to right. The leading edge of the high loft, nonwoven web 10 is to the right. The high loft, nonwoven web 10 exhibits a plurality of snugly stacked, approximately V, U or C-shaped structures 24. These V, U or C-shaped structures 24 are also depicted in

Fig. 1. Each of the approximately V, U or C-shaped structures 24 has an apex 26 which faces in the machine direction (MD). In other words, the approximately V or U shaped structure is rotated 90 degrees to a horizontal orientation with the apex of each facing to the right. The C-shaped structure is reversed in position so that the apex of each faces to the right. This unique structure occurs because of the way the fibers 12 are laid down during formation. This unique structure is important for it gives the high loft, nonwoven web 10 a very high recovery value. The high loft, nonwoven web 10 has a recovery value ranging from between about 20% to about 99% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes, according to the guidelines of the INDA Standard Test Method (IST 120.2 (01)). Desirably, the high loft, nonwoven web 10 has a recovery value ranging from between about 30% to about 95% according to the guidelines of the IST 120.2 (01). More desirably, the high loft, nonwoven web 10 has a recovery value ranging from between about 40% to about 90% according to the guidelines of the IST 120.2 (01). Even more desirably, the high loft, nonwoven web 10 has a recovery value ranging from between about 50% to about 80% according to the guidelines of the IST 120.2 (01).

It should be understood that each layer of the two layer web 10', shown in Fig. 3, and each layer of the three layered web 10'', shown in Fig. 4, also exhibits this plurality of snugly stacked, approximately V, U or C-shaped structures 24 if they are laminated offline, but they will show one snugly stacked structured, approximately V, U or C shaped structured, if they are comingled simultaneously from different spinning heads as shown in Fig. 9. This kind of comingled high loft structure could have different fiber size, different polymeric materials, and/or different fiber cross-section.

Referring again to Fig. 3, the two layered web 10' has a three dimensional structure with fibers oriented in the x, y and z directions. This two layer web 10' has a thickness  $t_1$  of from between about 5 millimeters to about 500 millimeters and a basis weight of from between about 50 g/m<sup>2</sup> to about 2,000 g/m<sup>2</sup>. The two layered web 10' does not have to be bonded but desirably is thermally or chemically bonded. Alternatively, the web 10' could be mechanically or hydro-mechanically bonded. Each of the two layers, 14 and 16, of the web 10' exhibits a vertical cross-section, when taken parallel to the machine direction (MD) during manufacture of the two layered web 10', which exhibits a plurality of snugly stacked, approximately V, U or C-shaped structures 24. Each of the approximately V, U or C-shaped structures 24 has an apex 26 facing in the machine direction (MD). In other words, the approximately V or U shaped structure is rotated 90 degrees to a horizontal

orientation with the apex of each facing to the right. The C-shaped structure is reversed in position so that the apex of each faces to the right. The two layered web 10' has a recovery value of from between about 20% to about 99% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes according to the guidelines of the IST 120.2 (01). Desirably, the two layered web 10' has a recovery value ranging from between about 30% to about 95% according to the guidelines of the IST 120.2 (01). More desirably, the two layered web 10' has a recovery value ranging from between about 40% to about 90% according to the guidelines of the IST 120.2 (01). Even more desirably, the two layered web 10' has a recovery value ranging from between about 50% to about 80% according to the guidelines of the IST 120.2 (01).

It should be understood that the two layer web 10' can be formed as two separate layers 14 and 16 from comingled fibrous materials where each layer has a different fiber size, is formed from a different material, has different fiber cross-sections, etc. Furthermore, the two layered web 10' could be laminated to one or more layers. The additional layers could be a thermoplastic film, a film, another nonwoven material, paper, cardboard, etc.

Referring again to Fig. 4, the three layered web 10" has a three dimensional structure with fibers oriented in the x, y and z directions. This three layer web 10" has a thickness  $t_2$  of from between about 5 millimeters to about 750 millimeters and a basis weight of from between about 50 g/m<sup>2</sup> to about 2,000 g/m<sup>2</sup>. The three layered web 10" does not have to be bonded but desirably is thermally or chemically bonded. Alternatively, the web 10" could be mechanically or hydro-mechanically bonded. Each of the three layers, 18, 20 and 22, of the web 10" exhibits a vertical cross-section, when taken parallel to the machine direction (MD) during manufacture of the web 10", which exhibits a plurality of snugly stacked, approximately V, U or C-shaped structures 24. Each of the approximately V, U or C-shaped structures 24 has an apex 26 facing in the machine direction (MD). In other words, the approximately V or U shaped structure is rotated 90 degrees to a horizontal orientation with the apex of each facing to the right. The C-shaped structure is reversed in position so that the apex of each faces to the right. The three layered web 10" has a recovery value of from between about 20% to about 99% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes according to IST 120.2 (01). Desirably, the three layered web 10 has a recovery value ranging from between about 30% to about 95% according to IST 120.2 (01). More desirably, the three layered web 10 has a recovery value ranging from between about 40% to about 90% according to IST

120.2 (01). Even more desirably, the three layered web 10 has a recovery value ranging from between about 50% to about 80% according to IST 120.2 (01).

It should also be recognized that an additive can be incorporated into the high loft, nonwoven web 10, 10' or 10". The additive (not shown) can be applied to the high loft, nonwoven web 10, 10' or 10" during manufacture. The additive can be applied in various ways, including but not limited to: being sprayed on, being sprinkled on, being extruded, being combined with, being painted on, being immersed, etc. The additive can be a gas, a liquid, a solid or a semi-solid. The additive can be selected from the group consisting of: a superabsorbent, absorbent particles, pulp fibers, polymers, nanoparticles, abrasive particulars, active particles, active compounds, ion exchange resins, zeolites, softening agents, plasticizers, ceramic particles pigments, dyes, flavorants, aromas, controlled release vesicles, binders, adhesives, tackifiers, surface modification agents, lubricating agents, emulsifiers, vitamins, peroxides, antimicrobials, deodorizers, fire retardants, flame retardants, antifoaming agents, anti-static agents, biocides, antifungals, degradation agents, stabilizing agents, conductivity modifying agents, or any combination thereof.

Referring now to Figs. 5 and 6, an alternative embodiment of high loft, nonwoven web 11 is shown having been formed as a single layer 14 with two major surfaces 28 and 30. The two major surfaces 28 and 30 are aligned opposite to one another. In Fig. 5, the two major surfaces include the upper surface 28 and the lower surface 30. By "two major surfaces" it is meant the two surfaces of the web 11 which have the greatest surface area. The web 11 has two major surfaces, 28 and 30, and both of these major surfaces 28 and 30 are textured. By "textured" it is meant a rough or grainy surface quality, as opposed to being smooth. The texture can be formed various ways during processing of the web 11. In Fig. 5, a plurality of protuberances 32 extends upward from the upper surface 28 and downward from the lower surface 30. By "protuberance" it is meant a bulge, knob or swelling that protrudes outward. Alternatively, indentations, cavities or depressions could be formed in the upper and/or lower surfaces, 28 and 30 respectively, to obtain a similar textured effect. Desirably, at least one of the two major surfaces, 28 and 30 of the web 11 is textured. More desirably, both of the two major surfaces, 28 and 30 of a web 11 are textured.

#### Apparatus

Referring to Fig. 7, an apparatus 34 is shown for producing a high loft, nonwoven web 10, 10', 10" or 11. The apparatus 34 is shown being oriented in a horizontal configuration, although it could be arranged vertically or at some other

angle relative to the vertical axis. The high loft, nonwoven web 10, 10', 10" or 11 has a three dimensional structure with fibers oriented in the x, y and z directions. The apparatus 34 includes a die 36 having a plurality of nozzles 38 each emitting, ejecting or extruding a filament 40. Each of the plurality of nozzles 38 has a distal end 42. The apparatus 34 can use air or gas to facilitate movement and drawing of the molten polymer from the plurality of nozzles 38 into a plurality of filaments. A pair of moving surfaces, 44 and 46, is located from between about 10 centimeters (cm) to about 150 cm of the distal end 42 of each of the plurality of nozzles 38. The pair of moving surfaces, 44 and 46, can be a first rotatable drum 48 and a second rotatable drum 50, as is shown in Fig. 7. Alternatively, the pair of moving surfaces, 44 and 46, can be a first conveyor belt 52 and a second conveyor belt 54, as is shown in Fig. 8. Other forms of moving surfaces, 44 and 46, known to those skilled in the art can also be employed.

When the pair of moving surfaces, 44 and 46, consists of a first rotatable drum 48 and a second rotatable drum 50, the first rotatable drum 48 will have a diameter  $d_1$  and the second rotatable drum 50 will have a diameter  $d_2$ . Desirably, the diameter  $d_1$  is approximately equal to the diameter  $d_2$ . More desirably, the diameters  $d_1$  and  $d_2$  are identical. The first and second rotatable drums, 48 and 50 respectively, will be aligned parallel to one another on the same plane  $X_1$ -- $X_1$ . It should be understood that the apparatus 34 is horizontally oriented so that the filaments 40 will move from left to right in a machine direction (MD) between the first and second rotatable drums, 48 and 50 respectively.

Still referring to Fig. 7, one can see that the first drum 48 rotates counterclockwise while the second drum 50 rotates clockwise. This specific rotation will cause the plurality of continuous filaments 40 to move in the machine direction (MD) away from the plurality of nozzles 38. The speed of the first and second rotatable drums, 48 and 50 respectively, can vary. Desirably, each of the first and second rotatable drums, 48 and 50 respectively, will rotate at the same speed. Alternatively, one of the first and second rotatable drums, 48 and 50 respectively, could rotate at a different speed than the other drum and therefore a different cross-sectional structure may be produced in the machine direction such as S or S-like shape. The speed of the first and second rotatable drums, 48 and 50 respectively, should be adjusted according to the basis weight of the material that is being produced, the thickness of the desired web 10, the kind of polymer being extruded, the polymer throughput through the plurality of nozzles 38, etc.

The first and second rotatable drums, 48 and 50 respectively, can be operated at room temperature. Alternatively, the first and second rotatable drums, 48

and 50 respectively, could be operated at an elevated temperature or at a temperature below room temperature. Desirably, the first and second rotatable drums, 48 and 50 respectively, are operated at room temperature.

The first and second rotatable drums, 48 and 50 respectively, can be hollow cylinders with their outer peripheries covered with a forming wire or screen. The forming wire or screen can be produced from a variety of different materials known to those skilled in the art. For example, the forming wire or screen could be made from a synthetic material, such as polyethylene terephthalate (PET). Alternatively, the forming wire or screen could be made from: metal, steel, aluminum, a plastic, a thermoplastics, etc. The first and second rotatable drums, 48 and 50 respectively, could also be constructed out of various materials, such as wood, steel, cast iron, aluminum, etc. Another option is to cover the outer peripheries of the first and second rotatable drums, 48 and 50 respectively, with metal belts. The metal belts could be ferrous or non-ferrous. The metal belts could contain a plurality of apertures, openings or holes arranged in a predetermined pattern or could be randomly arranged. The size and shape of the apertures, openings or holes can vary. As is known to those skilled in the art, each of the first and second rotatable drums, 48 and 50 respectively, can be equipped with adjustable vacuum chamber, if desired. Sometimes, it is advantageous to slightly heat the outer peripheries of the first and second rotatable drums, 48 and 50 respectively; so that the incoming filaments 40 will more readily form onto them. The reason for this is that the open mesh design of a wire, screen or a metal belt containing apertures, openings or holes can form a specific texture or pattern onto the outer surfaces of the high loft, nonwoven web 10, 10', 10" or 11 that is being produced. Such texture or pattern may enhance the sound insulation and/or thermal absorption properties of the finished web 10, 10', 10" or 11. This is an important attribute when the finished high loft, nonwoven web 10, 10', 10" or 11 is to be used for sound and/or thermal insulation purposes.

Still referring to Fig. 7, one will notice that each of the first and second rotatable drums, 48 and 50 respectively, has a central axis 56 and 58, respectively. Desirably, each of the central axes 56 and 58 are aligned on a common vertical plane, designated  $X_1-X_1$ . A horizontal distance measured from the distal end 42 of each nozzle 38 perpendicular to the vertical plane  $X_1-X_1$  established a Die-to-Collector Distance (DCD). This DCD distance can range from between about 10 cm to about 150 cm. Desirably, the DCD distance is less than about 100 cm. More desirably, the DCD distance is less than about 90 cm. Even more desirably, the DCD distance is less than about 80 cm. Most desirably, the DCD distance is less



than about 60 cm. The exact DCD distance is dependent upon a number of factors including but not limited to: the melt temperature of the polymer being extruded, the polymer throughput through the plurality of nozzles 38, etc. However, it has been found through experimentation, that the closer the moving surfaces 44 and 46 are  
5 located from the distal end 42 of each of the plurality of nozzles 38, the better the recovery value of the manufactured high loft, nonwoven web 10, 10', 10" or 11 is after compression. When the DCD distance ranges from between about 45 cm to about 75 cm, a high loft, nonwoven web 10, 10', 10" or 11 can be manufactured with a good recovery value after compression.

10 The outer peripheries of the first and second rotatable drums, 48 and 50 respectively, are spaced apart from one another thereby creating a convergence passage 60. By "convergent passage" it is meant a point of converging, to approach a point. This converging passage 60 narrows down to a dimension equal to a nip 62 established between the first and second rotatable drums, 48 and 50 respectively.  
15 The nip 62 can vary in dimension. The first and second rotating drums, 48 and 50 respectively, should be mounted such that the dimension of the nip 62 established therebetween can be easily adjusted. Generally, the nip 62 can range from between about 0.5 cm to about 25 cm. Desirably, the nip 62 is greater than about 0.5 cm. More desirably, the nip 62 ranges from between about 0.5 cm to about 10 cm. Even  
20 more desirably, the nip 62 ranges from between about 0.5 cm to about 8 cm. Most desirably, the nip 62 is less than about 5 cm.

The convergent passage 60 has an entry 64 and an exit 66 established by the circumference of the first and second rotatable drums, 48 and 50 respectively. As the plurality of filaments 40 are deposited at the entry 64 of the convergent passage  
25 60 they are directed and routed onto and between the pair of moving surfaces 44 and 46. The routing is facilitated by the rotation of the first and second rotatable drums, 48 and 50 respectively. The routing causes the plurality of filaments 40 to pass through the convergent passage 60 in descending travel from the entry 64 to the exit 66. The rotational movement of the first and second rotatable drums, 48 and 50  
30 respectively, will cause some of the plurality of filaments 40 to temporarily contact the outer peripheries of the first and second rotatable drums, 48 and 50 respectively. These filaments 40 will be compressed against the remaining filaments 40 passing through the nip 62 to create a 3-dimensional structure 68. The plurality of filaments 40 will be compressed at the nip 62 and this confined space helps the filaments 40,  
35 which are transformed into fibers 12 as they cool, to be aligned in the x, y and z directions. By "transformed" it is meant to change markedly the appearance or form of; to change the nature, function, or condition of; convert. Thus a 3-dimensional

structure 68 is produced instead of a 2-dimensional structure. The 3-dimensional structure 68 usually will not have a very good recovery value unless fiber-to-fiber bonds are created using some known bonding process to stabilize the formed 3-dimensional structure 68.

5 Still referring to Fig. 7, the 3-dimensional structure 68 is advanced in the machine direction (MD) in a horizontal direction. However, if the apparatus 34 is not horizontally oriented or if additional support is needed, a conveyor belt 70 can be utilized. The conveyor belt 70 can be constructed with a screen having a porous or open pattern to allow heat to pass therethrough freely. The conveyor belt 70 can  
10 move in a given direction over a plurality of rollers 72. Four rollers 72 are depicted in Fig. 7, although any number of rollers 72 can be utilized. One of the rollers 72 is the drive roller and the remaining rollers 72, 72 and 72 are idler or follower rollers. The conveyor belt 70 makes a continuous loop and is illustrated moving in a clockwise direction so as to advance the 3-dimensional structure 68 in the downward machine  
15 direction (MD).

It should be understood that some high loft, nonwoven webs 10 can be formed from certain materials and for certain uses, wherein bonding is not necessary. However, for most high loft, nonwoven webs 10, it is advantageous to subject the 3-dimensional structure 68 to a bonding process. Bonding generally imparts strength  
20 and integrity into the finished web 10. Various bonding techniques can be utilized. A single bonder or a pair of oppositely aligned bonders can be utilized.

Still referring to Fig. 7, a bonder 74 is shown located downstream of and in vertically alignment with the pair of moving surfaces 44 and 46 for bonding the 3-dimensional structure 68. The bonder 74 is located such that the 3-dimensional  
25 structure 68 passes therethrough. The bonder 74 can be a thermal bonder, such as: a through air bonder or an oven bonder. A thermal bonder can function by creating heat. For example, the heat can be created by a heated fluid, such as gases or liquid, burning a solid, such as coal, heating inert gases, using steam, using secondary radiation from nanoparticles, using infra-red heat, etc. The bonder 74  
30 itself can include a furnace, an oven, thermoelectric elements, etc., or any combination thereof. In addition, the bonder 74 can be a chemical bonder, a mechanical bonder, a hydro-mechanical bonder, needle bonder, a wet bonder, etc.

The heat from a thermal bonder will lock some of the fibers 12 to one another in the x, y and z directions. All the fibers 12 do not have to be bonded together, just  
35 enough to create the high loft, nonwoven web 10. The fibers 12 are created as the plurality of filaments 40 solidify in the 3-dimensional structure 68. By bonding some of the plurality of fibers 12 together, a high loft, nonwoven web 10 is create having a

thickness of less than about 250 mm, desirably, less than about 200 mm, and more desirably, less than about 100 mm. The high loft, nonwoven web 10 also has a basis weight ranging from between about 50 g/m<sup>2</sup> to about 3,000 g/m<sup>2</sup>, desirably, from between about 100 g/m<sup>2</sup> to about 2,000 g/m<sup>2</sup>, and more desirably, from between about 100 g/m<sup>2</sup> to about 600 g/m<sup>2</sup>. Furthermore, a vertical cross-section of the web 10, when taken parallel to its machine direction, exhibits a plurality of snugly stacked, approximately V, U, or C-shaped structures 24. Each of the approximately V, U or C-shaped structures 24 has an apex 26 facing in the machine direction. In other words, the approximately V or U shaped structure is rotated 90 degrees to a horizontal orientation with the apex of each facing to the right. The C-shaped structure is reversed in position so that the apex of each faces to the right. This high loft, nonwoven web 10 has a recovery value ranging from between about 20% to about 99% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes, according to IST 120.2 (01). The IST 120.2 (01) test requires the material to be compressed under a pressure of 0.25 psi for a time period of 30 minutes. Desirably, the high loft, nonwoven web 10 has a recovery value ranging from between about 30% to about 95% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes, according to IST 120.2 (01). More desirably, the high loft, nonwoven web 10 has a recovery value ranging from between about 40% to about 90% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes, according to IST 120.2 (01). Most desirably, the high loft, nonwoven web 10 has a recovery value ranging from between about 50% to about 80% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes, according to IST 120.2 (01).

Still referring to Fig. 7, the apparatus 34 may further include one or more dispensing mechanisms 76 and 78 for adding chemical binders, or dispensing one or more additives 80 to the high loft, nonwoven web 10. Two dispensing mechanisms 76 and 78 are illustrated in Fig. 7. Chemical bonding system can be utilized instead of the thermal bonding systems. Chemical binders may impart some new features to the web such as different surface chemistry, more stiffness or roughness. The exact number of dispensing mechanisms can vary. Typically, one or two dispensing mechanisms 76 or 78 are utilized to add one or more additives to the high loft, nonwoven web 10. The additive 80 can be any of those described above, as well as others known to those skilled in the art.

It should be understood that the high loft, nonwoven web 10 could also be partially or fully immersed in a liquid solution containing an additive 80. The liquid

solution could be chemically or electrically charged so as to cause the additive 80 to better adhere to the high loft, nonwoven web 10.

Still referring to Fig. 7, the apparatus 34 may also include a conditioning unit 82 situated downstream from the last dispensing mechanism 76 or 78. The conditioning unit 82 can vary in design and function. The conditioning unit 82 could be a dryer that can remove moisture from the web 10 by utilizing heat or some other process when the high loft, nonwoven web 10 has to be dried. Alternatively, the conditioning unit 82 could be a cooler that could blow cool air onto the high loft, nonwoven web 10 and reduce its temperature. Still further, the conditioning unit 82 could perform some other function, for example embossing the web 10, printing the web 10, combining the high loft, nonwoven web 10 with another layer, etc. Dryers and coolers are appliances well known to those skilled in the art.

Referring now to Fig. 8, another embodiment of an apparatus 34' is depicted wherein the pair of moving surfaces 44 and 46 is shown as a first conveyor belt 52 and a second conveyor belt 54. The orientation of the apparatus 34' is vertical although other orientations could also be employed. The first conveyor belt 52 moves in a counterclockwise direction while the second conveyor belt 54 moves in a clockwise direction. This arrangement causes the plurality of filaments 40 emitted, ejected or extruded from the plurality of nozzles 38 to move vertically downward in a machine direction (MD). The first and second conveyor belts, 52 and 54 respectively, can run at various speeds. Desirably, the first and second conveyor belts, 52 and 54 respectively, will run at the same speed.

The first and second conveyor belts, 52 and 54 respectively, converge toward one another at a point located farthest away from the distal end 42 of each of said plurality of nozzles 38. An opening 55, equivalent to the nip 62, is present between the first and second conveyor belts 52 and 54 respectively. The opening 55 occurs and is situated at a plane  $X_2$ -- $X_2$ . The plane  $X_2$ -- $X_2$  is equivalent to the plane  $X_1$ -- $X_1$ , shown in Fig. 7. A vertical distance measured from the distal end 42 of each nozzle 38 perpendicular to the plane  $X_2$ -- $X_2$  established a Die-to-Collector Distance (DCD). This DCD distance can range from between about 10 cm to about 150 cm. Desirably, the DCD distance is less than about 100 cm. More desirably, the DCD distance is less than about 90 cm. Even more desirably, the DCD distance is less than about 80 cm. Most desirably, the DCD distance is less than about 60 cm. The exact DCD distance is dependent upon a number of factors including but not limited to: the melting temperature of the polymer being extruded, the basis weight of the material being produced, the polymer throughput through the plurality of nozzles 38, and the inside diameter of each of the nozzles, etc.

As clearly shown in Fig. 8, the first and second conveyor belts, 52 and 54 respectively, are aligned at an angle  $\alpha$  to one another. The angle  $\alpha$  can vary. Desirably, the angle  $\alpha$  is less than about 90 degrees. More desirably, the angle  $\alpha$  is less than about 60 degrees. Even more desirably, the angle  $\alpha$  is less than about 50 degrees. Most desirably, the angle  $\alpha$  is less than about 45 degrees. An angle  $\alpha$  of from between about 15 degrees to about 45 degrees works well. This orientation creates a convergent passage 60 and a nip 62. The plurality of filaments 40 are deposited at the entry 64 of the convergent passage 60 as they are directed and routed onto and between the first and second conveyor belts, 52 and 54 respectively.

The routing is facilitated by the movement of the first and second conveyor belts, 52 and 54 respectively. The routing causes the plurality of filaments 40 to pass through the convergent passage 60 in descending travel from the entry 64 to the exit 66. The movement of the first and second conveyor belts, 52 and 54 respectively, will cause some of the plurality of filaments 40 to temporarily contact the outer peripheries of the first and second conveyor belts, 52 and 54 respectively. These filaments 40 will be compressed against the remaining filaments 40 passing through the nip 62 to create a 3-dimensional structure 68. The plurality of filaments 40 will be compressed at the nip 62 and this confined space helps the filaments 40, which are transformed into fibers 12 as they cool, to be aligned in the x, y and z directions. By "transformed" it is meant to change markedly the appearance or form of; to change the nature, function, or condition of; convert. Thus a 3-dimensional structure 68 is produced instead of a 2-dimensional structure. The 3-dimensional structure 68 usually will not have a very good recovery value unless fiber-to-fiber bonds are created using some known bonding process to stabilize the formed 3-dimensional structure 68.

Still referring to Fig. 8, the apparatus 34' also differs from the apparatus 34, shown in Fig. 7, in that the 3-dimensional structure 68 is advanced in a vertical, downward direction until it contacts a conveyor belt 84. The conveyor belt 84 is positioned perpendicular to the downward direction of the 3-dimensional structure 68. The conveyor belt 84 moves through a continuous loop in a clockwise direction. The conveyor belt 84 causes the 3-dimensional structure 68 to make a 90 degree turn to the right. This new horizontal, rightward movement is referred to as machine direction (MD').

The conveyor belt 84 is mounted on a plurality of rollers 86. Four rollers 86 are depicted in Fig. 8 although any number of rollers 86 can be utilized. One of the rollers 86 is the drive roller and the remaining rollers 86, 86 and 86 are idler or follower rollers.

It should be understood that some high loft, nonwoven webs 10 can be formed from certain materials and for certain uses, wherein bonding is not necessary. However, it is advantageous when producing most nonwoven webs 10 to subject the 3-dimensional structure 68 to a bonding process. Bonding generally imparts strength and integrity into the finished web 10. Various bonding techniques can be utilized. In Fig. 8, a single bonder 74 is utilized. Upon exiting the bonder 74, a high loft, nonwoven web 10 will be formed. The high loft, nonwoven web 10 has a thickness  $t$ .

Referring now to Fig. 9, still another apparatus 34" is shown which utilized a combination of a first meltblown die 88, a spunbond die 90 and a second meltblown die 92. The apparatus 34" is shown being oriented in a vertical configuration, although other configurations are possible. The spunbond die 90 is positioned between the first and second meltblown dies, 88 and 92 respectively. This die arrangement produces a comingled, high loft hybrid nonwoven web that may have different fiber size, different polymeric materials, and/or different fiber cross-section.

It should be understood that various combinations can be obtained using one or more spunbond dies, meltblown dies, spunmelt dies, etc. When one wishes to manufacture a two layer web 10', as shown in Fig. 3, two layers can be laminated inline or off-line. When one wishes to manufacture a three layer web 10', as shown in Fig. 4, three systems similar to Figure 7 can be utilized and the layers can be laminated inline or off-line with another ready-made web. Each die 88, 90 and 92 will emit, eject, extrude, spin, or otherwise route a plurality of filaments 40 in a vertical, horizontal or outward direction. The remaining equipment is similar to that shown and explained with reference to Fig. 7. One exception is that the Die-to-Collector Distance (DCD) is calculated by the distance from the middle spunbond die 90 to the plane  $X_1$ -- $X_1$ . Again, this DCD distance can range from between about 10 cm to about 150 cm. Desirably, the DCD distance is less than about 100 cm. More desirably, the DCD distance is less than about 90 cm. Even more desirably, the DCD distance is less than about 80 cm. Most desirably, the DCD distance is less than about 60 cm. The exact DCD distance is dependent upon a number of factors including but not limited to: the melt temperature of the polymer being extruded, the polymer throughput through the plurality of nozzles 38, etc. However, it has been found through experimentation, that the closer the moving surfaces 44 and 46 are located from the distal end 42 of each of the plurality of nozzles 38, the better the recovery value of the manufactured high loft, nonwoven web 10, 10', 10" or 11 is after compression. When the DCD distance ranges from between about 45 cm to

about 75 cm, a high loft, nonwoven web 10, 10', 10" or 11 can be manufactured with a good recovery value after compression.

A 3-dimensional structure 68 emerges from the exit 66 of the convergent passage 60. As explained above, it may be advantageous to bond the fibers 12 of the 3-dimensional web 10" together to increase the strength and improve the integrity of the web 10". A bonder 74 is positioned downstream of the first and second rotatable drums 48 and 50 respectively. The bonder 74 can be any of the various kinds of bonders explained above. Desirably, the bonder 74 is a thermal or chemical bonder.

It should be understood that in any of the three apparatuses 34, 34' or 34" described above, that one could add one or more features to them. For example, one could introduce natural or synthetic man-made fibers into the high loft, nonwoven web 10, 10', 10" or 11 during the manufacturing process. Likewise, non-thermoplastic materials could also be added to the webs 10, 10', 10" or 11 during manufacture.

Furthermore, one could spin or extrude multi-component fibers, fibers having different cross-sectional diameters, use curly fibers within the webs 10, 10', 10" or 11, or otherwise treat the fibers 12 in a particular way to obtain a unique finished high loft, nonwoven web 10, 10', 10" or 11.

It should also be recognized that the various processes, such as meltblown, spunbond, spunmelt, etc. may require that the filaments be attenuated at different temperatures, pressures, flow rates, etc. For example, the process air could be colder or hotter than the polymer melt.

#### Process

The process of forming the high loft, nonwoven web 10, 10', 10" or 11 will be explained with reference to Figs. 7 – 9. The process includes introducing a molten polymer to a die 36. The die 36 has a plurality of nozzles 38 each having a distal end 42. The molten polymer is emitted through the plurality of nozzles 38 to form a plurality of filaments 40. By "emitting" it is meant extruding, ejecting, spinning, forcing or discharging the molten polymer under pressure, in any of the known processes described above and/or known to those skilled in the art. The process also includes using air or gas streams to facilitate movement and drawing of the plurality of filaments 40. The filaments 40 are directed towards a pair of moving surfaces 44 and 46, located at a distance of from between about 10 cm to about 150 cm from the plurality of nozzles 38. The pair of moving surfaces 44 and 46 can be first and

second rotatable drums, 48 and 50 respectively, or can be first and second conveyor belts, 52 and 54 respectively.

The pair of moving surfaces 44 and 46 forms a convergent passage 60 having an entry 64 and an exit 66. The plurality of filaments 40 are deposited into the entry 64 of the convergent passage 60. The plurality of filaments 40 are then routed through the convergent passage 60 in descending travel from the entry 64 to the exit 66 and between the pair of moving surfaces 44 and 46 in a machine direction to form a 3-dimensional structure 68. In the 3-dimensional structure 68, the filaments 40 are transformed upon cooling into fibers 12 oriented in the x, y and z directions. The process further includes bonding the 3-dimensional structure 68 to form a high loft, nonwoven web 10, 10', 10" or 11 having a thickness  $t$ ,  $t_1$  or  $t_2$  of less than about 250 millimeters and a basis weight ranging from between about 50 g/m<sup>2</sup> to about 3,000 g/m<sup>2</sup>. The 3-dimensional structure 68 can be bonded using a variety of different bonders. Some bonders which can be used include but are not limited to: thermal bonding, through air bonding, oven bonding, chemical bonding, wet bonding, mechanical bonding or hydro-mechanical bonding.

A vertical cross-section of the high loft, nonwoven web 10, 10', 10" or 11, when taken parallel to the machine direction (MD), exhibits a plurality of snugly stacked, approximately V, U or C-shaped structures 24. Each of the approximately V, U or C-shaped structure 24 has an apex 26 facing in the machine direction (MD). In other words, the approximately V or U shaped structure is rotated 90 degrees to a horizontal orientation with the apex of each facing to the right. The C-shaped structure is reversed in position so that the apex of each faces to the right. The high loft, nonwoven web 10, 10', 10" or 11 has a recovery value ranging from between about 20% to about 99% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes.

Referring again to Figs. 3, 4 and 9, it is possible to utilize two separate and distinct dies 36 and 36 to produce a two layered web 10', see Fig. 3. One could also utilize three separate and distinct dies 36, 36 and 36 to produce a three layered web 10", see Fig. 4. Likewise, one could utilize four or more separate and distinct dies, 36, 36, 36 and 36 to produce a multi-layered web having 4 or more layers. Structure in these hybrid nonwoven high loft materials of the comingled fibers or the laminated layers may have different fiber size, different polymeric materials, and/or different fiber cross-section.

It should be understood that an additive 80 can be added to the high loft, nonwoven web 10, 10', 10" or 11 downstream of the bonder 74. The additive 80 can be any of those mentioned above. The additive 80 can be deposited onto the high



loft, nonwoven web 10, 10', 10" or 11, or it could be sprayed thereon. Alternatively, the high loft, nonwoven web 10, 10', 10" or 11 could be immersed in a liquid solution containing an additive 80.

It should also be understood that the high loft, nonwoven web 10, 10', 10" or 11 can be dried downstream of the bonder 74. Likewise, the high loft, nonwoven web 10, 10', 10" or 11 could be cooled downstream of the bonder 74. Such cooling could reduce the temperature of the high loft, nonwoven web 10, 10', 10" or 11 to room temperature or thereabout.

## Experiments:

### 1. Meltblowing Unit

A number of high loft, nonwovens sample webs were produced using a meltblowing pilot line that had a 381 mm meltblowing die with multi-row spinnerettes known as the Biax meltblowing (MB) die. This die is commercially available from Biax-Fiberfilm Corporation having an office at N992 Quality Drive, Suite B, Greenville, WI 54942. The meltblowing spinnerettes had 242 polymer nozzles. The inside diameter of each spinnerette was 0.508 millimeters (mm) while the outside diameter of each spinnerette was 0.711 mm. Each polymer nozzle was surrounded by an air nozzle where the blowing air was coming from the annular space between the polymer nozzle and the air nozzle. The diameter of each of the air nozzles was 1.4 mm. The Biax meltblowing (MB) die design is taught in U.S. Patent 5,476,616 and U.S. Patent Publication 2005/0056956 A1. Typical commercial Biax meltblowing (MB) dies have from between about 6,000 to about 11,000 nozzles per meter.

### 2. Process Conditions

Several examples of high loft, nonwoven webs were made using the pilot meltblowing line to prove the concept of this invention. It should be understood that the high loft, nonwoven webs could also have been made using spunbond equipment. Furthermore, it should be understood that the exact process conditions used to make these samples could be changed. Any variation of the process conditions, such as air temperature, polymer chemistry or type, polymer melt temperature, polymer throughput, air throughput, etc. could be changed.

The first seven (7) nonwoven web samples were made of polypropylene that was provided by Exxon-Mobil under the trade name: ACHIEVE 6936G1. This polypropylene had a typical melt flow rate of 1,550 grams per 10 minutes (according to ASTM test D 1238, 230 °C, 2.16 kg). The last two (2) nonwoven web samples

(samples 8 and 9) were made of polylactic acid that was provided by Natureworks under the trade name: INGENEO PLA 6202D. The polylactic acid had a melt flow rate of 15 grams (g) to 30 g per 10 minutes (according to ASTM test D 1238, 210 °C, 2.16 kg).

5

Polypropylene samples were fabricated at the following process conditions:

Polymer melt temperature: 190 °C

Air temperature: 170 °C

Polymer throughput: 0.26 g/hole/minute

10

Air pressure: 35 KPa

The basis weight of these samples varied from between about 150 g/m<sup>2</sup> to 500 g/m<sup>2</sup> by varying the speed of the first and second rotatable drums or by varying the speed of the first and second conveyor belts. The Die to Collector Distance (DCD) varied between about 30 centimeters (cm) to about 45 cm.

15

Polylactic acid samples were made at the following process conditions:

Polymer melt temperature: 260 °C

Air temperature: 260 °C

Polymer throughput: 1 g/hole/minute

20

Air pressure: 35 KPa

The basis weight was around 500 g/m<sup>2</sup> and the Die-to-Collector Distance (DCD) was around 75 cm.

Some of the samples were thermally bonded using an infra-red oven at a temperature of 120 °C and the dwell time (contact time) was about 3 seconds to about 5 seconds.

25

### **3. Characterization Tests**

30

#### **3.1 Basis weight**

Basis weight is defined as the mass per unit area and it can be measured in grams per meter squared (g/m<sup>2</sup>). The basis weight test is done according the INDA standard IST 130.1 which is equivalent to the ASTM standard ASTM D3776. Ten (10) different samples were die cut from different locations in a larger sample web and each one had an individual area equal to 100 cm<sup>2</sup>. The weight of each replicate was measured using a sensitive balance within ±0.1% of weight on the balance. The basis weight in grams/m<sup>2</sup> was measured by multiplying the average weight by 100.

35

### **3.2 Thickness of the high loft nonwoven**

- 5 Thickness is defined as the distance between one surface and an opposite surface of a single web measured under a specified pressure. For high loft, nonwoven webs, the thickness was measured according the INDA standard IST 120.2 (01). The apparatus include a thickness testing instrument that had: an anvil, a presser foot, and a scale indicating the distance between these two parallel plates.
- 10 The foot presser was 305 mm x 305 mm (12 inches x 12 inches) in size and had a weight of 288 grams. Five representative specimens of the fabric were die cut and tested in the standard atmosphere for testing as prescribed in ASTM D1776. Samples were handled carefully to avoid altering the natural state of the fabric. Each specimen was placed on the bottom plate and the presser foot was placed with care
- 15 on the top of the sample. The average thickness of these specimens is reported along with a standard deviation.

### **3.3 Compression and Recovery of the high loft nonwovens**

- 20 In this test, one measures the compression and recovery performance of the high loft, nonwoven web samples by observing the linear distance that a movable plane is displaced from a parallel surface by the high loft, nonwoven web samples while under a specified pressure. After a specified time interval, the pressure is removed and the recovery of the linear distance is measured. The performance of
- 25 the high loft, nonwoven webs for use in furniture, clothing, and insulation applications (acoustic or thermal) may be estimated from these compression and recovery values. The original thickness T1, measured in millimeters (mm), was measured according to the IST 120.2 (01). The presser foot was raised and the 288 gram weight was replaced with 16.33 Kg (36 pounds) to provide a pressure of 1720 Pa (0.25 psi). The
- 30 presser foot with the new weight was placed on top of the high loft, nonwoven webs samples for 30 minutes and then the compressed thickness T2 was measured. Finally, the presser foot was raised and replaced by the 36 pound weight with the 288 gram weight. After five (5) minutes, the presser foot was lowered to measure the thickness recovered, T3.

- 35 Percent compression =  $[(T1-T2)/T1] \times 100$

$$\text{Percent Recovery} = [T3/T1] \times 100$$

**Example 1**

In this example, the effects of the collector type on the high loft, nonwoven web properties were looked at. Sample 1 and 2 showed a big difference in thickness or caliper of the nonwoven web. The big difference is mainly due to collecting the spun fibers on a flat belt versus collecting them between two rotating drums having a nip gap of 2.5 cm. The dual drum collection system increased the thickness by 1,500% although both samples have the same mass per unit area. Sample 3 showed that by thermally bonding the high loft, nonwoven sample #2, one could enhance the recovery properties by 26%. Such enhancement will greatly increase the thermal insulation and acoustical properties of a web. With the proper tuning of the fiber formation conditions and the bonding conditions, the compression and recovery properties can be greatly enhanced, see Table 1 below.

**Table 1**

Table (1): Effect of Collector type on polypropylene high loft nonwoven samples								
Sample	DCD, (cm)	Collector type	Nip gap, (cm)	Bonding	Basis weight, (g/m <sup>2</sup> )	Thickness, (mm)	Percent compression (%)	Percent Recovery (%)
# 1	45	flat belt	NA	No	150.7	0.81	NA	NA
# 2	45	dual drum	2.5	No	147.8	13.6	72	53.6
# 3	45	dual drum	2.5	Thermally Bonded	142.6	12.6	72.4	67.7

**Example 2**

In this example, the effect of the Die-to-Collector Distance (DCD) on the compression-recovery properties of the high loft nonwoven web samples were looked at. The meltblown filaments were collected at a distance close to the die, where they are very tacky. This action created fiber to fiber bonding in the high loft, nonwoven web samples between the first and second rotatable drums and avoided the need for additional downstream bonding. This might work on equipment operating at a low polymer throughput to produce a high loft, nonwoven web with a basis weight of less than about 150 g/m<sup>2</sup>. However, when the polymer throughput and the basis weight increases, the blowing air causes the filaments to fly around and they prevent being

captured on the first and second rotatable drums because of the difficult air management at a closer Die-to-Collector Distance (DCD). Samples 2 and 3 were collector at a DCD distance of 45 cm from the die face. Samples 4 and 5 were collected at a DCD distance of 30 cm from the die face. As shown in Table 2, collecting the fibers at a closer DCD distance, as in sample 4, enhanced the fiber to fiber bonding and achieved similar recovery performance to sample 3, which was thermally bonded. Sample 5 was obtained by oven bonding sample #4. However, it was found that this additional bonding actually decreased the recovery properties of sample 5 by 28% because the additional bonding actually caused the fibers to become brittle.

**Table 2**

Table (2): Effect of Die-to-collector distance on polypropylene high loft nonwovens								
Sample	DCD, (cm)	Collector type	Nip gap, (cm)	Bonding	Basis weight, (g/m <sup>2</sup> )	Thickness, (mm)	Percent Compression (%)	Percent Recovery (%)
# 2	45	dual drum	2.5	No	147.8	13.6	72.3	53.6
# 3	45	dual drum	2.5	Thermally Bonded	142.6	12.6	72.4	67.7
# 4	30	dual drum	2.5	No	146.5	13.5	73.3	65.6
# 5	30	dual drum	2.5	Thermally Bonded	151.25	19.8	81.7	47.7

**Example 3**

In this example, the effect that basis weight had on the compression-recovery properties of the high loft, nonwoven web samples were looked at. As shown in Table 3, by increasing the mass per unit area, the compressibility decreased which is obvious because of the larger nonwoven mass passing between the nip of the first and second rotatable drums. It was also noticed that by increasing the basis weight, the percent recovery after compression also increased, which may be due to the larger number of fiber-to-fiber bonds that were created. Collecting the fibers of samples 6 and 7 at a closer Die-to-Collector Distance (DCD) was not successful on the pilot scale because of the difficult air management and the larger mass of filaments that blocked the way in front the blowing attenuation air.

**TABLE 3**

<b>Table (3): Effect of Basis Weight on polypropylene high loft nonwovens</b>								
Sample	DCD, (cm)	Collector type	Nip gap, (cm)	Bonding	Basis weight, (g/m <sup>2</sup> )	Thickness, (mm)	Percent compression (%)	Percent Recovery (%)
# 3	45	dual drum	2.5	Through Bonded	142.6	12.6	72.4	67.7
# 6	45	dual drum	2.5	Through Bonded	302.3	17.8	66.9	75.9
# 7	45	dual drum	2.5	Through Bonded	492.6	23.2	61.7	80.8

5           **Example 4**

In this example, the concept of collecting spunmelt fibers at the nip formed between two rotating drums, for different polymers, were looked at. Sample 8 and 9 were produced using polylactic acid resin. Despite the spinning difficulty of such polymer and the shrinkage effect that accompanied the web formation, two high loft, nonwoven samples were collected. As shown in Table 4, sample 8, which was not thermally bonded, had higher compressibility but lower recovery properties than sample 9 which was thermally bonded using the infra-red thermal oven. Sample 9 was also stronger than sample 8 during handling and had a better structure integrity as sample 9 was not falling apart because of the fiber-to-fiber bonds that were created during the post heat treatment. It is well known that structural integrity of the loose fibers can be enhanced by using other bonding techniques, such as through air bonding or chemical bonding.

**TABLE 4**

<b>Table (4): PLA high loft nonwovens</b>								
Sample	DCD, (cm)	Collector type	Nip gap, (cm)	Bonding	Basis weight, (g/m <sup>2</sup> )	Thickness, (mm)	Percent compression (%)	Percent Recovery (%)
# 8	75	dual drum	2.5	No	530	20.5	44.7	80.2
# 9	75	dual drum	2.5	Through Bonded	533	19.1	33.5	85.7

While the invention has been described in conjunction with several specific embodiments, it is to be understood that many alternatives, modifications and

variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, this invention is intended to embrace all such alternatives, modifications and variations which fall within the spirit and scope of the appended claims.

## CLAIMS

We claim:

1. A high loft, nonwoven web comprising a three dimensional structure with fibers oriented in the x, y and z directions, said web having a thickness of less than about 250 millimeters and a basis weight ranging from between about 50 g/m<sup>2</sup> to about 3,000 g/m<sup>2</sup>, and a vertical cross-section of said web, when taken parallel to a machine direction, exhibiting a plurality of snugly stacked, approximately V, U or C-shaped structures, with each V, U or C-shaped structure having an apex facing in said machine direction, and said web having a recovery value ranging from between about 20% to about 99% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes.
2. The high loft, nonwoven web of claim 1 wherein said web has a density ranging from between about 10 Kg/m<sup>3</sup> to about 250 Kg/m<sup>3</sup>.
3. The high loft, nonwoven web of claim 1 wherein said web is thermally bonded.
4. The high loft, nonwoven web of claim 1 wherein said web is chemically bonded.
5. The high loft, nonwoven web of claim 1 wherein said web is formed from polyolefin.
6. The high loft, nonwoven web of claim 1 wherein said web is formed from polypropylene having a melt flow rate ranging from between about 4 g/10 min. to about 6,000 g/10min at a temperature of 230 °C and at a pressure of 2.16 kg.
7. The high loft, nonwoven web of claim 1 wherein said web contains an additive.
8. The high loft, nonwoven web of claim 7 wherein said additive is selected from the group consisting of: a superabsorbent, absorbent particles, polymers, nanoparticles, abrasive particulars, active particles, active compounds, ion exchange resins, zeolites, softening agents, plasticizers, ceramic particles pigments,



dyes, flavorants, aromas, controlled release vesicles, binders, adhesives, tackifiers, surface modification agents, lubricating agents, emulsifiers, vitamins, peroxides, antimicrobials, deodorizers, fire retardants, flame retardants, antifoaming agents, anti-static agents, biocides, antifungals, degradation agents, stabilizing agents, conductivity modifying agents, or any combination thereof.

9. The high loft, nonwoven web of claim 1 wherein said web contains at least two separate and distinct layers, and said web has two major surfaces and at least one of these major surfaces is textured.

10. A high loft, nonwoven web comprising at least two layers each having a three dimensional structure with fibers oriented in the x, y and z directions, said web having a thickness of less than about 200 millimeters and a basis weight of from between about 50 g/m<sup>2</sup> to about 2,000 g/m<sup>2</sup>, said web being through air bonded, and a vertical cross-section of each layer of said web, when taken parallel to a machine direction, exhibiting a plurality of snugly stacked, approximately V, U or C-shaped structures, with each V, U or C-shaped structure having an apex facing in said machine direction, and said web having a recovery value ranging from between about 30% to about 95% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes.

11. The high loft, nonwoven web of claim 10 wherein said web is formed from a polymer selected from the group consisting of: polyolefins, polyesters, polyethylene terephthalates, polybutylene terephthalates, polycyclohexylene dimethylene terephthalates, polytrimethylene terephthalates, polymethyl methacrylates, polyamides, nylons, polyacrylics, polystyrenes, polyvinyls, polytetrafluoroethylenes, ultrahigh molecular weight polyethylenes, very high molecular weight polyethylenes, high molecular weight polyethylenes, polyether ether ketones, non-fibrous plasticized celluloses, polyethylenes, polypropylenes, polybutylenes, polymethylpentenes, low-density polyethylenes, linear low-density polyethylenes, high-density polyethylenes, polystyrenes, acrylonitrile-butadiene-styrenes, styrene-acrylonitriles, styrene-butadienes, styrene-maleic anhydrides, ethylene vinyl acetates, ethylene vinyl alcohols, polyvinyl chlorides, cellulose acetates, cellulose acetate butyrates, plasticized celluloses, cellulose propionates, ethyl celluloses, natural fibers, any derivative thereof, any polymer blend thereof, any copolymer thereof or any combination thereof.

12. The high loft, nonwoven web of claim 10 wherein said web has two major surfaces and at least one of these major surfaces is textured.

13. The high loft, nonwoven web of claim 10 wherein said web has two major surfaces and both of these major surfaces is textured.

14. The high loft, nonwoven web of claim 10 wherein said additive is selected from the group consisting of: a superabsorbent, absorbent particles, polymers, nanoparticles, abrasive particulars, active particles, active compounds, ion exchange resins, zeolites, softening agents, plasticizers, ceramic particles pigments, dyes, flavorants, aromas, controlled release vesicles, binders, adhesives, tackifiers, surface modification agents, lubricating agents, emulsifiers, vitamins, peroxides, antimicrobials, deodorizers, fire retardants, flame retardants, antifoaming agents, anti-static agents, biocides, antifungals, degradation agents, stabilizing agents, conductivity modifying agents, or any combination thereof.

15. A high loft, nonwoven web comprising at least two layers of fibers, each layer emitted from a different spinning head with a plurality of nozzles, said fibers being deposited on a forming wire to form a three dimensional structure with fibers oriented in the x, y and z directions, said web having a thickness of less than about 100 millimeters and a basis weight of from between about 50 g/m<sup>2</sup> to about 1,000 g/m<sup>2</sup>, said web being bonded, and a vertical cross-section of said web, when taken parallel to a machine direction, exhibiting a plurality of snugly stacked, approximately V, U or C-shaped structures, with each V, U or C-shaped structure having an apex facing in said machine direction, and said web having a recovery value ranging from between about 40% to about 90% after being compressed under a pressure of 0.25 psi for a time period of 30 minutes.

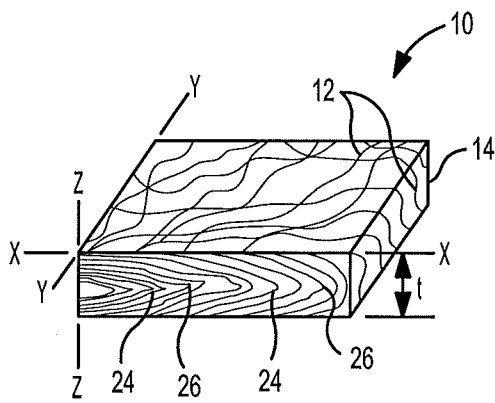
16. The high loft, nonwoven web of claim 15 wherein said web is thermally bonded.

17. The high loft, nonwoven web of claim 15 wherein said web is chemically bonded.

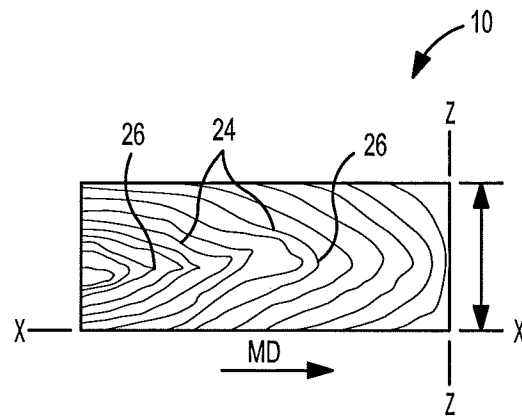
18. The high loft, nonwoven web of claim 15 wherein said web has two major surfaces and both of these major surfaces is textured.

19. The high loft, nonwoven web of claim 15 wherein said web is formed from a polymer which is selected from the group consisting of: polyolefins, polyesters, polyethylene terephthalates, polybutylene terephthalates, polycyclohexylene dimethylene terephthalates, polytrimethylene terephthalates, polymethyl methacrylates, polyamides, nylons, polyacrylics, polystyrenes, polyvinyls, polytetrafluoroethylenes, ultrahigh molecular weight polyethylenes, very high molecular weight polyethylenes, high molecular weight polyethylenes, polyether ether ketones, non-fibrous plasticized celluloses, polyethylenes, polypropylenes, polybutylenes, polymethylpentenes, low-density polyethylenes, linear low-density polyethylenes, high-density polyethylenes, polystyrenes, acrylonitrile-butadiene-styrenes, styrene-acrylonitriles, styrene-butadienes, styrene-maleic anhydrides, ethylene vinyl acetates, ethylene vinyl alcohols, polyvinyl chlorides, cellulose acetates, cellulose acetate butyrates, plasticized celluloses, cellulose propionates, ethyl celluloses, natural fibers, any derivative thereof, any polymer blend thereof, any copolymer thereof or any combination thereof.

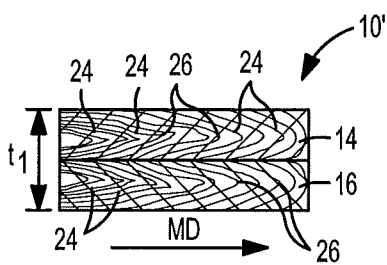
20. The high loft, nonwoven web of claim 10 wherein said web contains one or more additive selected from the group consisting of: a superabsorbent, absorbent particles, polymers, nanoparticles, abrasive particulars, active particles, active compounds, ion exchange resins, zeolites, softening agents, plasticizers, ceramic particles pigments, dyes, flavorants, aromas, controlled release vesicles, binders, adhesives, tackifiers, surface modification agents, lubricating agents, emulsifiers, vitamins, peroxides, antimicrobials, deodorizers, fire retardants, flame retardants, antifoaming agents, antistatics agents, biocides, antifungals, degradation agents, stabilizing agents, conductivity modifying agents, or any combination thereof.



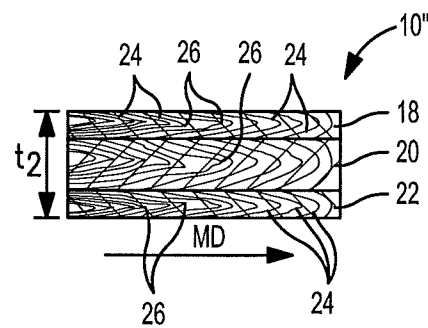
**FIG. 1**



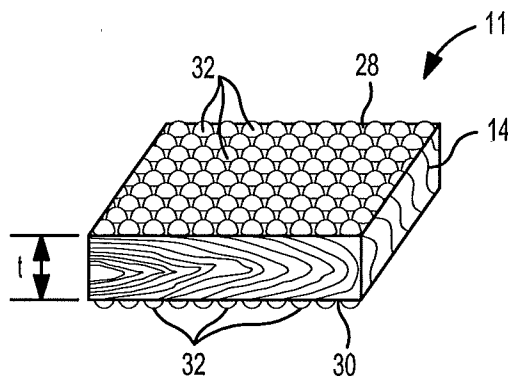
**FIG. 2**



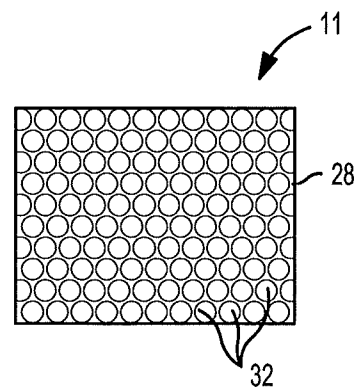
**FIG. 3**



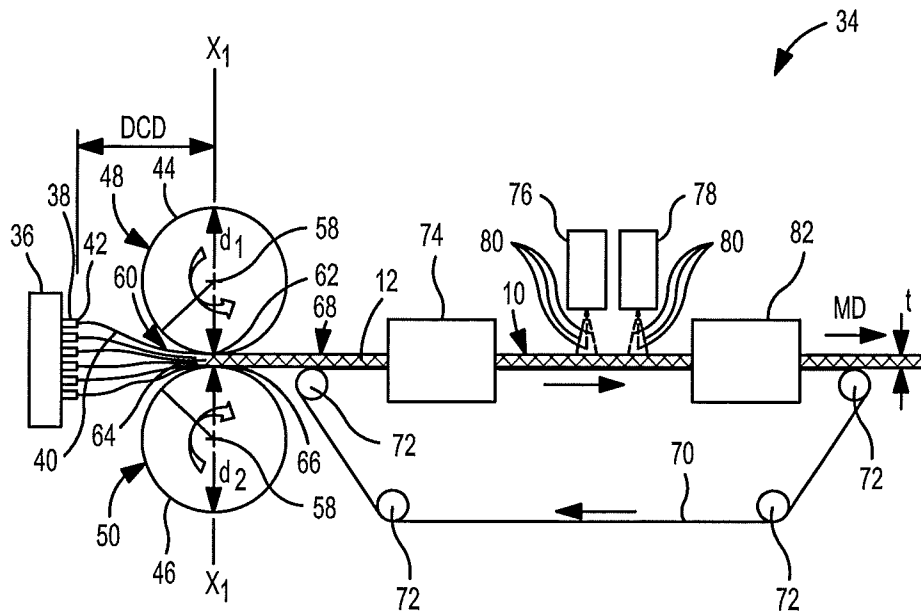
**FIG. 4**



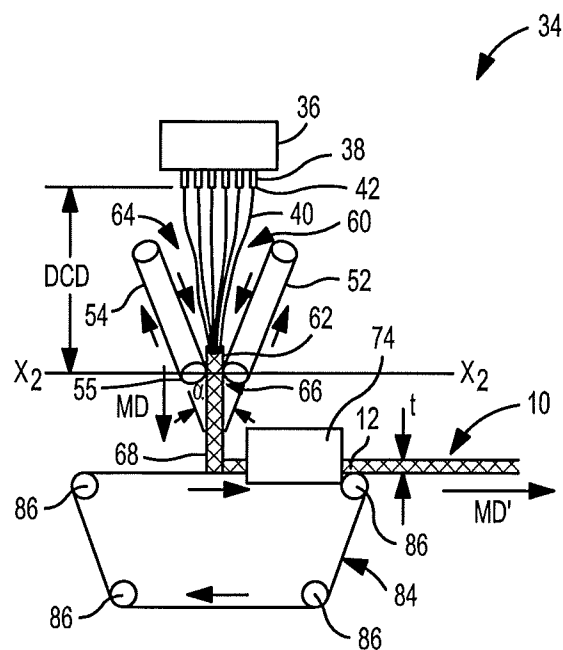
**FIG. 5**



**FIG. 6**



**FIG. 7**



**FIG. 8**

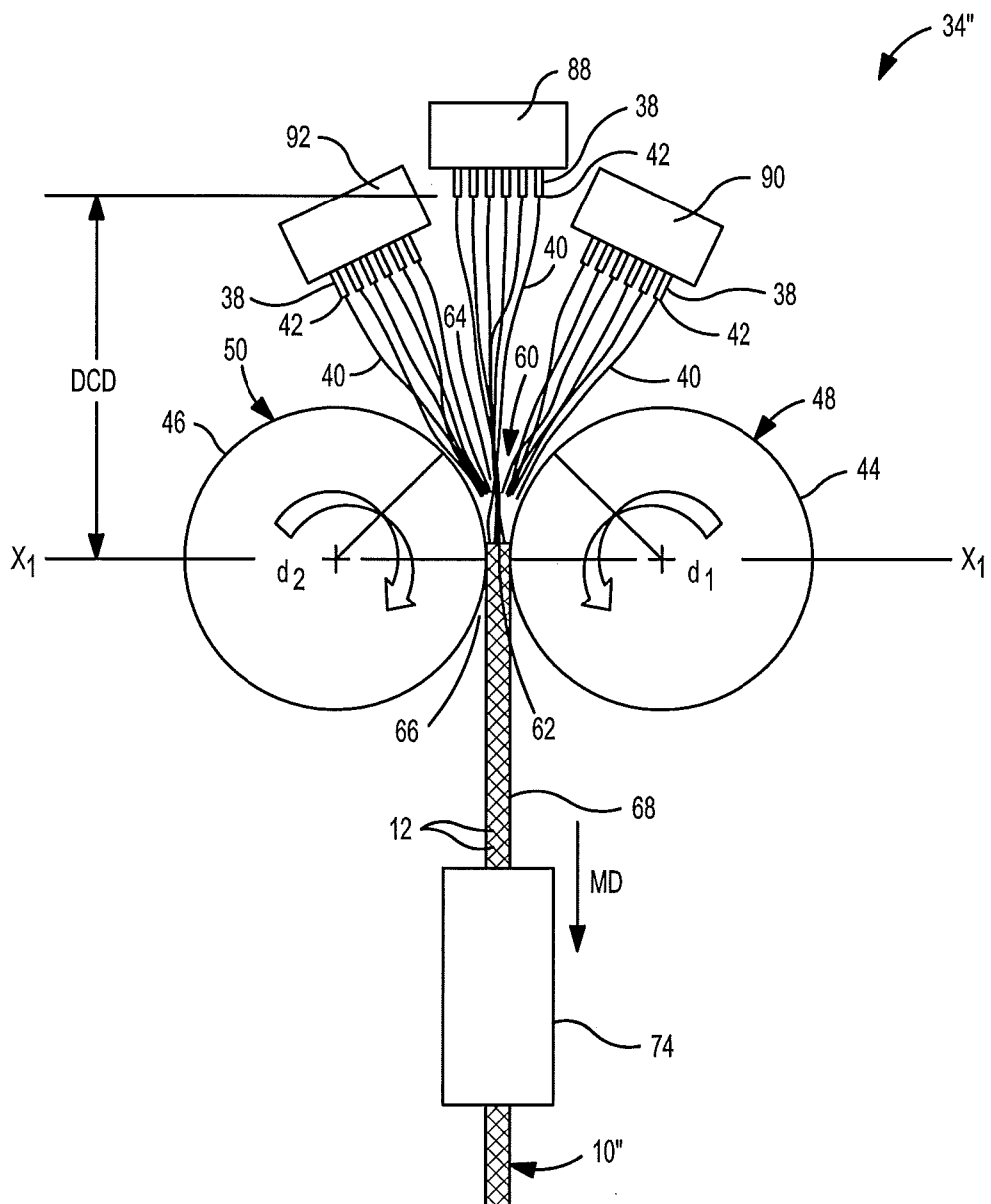


FIG. 9

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/013429

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. D04H3/02 D04H3/07 D04H3/14 D04H3/16 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) D04H		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/097155 A1 (OLSON DAVID A [US] ET AL) 20 May 2004 (2004-05-20)  abstract; paragraphs [0013], [0067]; claims 1,9; figures 1, 1a-1c; table 1 -----	1-7, 9-13, 15-19
X	WO 00/66824 A1 (KIMBERLY CLARK CO [US]) 9 November 2000 (2000-11-09) abstract; page 7, line 30 - page 8, line 2; figures -----	1,8,10, 14,15,20
A	US 4 375 446 A (FUJII SHIGEO [JP] ET AL) 1 March 1983 (1983-03-01) abstract; page 7, lines 30-31; figures page 8, lines 1-2; claims; figures -----  -/-	1-20
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search  2 April 2015		Date of mailing of the international search report  14/04/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer  Elsässer, Ralf

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/013429

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 740 302 A (SOEHNGEN J) 19 June 1973 (1973-06-19) claims; figures -----	1-20
A	DE 17 85 712 A1 (CELANESE CORP) 29 July 1976 (1976-07-29) claims; figures -----	1-20



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/013429

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004097155	A1	20-05-2004	AT 423235 T 15-03-2009
		AU 2003272699 A1 15-06-2004	
		BR 0315655 A 30-08-2005	
		CN 1714189 A 28-12-2005	
		EP 1570121 A1 07-09-2005	
		ES 2322142 T3 17-06-2009	
		JP 4571504 B2 27-10-2010	
		JP 2006506551 A 23-02-2006	
		JP 2010203033 A 16-09-2010	
		KR 20050075405 A 20-07-2005	
		MX PA05005174 A 18-08-2005	
		US 2004097155 A1 20-05-2004	
		WO 2004046443 A1 03-06-2004	
WO 0066824	A1	09-11-2000	AR 025837 A1 18-12-2002
		AU 4479300 A 17-11-2000	
		BR 0010020 A 15-01-2002	
		DE 10084561 B3 04-09-2014	
		DE 10084561 T1 21-03-2002	
		GB 2364071 A 16-01-2002	
		MX PA01011066 A 04-06-2002	
		US 6588080 B1 08-07-2003	
		US 2003213109 A1 20-11-2003	
		WO 0066824 A1 09-11-2000	
US 4375446	A	01-03-1983	BE 875978 A1 05-11-1979
		CA 1147113 A1 31-05-1983	
		DE 2948820 C2 14-03-1991	
		GB 2045300 A 29-10-1980	
		JP S6056825 B2 12-12-1985	
		JP S54147273 A 17-11-1979	
		US 4375446 A 01-03-1983	
		WO 7901014 A1 29-11-1979	
US 3740302	A	19-06-1973	NONE
DE 1785712	A1	29-07-1976	NONE