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(71) Applicant (for all designated States except US): **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **LEVIT, Mikhail, R.** [US/US]; 5120 Dorin Hill Court, Glen Allen, Virginia 23059 (US). **KHAN, Subhotosh** [IN/US]; 1100 Goswick Ridge Road, Midlothian, Virginia 23114 (US). **HENDREN, Gary, Lee** [US/US]; 12302 Shady Branch Court, Richmond, Virginia 23238 (US).

(74) Agent: **GOLIAN, Andrew, G.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

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(54) Title: HONEYCOMB FROM CONTROLLED POROSITY PAPER

(57) Abstract: This invention relates to an improved high performance honeycomb, methods for making the same, and articles including aerodynamic structures comprising the honeycomb, the honeycomb made with a paper that allows rapid impregnation of the honeycomb by structural resins while retarding excessive impregnation of node-line adhesives during manufacture. The honeycomb comprises a paper having a Gurley porosity of 2 seconds or greater and comprising high modulus fiber and thermoplastic binder having a melt point of from 120° C to 350° C, wherein at least 30 percent by weight of the total amount of thermoplastic material is in the form of discrete film-like particles in the paper, the particles having a film thickness of about 0.1 to 5 micrometers and a minimum dimension perpendicular to that thickness of at least 30 micrometers.



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Title of the Invention

Honeycomb from Controlled Porosity Paper

Background of the Invention

5 1. Field of the Invention.

 This invention relates to an improved high performance honeycomb comprising thermoplastic binder having a melt point of from 120° C to 350° C, methods for making the honeycomb, and articles comprising the honeycomb; the honeycomb is made with a paper that allows rapid
10 impregnation of the honeycomb by structural thermoset resins while retarding excessive impregnation of node-line adhesives during manufacture.

 2. Description of Related Art.

 Paper-based honeycomb is typically formed by (1) applying
15 adhesive resin to sheets of paper along predetermined lines, called node lines, (2) adhering several sheets of paper along these node lines to form a stack, with the node lines of each sheet offset to the adjacent sheets, (3) expanding the stack to form a honeycomb having defined cell walls, (4) impregnating the cell walls of the honeycomb with structural resin by
20 submerging the honeycomb in a liquid resin, and (5) curing the resin with heat. United States Patent Nos. 5,137,768 to Lin; 5,789,059 to Nomoto; and 6,544,622 to Nomoto; disclose honeycombs made from sheets made from high modulus para-aramid materials. These honeycombs are highly prized for structural applications due to their high stiffness and high
25 strength to weight ratio. Generally these honeycombs are made from papers comprising para-aramid fibers, pulp, and/or other fibrous materials plus a binder.

 United States Patent Nos. 6,551,456 and 6,458,244 to Wang et al. and Japanese Patent Application Publication 61-58,193 to Nishimura et
30 al., disclose papers made from aramid fibers combined with polyester fibers. It has been found that these papers have a very open or porous structure, allowing rapid impregnation of thermoset structural resins.

Unfortunately, if these aramid/polyester papers are used for honeycomb, the high porosity to resins can also allow rapid penetration of the node line adhesive resin through the paper. It is highly desired that the adhesive, when printed or applied to the surface of the paper, remain substantially on the surface of the paper and not penetrate through the paper to the opposite surface. Otherwise, the paper sheets are simply glued together and are impossible to expand into a uniform honeycomb structure. This problem is particularly critical for thin papers having a thickness of 75 micrometers or less that are highly desired for high-performance lightweight aircraft honeycombs.

Typically, the application or printing of the adhesive nodes lines is a relatively fast process, while impregnation of the structural resin is a somewhat slower process. Therefore what is needed is a honeycomb made from a paper that has properties that can control the rate of impregnation by the adhesive resin while maintaining overall good impregnation of structural resin.

Brief Summary of the Invention

This invention relates to a honeycomb having cells comprising a paper comprising 5 to 50 parts by weight thermoplastic material having a melting point of from 120° C to 350° C, and 50 to 95 parts by weight of a high modulus fiber having a modulus of 600 grams per denier (550 grams per dtex) or greater, based on the total amount of thermoplastic material and high modulus fiber in the paper; wherein at least 30 percent by weight of the total amount of thermoplastic material is in the form of discrete film-like particles in the paper, and the particles having a film thickness of about 0.1 to 5 micrometers and a minimum dimension perpendicular to that thickness of at least 30 micrometers, the film-like particles binding the high modulus fiber in the paper; and wherein the paper has a Gurley porosity of 2 seconds or greater.

One embodiment includes an article comprising the aforesaid honeycomb, with such articles including a panel or an aerodynamic structure.

Brief Description of the Drawings

Figures 1a and 1b are representations of views of a hexagonal shaped honeycomb.

5 Figure 2 is a representation of another view of a hexagonal cell shaped honeycomb.

Figure 3 is an illustration of honeycomb provided with facesheet(s).

Detailed Description of the Invention

10 This invention relates to a honeycomb made from a paper comprising high modulus fiber and thermoplastic material wherein the thermoplastic material is at least partly present in the paper in the form of discrete film-like particles. The honeycomb can be impregnated with many structural resins without unacceptable penetration by the node line
15 adhesive resins.

Figure 1a is one illustration of a honeycomb. Figure 1b is an orthogonal view of the honeycomb shown in Figure 1a and Figure 2 is a three-dimensional view of the honeycomb. Shown is honeycomb 1 having hexagonal cells 2. Hexagonal cells are shown; however, other geometric
20 arrangements are possible with square and flex-core cells being the other most common possible arrangements. Such cell types are well known in the art and reference can be made to *Honeycomb Technology* by T. Bitzer (Chapman & Hall, publishers, 1997) for additional information on possible geometric cell types.

25 In many embodiments, the honeycomb is provided with a structural or matrix resin, typically a thermoset resin that fully impregnates, saturates, or coats the cell walls of the honeycomb. The resin is then further crosslinked or cured to realize of the final properties (stiffness and strength) to the honeycomb. In some embodiments these structural resins
30 include epoxy resins, phenolic resins, acrylic resins, polyimide resins, and mixtures thereof.

The cell walls of the honeycomb are preferably formed from a paper comprising a high modulus fiber and a thermoplastic material. In some

embodiments the term paper is employed in its normal meaning and refers to a nonwoven sheet prepared using conventional wet-lay papermaking processes and equipment. However, the definition of paper in some embodiments includes, in general, any nonwoven sheet that requires a
5 binder material and has properties sufficient to provide an adequate honeycomb structure.

The thickness of the paper used in this invention is dependent upon the end use or desired properties of the honeycomb and in some embodiments is typically from 1 to 5 mils (25 to 130 micrometers) thick. In
10 some embodiments, the basis weight of the paper is from 0.5 to 6 ounces per square yard (15 to 200 grams per square meter).

The paper used in the honeycomb comprises 5 to 50 parts by weight thermoplastic material having a melting point of from 120° C to 350° C, and 50 to 95 parts by weight of a high modulus fiber having a
15 modulus of 600 grams per denier (550 grams per dtex) or greater, based on the total amount of thermoplastic material and high modulus fiber in the paper. At least 30 parts by weight of the thermoplastic material is in the form of discrete film-like particles having a film thickness of about 0.1 to 5 micrometers and having a minimum dimension perpendicular to that
20 thickness of at least 30 micrometers. The film-like particles act as a binder for the high modulus fiber in the paper and by their nature create a paper having a Gurley porosity of 2 seconds or greater.

In some embodiments the high modulus fiber is present in the paper in an amount of from about 60 to 80 parts by weight, and in some
25 embodiments the thermoplastic material is present in the paper in an amount of from 20 to 40 parts by weight.

In some embodiments, the maximum dimension of the thermoplastic film-like particles perpendicular to the thickness is at most
1.5 mm.

30 The paper can also include inorganic particles and representative particles include mica, vermiculite, and the like; the addition of these particles can impart properties such as improved fire resistance, thermal

conductivity, dimensional stability, and the like to the paper and the final honeycomb.

The paper used in this invention can be formed on equipment of any scale, from laboratory screens to commercial-sized papermaking machinery, including such commonly used machines as Fourdrinier or inclined wire paper machines. A typical process involves making a dispersion of high modulus fibrous material such as floc and/or pulp and a binder material in an aqueous liquid, draining the liquid from the dispersion to yield a wet composition and drying the wet paper composition. The dispersion can be made either by dispersing the fibers and then adding the binder material or by dispersing the binder material and then adding the fibers. The final dispersion can also be made by combining a dispersion of fibers with a dispersion of the binder material; the dispersion can optionally include other additives such as inorganic materials. If the binder material is a fiber, the fiber can be added to the dispersion by first making a mixture with high modulus fibers, or the fiber can be added separately to the dispersion. The concentration of fibers in the dispersion can range from 0.01 to 1.0 weight percent based on the total weight of the dispersion. The concentration of a binder material in the dispersion can be up to 50 weight percent based on the total weight of solids. In a typical process, the aqueous liquid of the dispersion is generally water, but may include various other materials such as pH-adjusting materials, forming aids, surfactants, defoamers and the like. The aqueous liquid is usually drained from the dispersion by conducting the dispersion onto a screen or other perforated support, retaining the dispersed solids and then passing the liquid to yield a wet paper composition. The wet composition, once formed on the support, is usually further dewatered by vacuum or other pressure forces and further dried by evaporating the remaining liquid.

In one preferred embodiment high modulus fibrous material and a thermoplastic binder, such as a mixture of short fibers or short fibers and binder particles, can be slurried together to form a mix that is converted to paper on a wire screen or belt. Reference is made to United States Patent and Patent Application Nos. 3,756,908 to Gross; 4,698,267 and 4,729,921

to Tokarsky; 5,026, 456 to Hesler et al.; 5,223,094 to Kirayoglu et al.; 5,314,742 to Kirayoglu et al.; 6,458,244 and 6,551,456 to Wang et al.; and 6,929,848 and 2003-0082974 to Samuels et al. for illustrative processes for forming papers from various types of fibrous material and binders.

5 Once the paper is formed, it is preferably hot calendered. This can increase the density and strength of the paper. Generally one or more layers of the paper are calendered in the nip between metal-metal, metal-composite, or composite-composite rolls. Alternatively, one or more layers of the paper can be compressed in a platen press at a pressure,
10 temperature, and time that are optimal for a particular composition and final application. Calendering paper in this manner also decreases the porosity of the formed paper, and in some preferred embodiments the paper used in the honeycomb is calendered paper. Heat-treatment of the paper, such as from radiant heaters or un-nipped rolls, as an independent
15 step before, after, or instead of calendering or compression, can be conducted if strengthening or some other property modification is desired without, or in addition to, densification.

 The papers useful in this invention have a Gurley porosity of 2 seconds or greater. In some embodiments the papers have Gurley
20 porosity of from 2 to about 20 seconds, and in some preferred embodiments the papers have a Gurley porosity of about 5 to 10 seconds. A paper having a porosity of less than 2 seconds is believed to allow uncontrolled impregnation of the paper by both adhesives and structural resins, while papers having a porosity of more than 20 seconds are not as
25 desirable because it is believed that in some cases the low porosity will retard structural resin impregnation of the paper to the extent that the rate of dipping/impregnation process of the honeycomb is made not very practical.

 The honeycomb comprises high modulus fibers; as used herein
30 high modulus fibers are those having a tensile or Young's modulus of 600 grams per denier (550 grams per dtex) or greater. High modulus of the fiber provides necessary stiffness of the final honeycomb structure and corresponding panel. In a preferred embodiment, the Young's modulus of

the fiber is 900 grams per denier (820 grams per dtex) or greater. In the preferred embodiment, the fiber tenacity is at least 21 grams per denier (19 grams per dtex) and its elongation is at least 2% so as to provide a high level of mechanical properties to the final honeycomb structure.

5 In a preferred embodiment the high modulus fiber is heat resistant fiber. By "heat resistant fiber" it is meant that the fiber preferably retains 90 percent of its fiber weight when heated in air to 500° C at a rate of 20 degrees Celsius per minute. Such fiber is normally flame resistant, meaning the fiber or a fabric made from the fiber has a Limiting Oxygen
10 Index (LOI) such that the fiber or fabric will not support a flame in air, the preferred LOI range being about 26 and higher.

 The high modulus fibers can be in the form of a floc or a pulp or a mixture thereof. By "floc" is meant fibers having a length of 2 to 25 millimeters, preferably 3 to 7 millimeters and a diameter of 3 to 20
15 micrometers, preferably 5 to 14 micrometers. Floc is generally made by cutting continuous spun filaments into specific-length pieces. If the floc length is less than 2 millimeters, it is generally too short to provide a paper with adequate strength; if the floc length is more than 25 millimeters, it is very difficult to form uniform wet-laid webs. Floc having a diameter of less
20 than 5 micrometers, and especially less than 3 micrometers, is difficult to produce with adequate cross sectional uniformity and reproducibility; if the floc diameter is more than 20 micrometers, it is very difficult to form uniform papers of light to medium basis weights.

 The term "pulp", as used herein, means particles of high modulus
25 material having a stalk and fibrils extending generally therefrom, wherein the stalk is generally columnar and about 10 to 50 micrometers in diameter and the fibrils are fine, hair-like members generally attached to the stalk measuring only a fraction of a micrometer or a few micrometers in diameter and about 10 to 100 micrometers long.

30 In some embodiments, the high modulus fibers useful in this invention include fiber made from para-aramid, polybenzazole, polypyridazole polymer or mixtures thereof. In some embodiments, the high modulus fibers useful in this invention include carbon fiber. In one

preferred embodiment, the high modulus fiber is made from aramid polymer, especially para-aramid polymer. In an especially preferred embodiment the high modulus fiber is poly(paraphenylene terephthalamide).

5 As employed herein the term aramid means a polyamide wherein at least 85% of the amide (-CONH-) linkages are attached directly to two aromatic rings. "Para-aramid" means the two rings or radicals are para oriented with respect to each other along the molecular chain. Additives can be used with the aramid. In fact, it has been found that up to as much as 10 percent, by weight, of other polymeric material can be blended with the aramid or that copolymers can be used having as much as 10 percent of other diamine substituted for the diamine of the aramid or as much as 10 percent of other diacid chloride substituted for the diacid chloride of the aramid. In some embodiments the preferred para-aramid is poly(paraphenylene terephthalamide). Methods for making para-aramid fibers useful in this invention are generally disclosed in, for example, US Patent Nos. 3,869,430; 3,869,429; and 3,767,756. Such aromatic polyamide fibers and various forms of these fibers are available from E. I. du Pont de Nemours and Company, Wilmington, Delaware under the trademark Kevlar® fibers and from Teijin, Ltd., under the trademark Twaron®.

Commercially available polybenzazole fibers useful in this invention include Zylon® PBO-AS (Poly(p-phenylene-2,6-benzobisoxazole) fiber, Zylon® PBO-HM (Poly(p-phenylene-2,6-benzobisoxazole)) fiber, available from Toyobo, Japan. Commercially available carbon fibers useful in this invention include Tenax® fibers available from Toho Tenax America, Inc.

The honeycomb has 5 to 50 parts by weight thermoplastic material having a melting point of from 120° to 350° C. Thermoplastic is meant to have its traditional polymer definition; these materials flow in the manner of a viscous liquid when heated and solidify when cooled and do so reversibly time and time again on subsequent heating and cooling steps. In some other preferred embodiments the melting point of the thermoplastic is from 180° to 300° C. In some other preferred

embodiments the melting point of the thermoplastic is 220° to 250° C.

While papers can be made with thermoplastic material having a melt point lower than 120° C, this paper can be susceptible to undesirable melt flow, sticking, and other problems after paper manufacture. For example,

5 during honeycomb manufacture, after node line adhesive is applied to the paper, generally heat is applied to remove solvent from the adhesive. In another step, the sheets of paper are pressed together to adhere the sheets at the node lines. During either of these steps, if the paper has a low melt point thermoplastic material, that material can flow and

10 undesirably adhere the paper sheets to manufacturing equipment and/or other sheets. Therefore, preferably the thermoplastic materials used in the papers can melt or flow during the formation and calendering of the paper, but do not appreciably melt or flow during the manufacture of honeycomb. Thermoplastic materials having a melt point above 350 ° C
15 are undesired because they require such high temperatures to soften that other components in the paper may begin to degrade during paper manufacture. In those embodiments where more than one type of thermoplastic material is present then at least 30% of the thermoplastic material should have melting point not above 350° C.

20 The thermoplastic material binds the high modulus fiber in the paper used in the honeycomb. The thermoplastic material can be in the form of flakes, particles, fibrils, floc or mixtures thereof. When incorporated into papers, these materials can form discrete film-like particles having a film thickness of about 0.1 to 5 micrometers and a
25 minimum dimension perpendicular to that thickness of at least 30 micrometers. In one preferred embodiment, the maximum dimension of the particle perpendicular to the thickness is at most 1.5 mm. The papers used in the honeycombs, and the honeycombs themselves, have at least 30 weight percent of the thermoplastic material present in the form of
30 these discrete film-like particles. By "discrete" it is meant the particles form islands of film-like particles in a sea of high modulus fibers, and while there may be some overlap of film-like particles they do not form a continuous film of thermoplastic material in the plane of the paper. This

allows relatively full movement of any matrix resins that are used to impregnate the honeycomb cell walls made from the paper. The presence and amount of such particles in the paper and the honeycomb can be determined by optical methods, such as by inspection of a sample of
5 paper or honeycomb suitably prepared and viewed under adequate power to measure the size of the particles and count the average number of particles in a unit sample.

The thermoplastic material useful in this invention includes thermoplastic material selected from the group consisting of polyester,
10 polyolefin, polyamide, polyetherketone, polyetheretherketone, polyamide-imide, polyether-imide, polyphenylene sulfide, and mixtures thereof.

In some preferred embodiments the thermoplastic material includes polypropylene or polyester polymers and/or copolymers. In some
embodiments polyester polymer flakes and fibrils are the preferred binder;
15 however it is intended that any material that forms discrete film-like particles as described previously could be used. If a binder powder is used, the preferred binder powder is a thermoplastic binder powder such as copolyester Griltex EMS 6E adhesive powder.

The term "fibrils" as used herein, means a very finely-divided
20 polymer product of small, filmy, essentially two-dimensional particles having a length and width on the order of 100 to 1000 micrometers and a thickness only on the order of 0.1 to 1 micrometer. Fibrils are typically made by streaming a polymer solution into a coagulating bath of liquid that is immiscible with the solvent of the solution. The stream of polymer
25 solution is subjected to strenuous shearing forces and turbulence as the polymer is coagulated.

In some embodiments, the preferred thermoplastic polyester used in the paper in this invention is polyethylene terephthalate (PET) or polyethylene naphthalate (PEN) polymers. These polymers may include a
30 variety of comonomers, including diethylene glycol, cyclohexanedimethanol, poly(ethylene glycol), glutaric acid, azelaic acid, sebacic acid, isophthalic acid, and the like. In addition to these comonomers, branching agents like trimesic acid, pyromellitic acid,

trimethylolpropane and trimethylololthane, and pentaerythritol may be used. The PET may be obtained by known polymerization techniques from either terephthalic acid or its lower alkyl esters (e.g. dimethyl terephthalate) and ethylene glycol or blends or mixtures of these. PEN
5 may be obtained by known polymerization techniques from 2,6-naphthalene dicarboxylic acid and ethylene glycol.

In other embodiments, the preferred thermoplastic polyesters used are liquid crystalline polyesters. By a "liquid crystalline polyester" (LCP) herein is meant a polyester polymer that is anisotropic when tested using
10 the TOT test or any reasonable variation thereof, as described in U.S. Patent 4,118,372, which is hereby included by reference. One preferred form of LCP is "all aromatic", that is all of the groups in the polymer main chain are aromatic (except for the linking groups such as ester groups), but side groups that are not aromatic may be present. LCP useful as
15 thermoplastic material in this invention has melting point up to 350° C. Melting points are measured per test method ASTM D3418. Melting points are taken as the maximum of the melting endotherm, and are measured on the second heat at a heating rate of 10°C/min. If more than one melting point is present the melting point of the polymer is taken as
20 the highest of the melting points. A preferred LCP for this invention include corresponding grades of Zenite® available from E. I. du Pont de Nemours and Company, and Vectra® LCP available from Ticona Co.

Other materials, particularly those often found in or made for use in thermoplastic compositions may also be present in the thermoplastic
25 material. These materials should preferably be chemically inert and reasonably thermally stable under the operating environment of the honeycomb. Such materials may include, for example, one or more of fillers, reinforcing agents, pigments and nucleating agents. Other polymers may also be present, thus forming polymer blends. In some
30 embodiments, other polymers are present it is preferred that they are less than 25 weight percent of the composition. In another preferred embodiment, other polymers are not present in the thermoplastic material

except for a small total amount (less than 5 weight percent) of polymers such as those that function as lubricants and processing aids.

One embodiment of the invention is an article comprising a honeycomb made from a paper comprising high modulus fiber and thermoplastic material wherein the thermoplastic material is at least partly present in the paper in the form of discrete film-like particles. When used in articles the honeycomb can function, if desired, as a structural component. In some preferred embodiments, the honeycomb is used at least in part in an aerodynamic structure. In some embodiments, the honeycomb has use as a structural component in such things as overhead storage bins and wing to body fairings on commercial airliners. Due to the lightweight structural properties of honeycomb, one preferred use is in aerodynamic structures wherein lighter weights allow savings in fuel or the power required to propel an object through the air.

Another embodiment of the invention is a panel comprising a honeycomb made from a paper comprising high modulus fiber and thermoplastic material wherein the thermoplastic material is at least partly present in the paper in the form of discrete film-like particles. One or more facesheets may be attached to the face of the honeycomb to form a panel. Facesheets provide integrity to the structure and help to realize the mechanical properties of the honeycomb core. Also, facesheets can seal the cells of the honeycomb to prevent material from the cells, or the facesheets can help retain material in the cells. Figure 3 shows honeycomb **5** having a facesheet **6** attached to one face by use of an adhesive. A second facesheet **7** is attached to the opposing face of the honeycomb, and the honeycomb with the two opposing facesheets attached form a panel. Additional layers of material **8** can be attached to either side of the panel as desired. In some preferred embodiments face sheets applied to both sides of the honeycomb contain two layers of material. In some preferred embodiments, the facesheet comprises a woven fabric or a crossplied unidirectional fabric. In some embodiments crossplied unidirectional fabric is a 0/90 crossply. If desired, the facesheet can have a decorative surface, such as embossing or other treatment to

form an outer surface that is pleasing to the eye. Fabrics containing glass fiber and/or carbon and/or other high strength and high modulus fibers are useful as facesheet material.

In some embodiments the honeycomb can be made by methods
5 such as those described in United States Patent Nos. 5,137,768;
5,789,059; 6,544,622; 3,519,510; and 5,514,444. These methods for
making honeycomb generally require the application or printing of a
number of lines of adhesive (node lines) at a certain width and pitch on
one surface of the high modulus paper, followed by drying of the adhesive.
10 Typically the adhesive resin is selected from epoxy resins, phenolic resins,
acrylic resins, polyimide resins and other resins, however, it is preferred
that a thermoset resin be used.

After application of node lines, the high modulus paper is cut at a
predetermined interval to form a plurality of sheets. The cut sheets are
15 piled one on top of the other such that each of the sheets is shifted to the
other by half a pitch or a half the interval of the applied adhesive. Each of
the piled high modulus fiber-containing paper sheets are then bonded to
each other along the node lines by the application of pressure and heat.
The bonded sheets are then pulled apart or expanded in directions
20 perpendicular to the plane of the sheets to form a honeycomb having cells.
Consequently, the formed honeycomb cells are composed of a planar
assembly of hollow, columnar cells separated by cell walls made of paper
sheets that were bonded to each other along a number of lines and which
were expanded.

25 In some embodiments, the honeycomb is then typically
impregnated with a structural resin after it is expanded. Typically this is
accomplished by dipping the expanded honeycomb into a bath of
thermoset resin, however, other resins or means such as sprays could be
employed to coat and fully impregnate and/or saturate the expanded
30 honeycomb. After the honeycomb is fully impregnated with resin, the resin
is then cured by heating the saturated honeycomb to crosslink the resin.
Generally this temperature is in the range of 150° C to 180° C for many
thermoset resins.

The honeycomb before or after resin impregnation and curing, may be cut into slices. In this way, multiple thin sections or slices of honeycomb can be obtained from a large block of honeycomb. The honeycomb is generally sliced perpendicular to the plane of the cell edges so that the cellular nature of the honeycomb is preserved.

The honeycomb can further comprise inorganic particles, and depending on the particle shape, the particular paper composition, and/or other reasons, these particles can be incorporated into the paper during papermaking (for example, mica flakes, vermiculite, and the like) or into they may be incorporated into the matrix or structural resin (for example, silica powder, metal oxides, and the like).

Test Methods

Gurley Porosity for papers is determined by measuring air resistance in seconds per 100 milliliters of cylinder displacement for approximately 6.4 square centimeters circular area of a paper using a pressure differential of 1.22 kPa in accordance with TAPPI T460.

Fiber denier is measured using ASTM D1907. Fiber modulus, tenacity, and elongation are measured using ASTM D885. Paper density is calculated using the paper thickness as measured by ASTM D374 and the basis weight as measured by ASTM D646.

Examples

The examples below demonstrate that the discrete film-like particles of thermoplastic material can be incorporated into the final paper structure by either choosing appropriately shaped raw materials (Example 1) or by transforming the original shape of the thermoplastic material into the desired film-like shape by optimum steps in the papermaking process (Example 2). Comparative Examples 1 and 2 illustrate that if the discrete film-like particles are not incorporated in the paper composition initially, or not created in the paper during the papermaking process, the Gurley porosity numbers will be too low and the node line adhesive will easily

penetrate through the paper thickness, making difficult or impossible to prepare good quality honeycomb.

Example 1

5 An aramid/thermoplastic paper having a composition of 52 weight percent para-aramid floc, 18 weight percent para-aramid pulp, 10 weight percent polyester floc, and 20 weight percent polyester fibrids is formed on conventional wet-lay paper forming equipment with a drying section consisting of heated cylinders (cans) having a temperature of about
10 150° C. The paper therefore contains 70 weight percent high modulus fiber and 30 weight percent thermoplastic material.

 The para-aramid floc is poly (para-phenylene terephthalamide) fiber sold by E. I. du Pont de Nemours and Company of Wilmington, DE (DuPont) under the trademark KEVLAR® 49 and has a nominal filament
15 linear density of 1.5 denier per filament (1.7 dtex per filament) and a nominal cut length of 6.7 mm. This fiber has a tensile modulus of about 930 grams/denier (850 grams/dtex), a tensile strength of about 24 grams/denier (22 grams/dtex), and an elongation of about 2.5 percent. The para-aramid pulp is poly (paraphenylene terephthalamide) pulp type
20 1F361 also sold by DuPont under the KEVLAR® trade name. The polyester floc is poly (ethylene terephthalate) floc 106A75 sold by Invista Company, Wichita, KS, having a nominal filament linear density of 2.1 dpf (2.4 dtex) and a nominal cut length of 6 mm long. The polyester fibrids are obtainable from the process described in US Patent 2,999,788, example
25 176, using a co-polymer containing 80% polyethylene terephthalate and 20% of polyethylene isophthalate. The average thickness of a fibrid is about 1 micron, the minimum dimension in the filmy plane of the fibrid is about 40 micrometers, and maximum dimension in plane is about 1.3 mm.

 After forming, the paper is calendered in the nip of two metal
30 calender rolls operating at a temperature of 260° C with a linear pressure in the nip of 1200 N/cm. The final paper has a basis weight of 31 g/m², a thickness of 1.5 mils (38 micrometers), and a measured Gurley porosity of 5 seconds.

A honeycomb is then formed from the calendered paper in the following manner. Node lines of adhesive resin are applied to the paper surface with the width of the lines of adhesive being 1.78 mm. The pitch, or the linear distance between the start of one line and the next line, is 5.33 mm. The adhesive resin is a 50% solids solution comprising 70 parts by weight of an epoxy resin identified as Epon 826 sold by Shell Chemical Co.; 30 parts by weight of an elastomer-modified epoxy resin identified as Heloxy WC 8006 sold by Wilmington Chemical Corp, Wilmington, DE, USA; 54 parts by weight of a bisphenol A - formaldehyde resin curing agent identified as UCAR BRWE 5400 sold by Union Carbide Corp.; 0.6 parts by weight of 2-methylimidazole as a curing catalyst, in a glycol ether solvent identified as Dowanol PM sold by The Dow Chemical Company; 7 parts by weight of a polyether resin identified as Eponol 55-B-40 sold by Miller-Stephenson Chemical Co.; and 1.5 parts by weight of fumed silica identified as Cab-O-Sil sold by Cabot Corp. The adhesive is partially dried on the paper in an oven at 130° C for 6.5 minutes. No noticeable strike through of the adhesive is observed on the paper.

The sheet with the adhesive node lines is cut parallel to the node lines to form 50 smaller sheets. The cut sheets are stacked one on top of the other, such that each of the sheets is shifted to the other by half a pitch or a half the interval of the applied adhesive node lines. The shift occurs alternately to one side or the other, so that the final stack is uniformly vertical. The stack of sheets is then hot-pressed at 345 kPa at a first temperature of 140° C for 30 minutes and then at a temperature of 177° C for 40 minutes, causing the adhesive node lines to melt; once the heat is removed the adhesive then hardens to bond the sheets with each other. Using an expansion frame, the bonded aramid sheets are then expanded in the direction counter to the stacking direction to form cells having a equilateral cross section. Each of the sheets are extended between each other such that the sheets are folded along the edges of the bonded node lines and the portions not bonded are extended in the direction of the tensile force to separate the sheets from each other.

The expanded honeycomb is then placed in an impregnating bath containing a solution of phenolic resin PLYOPHEN 23900 from the Durez Corporation. After impregnating with resin, the honeycomb is taken out from the bath and is dried in a drying furnace using hot air. The
5 honeycomb is heated from room temperature to 82° C in this manner and then this temperature is maintained for 15 minutes. The temperature is then increased to 121° C and this temperature is maintained for another 15 minutes, followed by increasing the temperature to 182° C and holding at this temperature for 60 minutes. After that, the impregnation and drying
10 processes are repeated once more. The final honeycomb has a bulk density of about 40 kg/m³.

Comparative Example 1

A paper is made via wet-lay and calendering as in Example 1
15 except that the 30 weight percent thermoplastic material is entirely the polyester floc as mentioned in Example 1. The final paper has a basis weight of 31 g/m², a thickness of 1.6 mils (41 micrometers) and Gurley porosity of about 0.3 seconds. The porosity of this paper is such that the node line adhesive of Example 1 will penetrate through the paper and
20 prevent the expansion of a stack of sheets to make a uniform honeycomb.

Example 2

An aramid/thermoplastic paper having a composition of 50 weight percent para-aramid floc and 50 weight percent polyethylene terephthalate
25 floc is formed on conventional wet-lay paper forming equipment with a drying section consisting of a thru-air dryer operating at an air temperature of about 260° C. The paper therefore contains 50 weight percent high modulus fiber and 50 weight percent thermoplastic material. The para-aramid floc and polyester floc are the same as in Example 1. After
30 forming, the paper is calendered as in Example 1.

The final paper has a basis weight of 85 g/m², a thickness 4.0 mils (102 micrometers) and a Gurley porosity of 4 seconds. The use of high heat in the drying section partially softens or liquefies about 40 percent of

the thermoplastic polyester floc in paper, and after calendering the thermoplastic material is in the form of discrete film-like particles having a film thickness from about 0.5 to about 5 micrometers and a minimum dimension perpendicular to that thickness of at least 30 micrometers.

- 5 Node lines of same adhesive of Example 1 are applied to the paper surface as in that example, except the lines are applied at a width of 2.67 mm and a pitch of 8.0 mm. No noticeable strike through of the adhesive is observed. The steps of Example 1 are repeated to expand the honeycomb, and then impregnate the honeycomb with the same
- 10 thermoset resin as in Example 1 and then dry and cure the resin; however in this example the impregnation and drying cycle was repeated for a total of 12 times. The final honeycomb has a bulk density of about 130 kg/m³.

Comparative Example 2

- 15 A paper is made via wet-lay and calendering as in Example 1 except that the drying sections consists of a thru-air dryer operating at 150° C versus the 260° C as mentioned in Example 1. The final paper has basis weight of 85 g/m², thickness 4.0 mils (102 micrometers) and Gurley porosity 1 second. Upon inspection only about 5% of the thermoplastic
- 20 material in the final paper is in the form of discrete film-like particles having a film thickness from about 0.5 to about 5 micrometers and a minimum dimension perpendicular to that thickness of at least 30 micrometers

- Node lines of adhesive are applied to the paper surface as in Example 2, however, noticeable strike through of the adhesive is
- 25 observed. The process for making a honeycomb in Example 2 is repeated however no useable honeycomb is obtained due to difficulties in expanding the stack of sheets and the resulting significant quantity of unopened and damaged cells.

Claims

1. A honeycomb having cells comprising a paper, the paper comprising:
 - 5 a) 5 to 50 parts by weight thermoplastic material having a melting point of from 120° C to 350° C, and
 - b) 50 to 95 parts by weight of a high modulus fiber having a modulus of 600 grams per denier (550 grams per dtex) or greater, based on the total amount of thermoplastic material
10 and high modulus fiber in the paper,
wherein at least 30 percent by weight of the total amount of thermoplastic material is in the form of discrete film-like particles in the paper, the particles having a film thickness of about 0.1 to 5 micrometers and a minimum dimension perpendicular to that thickness of at least 30
15 micrometers, the film-like particles binding the high modulus fiber in the paper; and
wherein the paper has a Gurley porosity of 2 seconds or greater.
2. The honeycomb of claim 1 wherein the paper has a Gurley porosity
20 of from 2 to 20 seconds.
3. The honeycomb of claim 2 wherein the paper has a Gurley porosity of from 5 to 10 seconds.
- 25 4. The honeycomb of claim 1 wherein the high modulus fiber is present in an amount of from about 60 to 80 parts by weight.
5. The honeycomb of claim 1 wherein the thermoplastic material is present in an amount of from 20 to 40 parts by weight.
30
6. The honeycomb of claim 1 wherein the thermoplastic material has a melting point of from 180° C to 300° C.

7. The honeycomb of claim 1 wherein the maximum dimension of the particle perpendicular to the thickness is at most 1.5 mm.
8. The honeycomb of claim 1 further comprising a thermoset matrix
5 resin.
9. The honeycomb of claim 1 further comprising inorganic particles.
10. The honeycomb of claim 1 wherein the high modulus fiber
10 comprises para-aramid fiber.
11. The honeycomb of claim 10 wherein the para-aramid fiber is poly (paraphenylene terephthalamide) fiber.
- 15 12. The honeycomb of claim 1 wherein the high modulus fiber is selected from the group consisting of polybenzazole fiber, polypyridazole fiber, carbon fiber, and mixtures thereof.
13. The honeycomb of claim 1 wherein the thermoplastic material
20 comprises polyester.
14. The honeycomb of claim 1 wherein the thermoplastic material is selected from the group consisting of polyolefin, polyamide, polyetherketone, polyetheretherketone, polyamide-imide, polyether-imide,
25 polyphenylene sulfide, and mixtures thereof.
15. An article comprising the honeycomb of claim 1.
16. An aerodynamic structure comprising the honeycomb of claim 1.
30
17. A panel comprising the honeycomb of claim 1 and a facesheet attached to a face of the honeycomb.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/025704

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H13/00 D21H27/00 B31D3/02

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)
D21H B31D

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 05 278154 A (TEIJIN LTD) 26 October 1993 (1993-10-26) abstract	1,15-17
A	US 5 137 768 A (LIN PUI-YAN [US]) 11 August 1992 (1992-08-11) cited in the application the whole document	1,15-17
A	US 3 756 908 A (GROSS G) 4 September 1973 (1973-09-04) cited in the application examples	1,15
A	US 3 869 430 A (BLADES HERBERT) 4 March 1975 (1975-03-04) cited in the application examples	1,15
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Naeslund, Per

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2007/025704

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2005/068288 A (AIRBUS GMBH [DE]; MUELLER RAINER [DE]; TURANSKI PETER [DE]; OESTEREICH) 28 July 2005 (2005-07-28) the whole document -----	1
A	EP 1 329 567 A (HANKUK FIBER GLASS CO LTD [KR]) 23 July 2003 (2003-07-23) claims -----	1
A	WO 92/05950 A (DU PONT [US]) 16 April 1992 (1992-04-16) claims -----	1
A	JP 62 258801 A (DAINIPPON INK & CHEMICALS) 11 November 1987 (1987-11-11) abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2007/025704

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 5278154	A	26-10-1993	NONE	
US 5137768	A	11-08-1992	CA 2046947 A1	17-01-1992
			DE 69108623 D1	11-05-1995
			DE 69108623 T2	12-10-1995
			EP 0467286 A1	22-01-1992
			JP 3518608 B2	12-04-2004
			JP 4226745 A	17-08-1992
US 3756908	A	04-09-1973	DE 2209076 A1	07-09-1972
			FR 2127801 A5	13-10-1972
			GB 1336691 A	07-11-1973
US 3869430	A	04-03-1975	NONE	
WO 2005068288	A	28-07-2005	BR PI0506464 A	21-02-2007
			CA 2548774 A1	28-07-2005
			CN 1906081 A	31-01-2007
			DE 102004001080 A1	04-08-2005
			EP 1701880 A1	20-09-2006
			JP 2007521184 T	02-08-2007
			US 2007003733 A1	04-01-2007
EP 1329567	A	23-07-2003	JP 2002144460 A	21-05-2002
			KR 20020032221 A	03-05-2002
			US 2003126830 A1	10-07-2003
WO 9205950	A	16-04-1992	AU 656741 B2	16-02-1995
			AU 8745591 A	28-04-1992
			BR 9107260 A	22-03-1994
			CA 2092433 A1	10-04-1992
			DE 69109686 D1	14-06-1995
			DE 69109686 T2	12-10-1995
			EP 0552231 A1	28-07-1993
			ES 2073175 T3	01-08-1995
			JP 3046839 B2	29-05-2000
			JP 6510489 T	24-11-1994
			KR 176728 B1	01-05-1999
			US 5407516 A	18-04-1995
			US 5328744 A	12-07-1994
JP 62258801	A	11-11-1987	NONE	