(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 February 2012 (02.02.2012)

PCT

(10) International Publication Number
WO 2012/016234 A1

(51) International Patent Classification:
B29C 70/02 (2006.01) ***B29C 70/52*** (2006.01)

(21) International Application Number:
PCT/US2011/046097

(22) International Filing Date:
1 August 2011 (01.08.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/369,408 30 July 2010 (30.07.2010) US

(71) Applicant *(for all designated States except US)*: **OCV INTELLECTUAL CAPITAL, LLC** [US/US]; One Owens Corning Parkway, Toledo, OH 43659 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **SPOO, Kevin, J.** [US/US]; 1808 Sutton Place, Newwark, OH 43055 (US). **KONIECZKA, Keith, M.** [US/US]; 7732 County Road 13, Wauseon, OH 43567 (US).

(74) Agent: **RAULERSON, Billy, C.**; Calfee, Halter & Griswold Llp, 800 Superior Ave., Ste. 1400, Cleveland, OH 44114 (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, 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, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, 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, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, 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, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

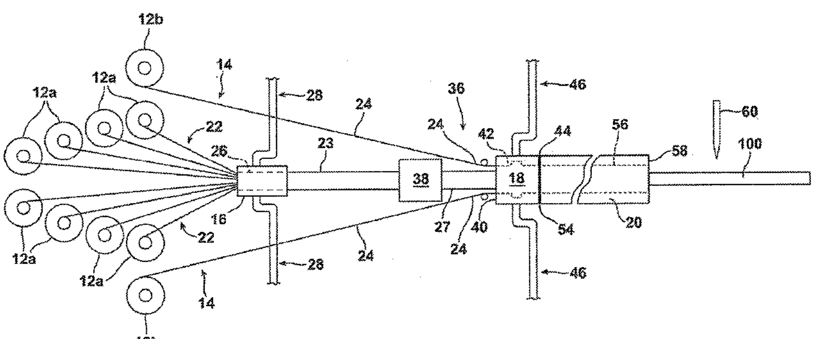
— *of inventorship (Rule 4.17(iv))*

Published:

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

(54) Title: PULTRUDED ARTICLE AND PROCESS FOR FORMING SAME

FIG. 1



(57) Abstract: A pultrusion process incorporates one or more filler materials to impart a desired functionality to the exterior of a pultruded article (100). In the process, at least one inner layer or core (23) is impregnated with a first resin material (29). The impregnated inner layer (23) may then be combined with at least one exterior layer (24) to form a reinforcement pack (36). An injection die (18) injects a resin material containing a functional filler material (74) to the outer layers (24) of the reinforcement pack (36) to the exclusion of the placement of a functional filler material (74) in the inner layers. Advantageously, the functional filler material (74) added to the external layers (24) does not displace the fibers in the continuous reinforcement material forming the exterior layers. As a result, the structural integrity of the exterior layers (24) of the pultruded article (100) is maintained and a superior and stronger end product is formed.

WO 2012/016234 A1

PULTRUDED ARTICLE AND PROCESS FOR FORMING SAME

RELATED APPLICATION

[0001] The present application claims the benefit of pending United States provisional patent application serial number 61/369,408 filed on July 30, 2010 for PULTRUDED ARTICLE HAVING A FUNCTIONAL OUTER LAYER AND PROCESS FOR FORMING SAME, the entire disclosure of which is fully incorporated herein by reference.

FIELD

[0002] The general inventive concepts relate generally to a pultrusion process, and more particularly, to a pultrusion process that utilizes an injection die to add functional fillers selectively to the exterior surface of a pultruded article.

BACKGROUND

[0003] Glass fibers are useful in a variety of technologies, and may be used in the form of continuous or chopped filaments, strands, rovings, woven fabrics, nonwoven mats, meshes, and scrims to reinforce polymers. Reinforced polymeric composites can be formed from a polymeric matrix material, reinforcing material, or any other desired components in a variety of ways. Such composites are formed using glass fiber reinforcements which provide dimensional stability and excellent mechanical properties to the resulting composites. For example, glass fibers provide dimensional stability as they do not shrink or stretch in response to changes in atmospheric conditions. Further, glass fibers have high tensile strength, heat resistance, moisture resistance, and high thermal conductivity.

[0004] Continuous glass fibers and/or glass mats are commonly used as reinforcements in pultrusion processes to form pultruded parts. Generally, pultrusion involves impregnating continuous fibers and/or continuous fibers/mat combinations with a suitable resin material and passing the impregnated fibers and/or mat through a heated die. The continuous fibers are impregnated with a liquid resin material, such as by passing the fibers through a resin bath, to wet or coat the individual fibers within the roving. The coated fibers and/or mat are then consolidated and passed through a pultrusion die where the fibers and mat are formed into a desired shape, heated, and the resin is cured to hold the fibers and mat together. The composite part exiting the heated die is then cut to a desired length. In this manner, the continuous fibers are impregnated with a polymer resin, and the resin and fibers are shaped into the form of the composite. The continuous nature of the pultrusion process advantageously enables composites of any desired length to be produced.

[0005] However, there are known problems associated with pultrusion processes that rely on resin baths. These include the use of volatile unsaturated monomers such as styrene and/or methyl methacrylate. These monomers are highly reactive and some are potent solvents. They can easily swell and degrade a binder located on the reinforcement mat, weakening the reinforcement structure. In addition, resin baths typically involve volatile organic compounds (VOCs), the emission of which is strictly monitored and limited by various governmental agencies and regulations, and compliance with these regulations can be very costly. Finally, resin baths tend to generate a significant amount of waste in the resin material, which unfavorably increases operating expenses.

[0006] As a result of these drawbacks, resin injection has been utilized to impregnate the continuous fibers during the pultrusion process. For example, as dry fiber is fed through the injection die, resin is injected such that the fibers are coated with a resin material. Initially, pultrusion processes utilized only a single resin, but over time selective impregnation of multiple reinforcement layers with different resins became a desirable feature, such as taught in U.S. Patent No. 5,783,013 to Beckman, et al., which is incorporated herein by reference in its entirety. According to the disclosure in the '013 patent, the pultruded part may have inner and outer portions with different properties (e.g., strength vs. flexibility), due to the portions being formed from two different resin materials.

[0007] Other conventional processes have added various fillers to resin mixtures used with pultruded parts. Fillers are added mainly to reduce costs, but may also provide other benefits. For example, clays or pigments may be added to improve the finish of the pultruded parts. Other fillers may impart particular properties, such as corrosion resistance, to the pultruded parts.

[0008] A problem with use of fillers, however, is that they can interfere with the formation of strong composite articles by interfering with the ability of the resin to completely impregnate the reinforcement (whether roving or mat) and sufficiently cover or encase the fibrous materials. This typically weakens the reinforcement and, ultimately, the pultruded article. Additionally, when modifications are made to the process to ensure complete impregnation of the reinforcement, the increased volume of the filler displaces some of the glass fiber which reduces the structural capability of the pultruded shape.

[0009] Conventional pultrusion processes possess many desirable attributes, such as the ability to form elongated structures of uniform cross-section and the ability to provide a pultruded part with multiple resin systems and different functionalities. However, an unmet need exists for improved pultrusion processes that overcome the aforementioned drawbacks of the conventional processes. Accordingly, there exists a need in the art for a pultrusion process that imparts specific, desired features into the resin mix and into specific locations in the pultruded part.

SUMMARY

[0010] The general inventive concepts provide a process for forming a pultruded article having a desired functionality in an outer layer. The process includes: (1) impregnating at least one first continuous reinforcement material with a first resin material *to form an impregnated inner layer; (2) contacting the impregnated inner layer with at* least one second continuous reinforcement material to form a reinforcement pack; (3) impregnating the reinforcement pack with at least one second resin material containing one or more functional filler materials to form an impregnated reinforcement pack; and (4) curing the impregnated reinforcement pack to form a pultruded article having an outer layer. The functional filler material becomes impregnated throughout the second continuous reinforcement material to impart a desired functionality to the outer layer of the pultruded article substantially without becoming impregnated in the first continuous reinforcement material.

[0011] In one or more exemplary embodiments of the general inventive concepts, the continuous reinforcement material forming the inner layer is formed of continuous glass fiber rovings and the continuous reinforcement material forming the outer layer is a glass mat, such as a continuous filament mat, a non-woven mat, or a chopped strand mat. The functional filler material desirably has a particle size that is at least half the size of the diameter of the filaments of the rovings forming the interior layer adjacent to the exterior mat. The functional filler material is positioned in the exterior surface of the pultruded article to the exclusion of the placement of the functional filler material in the inner core or layer forming the interior portion of the pultruded article. Additionally, the functional filler material in the second resin system fills the spaces within the architecture of the exterior glass mat without displacing any structural reinforcement. As a result, the structural integrity of the exterior layers of the pultruded product is maintained and a superior and stronger end product is formed. Furthermore, in accordance with the general inventive concepts, the exterior of the pultruded article may have imparted thereto a desired functionality through a selection of desired functional filler materials.

[0012] In one or more exemplary embodiments of the general inventive concepts, a process for forming a pultruded article, including the step of impregnating at least one first continuous reinforcement material with a first resin material, further comprises impregnating at least two continuous reinforcement materials -- a primary and a secondary -- with resin materials that may be the same or different and consolidating them into a combined impregnated inner layer prior to contacting the impregnated inner layer with the second continuous reinforcement material.

[0013] In one or more exemplary embodiments of the general inventive concepts, a pultruded article is provided, the pultruded article comprising: a first continuous reinforcement material impregnated with a first resin material to form an impregnated inner layer; and a second continuous reinforcement material adjacent the impregnated inner layer and impregnated with a second resin material containing at least one functional filler material to form an impregnated reinforcement pack, the impregnated reinforcement pack being shaped and cured by a die to form the pultruded article. The first and second resins are allowed to intermix at an interface where the second continuous reinforcement material lies adjacent said impregnated inner layer, and wherein the at least one functional filler material is incorporated into the second continuous reinforcement material but not the first continuous reinforcement material.

[0014] In one or more exemplary embodiments of the general inventive concepts, when the exterior layers are formed of an exterior mat, the functional filler material has a particle size that is at least half the size of the diameter of the rovings forming the interior layer adjacent to the exterior mat.

[0015] An exemplary advantage attributable to the general inventive concepts is that the filled resin material permits the inclusion of desired properties to the exterior surface of the pultruded article, without any substantial decrease in the structural capability of the external layer of the final pultruded article as a result of the inclusion of one or more filler materials into the continuous exterior layers.

[0016] Another exemplary advantage attributable to the general inventive concepts is that the first reinforcement material, e.g., rovings, acts to filter the functional filler material to keep it in the outer layer or at the exterior surface of the pultruded article, while the functional filler material fills the spaces within the architecture of the exterior mats forming the continuous exterior layers without displacing any of the structural reinforcement.

[0017] Another exemplary advantage attributable to the general inventive concepts is that less functional filler material is required to achieve the desired property compared to conventional pultrusion processes in which the filler material is distributed throughout the pultruded article. According to the general inventive concepts, the desired functional filler materials are intentionally placed in the exterior surface of the pultruded article to the exclusion of placement of the functional filler material in the inner layers.

[0018] The foregoing and other objects, features, and advantages of the general inventive concepts will appear more fully hereinafter from a consideration of the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] The general *inventive concepts will be more readily apparent upon* consideration of the following detailed disclosure, especially when taken in conjunction with the accompanying drawings wherein:

[0020] FIG. 1 is a schematic illustration of a pultrusion process utilizing an injection die to impregnate functional fillers into the exterior of the pultruded article, according to one exemplary embodiment; and

[0021] FIG. 2 is a schematic illustration of a pultrusion process utilizing an injection die to impregnate functional fillers into the exterior of the pultruded article, according to another exemplary embodiment.

[0022] FIG. 3 is a schematic cross-sectional illustration of a pultruded article, according to one exemplary embodiment.

DETAILED DESCRIPTION

[0023] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the subject matter presented herein belongs. Although other methods and materials similar or equivalent to those described herein can be used in the practice or testing of various embodiments of the general inventive concepts, the exemplary methods and materials described herein are intended to enable others to comprehend and practice the general inventive concepts. All references cited herein, including published or corresponding U.S. or foreign patent applications, issued U.S. or foreign patents, or any other references, are each incorporated herein by reference in their entireties, including all data, tables, figures, and text presented in the cited references.

[0024] In the drawings, the thickness of the lines, layers, and regions may be exaggerated for clarity. It is to be noted that like numbers found throughout the figures denote like elements. It will be understood that when an element is referred to as being "on," another element, it can be directly on or against the other element, or intervening elements may be present. It is also to be understood that the term "filler" and "filler material" may be used interchangeably herein. In addition, the terms "inner" and "interior" may be used interchangeably; "outer" and "exterior" may be used interchangeably; and "functional" and "functionalized" may be used interchangeably.

[0025] "Continuous" as used herein means that the material is or contains unidirectional fibers that may extend for the complete length of a pultruded article. Continuous fibers are produced in reels or packages typically extending from at least 100 feet up to or exceeding tens of thousands of feet in length. Such materials are generally wound onto creels, spools, cakes, bobbins or the like, and stored until used. "Continuous" may refer to individual or grouped unidirectional fibers, as in filaments, strands or rovings, such as Type 30® Single End rovings, available from Owens Corning, Toledo, OH; or to 2-dimensional or 3-dimensional matrices of such continuous fibers with other discontinuous fibers, such as veils and mats.

[0026] The general inventive concepts encompass a pultrusion process that incorporates one or more functional filler materials that impart a desired functionality to the exterior of the pultruded article. In one exemplary embodiment of the pultrusion process, a first resin is used to wet the reinforcements with the exception of the exterior layers. This impregnated reinforcement material, together with the "dry" exterior layers, then passes to an injection die where a resin containing the functional filler material is injected into the exterior layers. As a result, the exterior of the pultruded article has imparted thereto a desired functionality through the selection of the filler materials.

[0027] The pultrusion process is useful for manufacturing a wide variety of pultruded articles, including but not limited to window and door frames, automobile, truck and bus parts, ladders, grating, utility poles, and building panels. It is particularly well suited for manufacturing pultruded articles where a certain functionality is desired but where the loss of strength caused by the use of most fillers would not be satisfactory.

[0028] A resin-injected pultrusion process, according to one exemplary embodiment of the general inventive concepts is depicted generally in Fig. 1. In the disclosed process, two separate resin systems are utilized to form the final pultruded article. As shown in Fig. 1, spools 12a, 12b provide continuous reinforcement materials 14, 22, respectively, which are utilized to form a pultruded part 100. Specifically, spools 12a supply continuous reinforcement material 22 that form the inner layers 23 in the reinforcement pack 36 and spools 12b supply continuous reinforcement material 14 that form the outer layers in the reinforcement pack 36. It is to be appreciated that although ten total spools are illustrated, more or fewer spools may be utilized to form the pultruded article 100.

[0029] The continuous reinforcement materials 14, 22 may take many shapes and forms. They may have individual fibers or fibers grouped into bundles (or some of both); they may be in the form of 2-dimensional, essentially mono-layer matrices or 3-dimensional, lofted matrices (or some of both); their fibers may be unidirectional or multi-directional (or some of both); and they may include continuous or discontinuous fibers (or some of both). However, for pultrusion, at least some of the reinforcement material fibers must be continuous and unidirectional in order to be "pulled" through the processing equipment as is characteristic of pultrusion. Continuous, unidirectional reinforcements include fibers, rovings, bundles of fibers, and yarns; and multi-directional reinforcements include mats, polymer cloths, veils, fabrics, or combinations thereof A continuous reinforcement may have multiple types and orientations of fibers, e.g., rovings embedded in a fibrous mat.

[0030] The fibers, either individually or forming the fibrous structures, may be any type of continuous glass fiber, such as A-type glass fibers, C-type glass fibers, E-type glass fibers, R-type glass fibers, S-type glass fibers, E-CR-type glass fibers (e.g., Advantex® glass fibers commercially available from Owens Corning). The diameter of filaments making up glass rovings are typically within the range of 11 to 32 microns, but may range from about 8 to 40 microns or even fall outside this range.

[0031] The continuous fibers may also include or be mineral fibers, carbon fibers, ceramic fibers, natural fibers, and/or synthetic fibers. The term "natural fiber" as used in conjunction with the general inventive concepts refers to plant fibers extracted from any part of a plant, including, but not limited to, the stem, seeds, leaves, roots, or bast.

Examples of natural fibers suitable for use as the reinforcing fiber material include basalt, cotton, jute, bamboo, ramie, bagasse, hemp, coir, linen, kenaf, sisal, flax, henequen, and combinations thereof. The term "synthetic fibers" as used herein is meant to indicate any man-made fiber having suitable reinforcing characteristics, such as, for example, polyester, polyethylene, polyethylene terephthalate, polypropylene, polyamide, aramid, and/or polyaramid fibers.

[0032] The interior layer or core 23 and the outer layer 14 need not, and typically will not, be identical. In one or more exemplary embodiments of the general inventive concepts, the outer continuous reinforcement material 14 is a fibrous mat structure formed from glass fibers (e.g., a continuous filament mat into which the functional filler materials can penetrate) and the continuous reinforcement material 22 that forms the interior layers 23 is a plurality of continuous glass fiber rovings.

[0033] Referring to Fig. 1, the continuous reinforcement material 22 forming the inner layers 23 passes through the impregnation die 16 where the reinforcement material 22 is impregnated with at least one first resin material 29 (not shown in Fig 1). The impregnation die 16 generally contains a passageway 26 for passing the continuous reinforcement material 22 forming the inner layers 23 therethrough. A resin supply system 28 in fluid communication with the impregnation die 16 supplies a first resin material 29 to the die 16. Additional resin supply systems may also be coupled to the impregnation die 16 to supply additional resin materials as desired. Desirably, the resin material is supplied to the impregnation die 16 at a constant or substantially constant pressure. The impregnated interior layers may then be fed through a shaping die 38, where excess resin is removed and the layers are shaped into a consolidated structure 27.

[0034] After the inner layers exit the shaping die 38, the consolidated structure 27 is combined with the outer layers 24 to form a reinforcement pack 36. The reinforcement pack 36 then enters into an injection die 18, which generally includes an entry portion 40, an internal passageway 42, and an exit portion 44. In operation, the reinforcement pack 36 enters the injection die 18 through the entry portion 40 and moves into the internal passageway 42. As the reinforcement pack 36 passes through the injection die 18, the pack 36 is compressed and impregnated with a second resin material.

[0035] In the exemplary embodiment illustrated in Fig. 1, the injection die 18 is sealingly coupled or integrally formed with the curing die 20. Therefore, as the impregnated reinforcement pack 36 exits the injection die 18, it immediately enters the curing die 20. As a result, the impregnated reinforcement pack is not exposed to the atmosphere or the surrounding environment, which could expose the reinforcement pack to unwanted contaminants. In addition, the impregnated reinforcement pack 36 is maintained under constant pressure, thereby minimizing any unwanted expansion. In another exemplary embodiment (not illustrated), the injection die 18 is separate from and not coupled to the curing die 20 or any other die. Such an independent injection die 18 acts to provide the same function, namely to inject at least one second resin material into the impregnated reinforcement pack 36.

[0036] The second resin material is supplied to the injection die 18 by one or more second resin supply systems 46. Similar to the first resin supply system 28, the second resin supply system 46 is in fluid communication with the injection die 18 and the resin is fed to the injection die 18 under constant or substantially constant pressure. One or more resin systems may be utilized to inject multiple resins into the injection die 18. Inside the die 18, the second resin material 47 saturates and impregnates the outer layers 24 and contacts the inner layers 23 of the impregnated reinforcement pack 36. As discussed herein, a functional filler material 74 within the second resin material 47 is unable to enter or pass through the inner layers 23. The first and second resin materials 29, 47 may be the same or different. When the resin materials 29, 47 are different, different properties can be imparted to the inner and outer layers 23, 24.

[0037] In an exemplary embodiment, depicted in Fig. 3, the second resin material 47 is applied to the outer reinforcement material 14 before the first resin material 29 has had time to substantially cure. By applying the second resin material 47 before the curing of the first resin material 29, the first and second resin materials have the ability to combine or mix at the adjacent interior and exterior layers 23, 24 as shown, for example, at A and A' in Fig. 3. As a result, a portion of the first resin material 29 may migrate into one or more of the exterior layers 24 while a portion of the second resin material 47 (exclusive of the filler material 74) migrates into one or more of the interior layers 23. This migration and intermixing of resin materials reduces the likelihood of voids or zones of little or no resin material at the interface between the interior and exterior layers 23, 24. Voids or zones of little or no resin material tend to weaken the final pultruded article and decrease its overall performance. In addition, impregnation of the pack 36 with the second resin material 47 prior to the first resin material 29 fully curing results in superior bonding of adjacent or interface interior and exterior layers 23, 24. Notably, no functional filler material 74 passes into the inner layer 23 or contacts the inner continuous reinforcement material 22.

[0038] The steps of the adding reinforcement material and impregnating with resin to form multilayer reinforcement packs may be repeated if desired to create third and subsequent reinforced layers, so long as at least one layer, usually the outermost layer, contains a functionalized filler material.

[0039] Resins useful for pultruded articles are well known to those skilled in the art. Generally, such resins are selected from among polyesters, polyvinyl esters, polyurethanes, epoxy resins and phenolic resins. Suitable thermoplastic resins include, for example, unsaturated polyester resins based on maleic-5 anhydride, isophthalic acid, terephthalic acid, orthophthalic acid, dicyclopentadiene, and vinyl ester chemistries. Other suitable resins include polyamides, copolyamides polyolefins and polyetherketoneketone (PEKK). The resin in the inner layer 23 may be the same or different from the resin in the outer layer 24.

[0040] Unlike the first resin material 29 that impregnates the inner layers 23 with only a resin material, the second resin material 47 contains one or more functionalized filler materials 74. Filler materials may conveniently be categorized into groups according to the purpose for which they are included in a pultruded article. By way of example, fillers may be divided into three broad groups, although such categorizations are generalizations and overlaps are likely to occur: (1) fillers that are primarily cost-reducers and essentially impart no other intended or desired property; (2) fillers that are selected to impart a particular aesthetic finish to the pultruded article, such as pigments and smoothing fillers; and (3) fillers that are selected to impart desired physical or mechanical properties.

[0041] A "functionalized filler material," as used herein, is a compound or material, or combinations of compounds or materials, that fall into the third category, and are selected for their ability to impart a particular or desired mechanical or physical feature or property to the pultruded article or to at least its outer layer. While color and smoothness might be considered a "desired" physical property, they are nonetheless excluded from the definition of "functionalized fillers" for purposes of this application, unless such filler also has a desired functional property and could also be classified in the third category.

[0042] Examples of fillers of the first type include calcium carbonate, wood flour, fly ash and recycled plastic grinds. Examples of fillers of the second type include clays like kaolin or talc; and pigments like carbon black, titanium dioxide, as well as all other pigments.

[0043] Functionalized filler materials 74 of the third type may be further divided and categorized based on the property or feature they impart; and further still on the mechanism by which they achieve that purpose. Thus, functionalized fillers may be fire or flame retardants, electrical conductors or insulators, corrosion resistors, density increasors or decreasors, and the like. Flame retardant fillers may function by releasing water, free radical scavenging, char formation catalysts or insulators, or smoke suppressants. Density increasors generally act by adding highly dense filler materials, and density decreasors work by adding lower density material, generally by entrapping air or other gas within the filler. Density decreasors may be organic or inorganic. Typically, density decreasors afford lighter weight pultruded articles without loss of strength. Some specific examples of density decreasor functionalized fillers are given in Table 1. Some specific examples of flame retardant functionalized fillers are given in Table 2.

[0044] **Table 1: Density decreasor functionalized fillers**

Type	Material	Typical usage concentration	Tradename (Supplier)
Organic (Henkel)	polymeric (acrylonitrile co-polymer or polyvinylidene chloride)	0 - 10% by wt.	Dualite™
Inorganic (Silbrico	perlite	0 - 15% by wt.	Silcell™ Corp)
Inorganic (3M)	glass microspheres	0 - 15% by wt.	Scotchlite™
Inorganic	ceramic microspheres	0 - 15% by wt.	__(3M)

[0045] **Table 2: Flame retardant functionalized fillers**

Mechanism	Material	Typical usage concentration	Tradename (Supplier)
-Water releasing agents	Metal oxides, eg MgOH Alumina trihydrate (ATH)	20 - 60% by wt.	Hymod™ or Micral™(Huber Engineered Minerals)
-Free radical scavengers	Bromine or chlorine-containing organic compounds, e.g., Decabromo-	10 - 25% by wt. based on halogen content.	DE83R (Chemtura) Hetron 1540

	diphenyl ether; Decabromo-diphenyl oxide; Hexabromocyclo-dodecane; Tetrabromobisphenol A		(Ashland)
Halogen synergists	Antimony trioxide	2 - 5% based on Sb_2O_3 content	_____,(Plasticolors) Nyacol™(Nyacol NanoTechnologies)
	Antimony pentoxide	2 - 7% based on Sb_2O_5 content	
Char forming	Phosphorous containing intumescents	5 - 25% based on elemental phosphorous content	Mel-Ban™(Hummel catalysts Croton) Exolit™ (Clariant)
Char forming insulators	Expanded graphite	0 - 5% by wt.	
Smoke suppressants	Zinc borate	1 -7% by wt.	Firebrake™(US Borax)

[0046] In addition, although the second resin 47 is likely, to some extent, impregnate the reinforcement material in both the inner and outer layers 23, 24, the functional filler material 74 is impregnated into and remains in the exterior layers 24 only. As a result, the functionalized fillers can impart their intended properties to the outer layer 24 without significantly impacting the strength of the pultruded part 100, as in the case of conventional pultrusion processes, and do not require having to cure the first resin layer before applying the second resin. This is important to allow the two resin layers to intermix and bond together more strongly as previously discussed. Without intending to be bound by any particular theory, it is believed this occurs as a result of two factors. First, in impregnating the first resin into the reinforcement materials, sufficient pressure is applied to force the resin into all the crevices and air spaces around the reinforcement fibers, thus leaving no voids or gaps into which filler might enter. Second, by selecting functionalized fillers of a certain size (discussed herein), it has been found that the fillers completely impregnate the second reinforcement matrix, but are unable to enter and impregnate the first reinforcement layer.

[0047] In some exemplary embodiments, the continuous reinforcement material 14 is a mat, such as a continuous filament mat or chopped strand mat. Additionally, the functional filler material 74 has a particle size that is at least half the size of the diameter of the filaments of the continuous, unidirectional reinforcement materials 22 (e.g., rovings) forming the interior layers 23 adjacent to the exterior mat 14. Utilizing a particle size that is greater than or equal to half the size of the diameter of the reinforcement materials 22 restricts the flow or entry of the functional filler material 74 into the reinforcement materials 22, thereby leaving the functional filler material 74 in the exterior surface of the pultruded article. Thus, the rovings act to filter the resin material such that the resin itself can pass into the inner layers or cores but the functional filler material 74 is forced to remain in the outer layers.

[0048] Also, the functional filler material 74 in the second resin system 47 fills the spaces within the architecture of the exterior mat 14 without substantially displacing any structural reinforcement therein. As used herein, the term "substantially displacing" or "substantial displacement" is meant to denote that there is no displacement of the structural reinforcement or almost no displacement of the structural reinforcement so as not to reduce the structural performance of the pultruded article. As a result of this lack of displacement of the structural reinforcement within the outer layers, the structural integrity of the exterior layers of the pultruded product is maintained and a superior and stronger end product is formed, particularly when compared to conventional pultruded articles where the filler materials displace fibers and reduce the structural capability of the final pultruded article. In addition, because the functional filler material 74 is not integrated into the roving 22, the pultruded article retains its structural integrity and strength.

[0049] The functional filler material 74 may have a median particle size from about 2 microns to about 1000 microns, and in some exemplary embodiments, from about 8 microns to about 300 microns. By contrast, sizes of the reinforcement matrix (e.g., about 11-32 microns) are often significantly smaller than this. In addition, the functional filler material 74 may be present in the second resin material in an amount from about 2 to about 60% by weight, and in some exemplary embodiments in an amount from about 5 to about 35% by weight, of the second resin material 47.

[0050] Turning back to Fig. 1, once the impregnated pack leaves the impregnation die 18, it enters the curing die 20 where the impregnated pack is shaped and cured into its final intended shape to form the final pultruded article 100. The curing die 20 may contain an entry 54, a central passage 56, and an exit 58. Additionally, in some exemplary embodiments, the pultruded article 100 may be cut by a cutting apparatus 60 located externally and downstream from the curing die 20. Conventional pulling means (not shown) are provided downstream from the curing die 20 for pulling the reinforcement materials 14, 22 from the spools 12a, 12b sequentially through the impregnation die 16, the shaping die 38, the impregnation die 18, and the curing die 20.

[0051] In another exemplary embodiment, depicted in Fig. 2, multiple resins may be applied to different sets of layers within a reinforcement pack to impart differing properties across the final pultruded product. As shown in Fig. 2, spools 13a and 13b provide primary and secondary first reinforcement materials 62, 64 that are utilized to form a pultruded part 110. The primary first continuous reinforcement materials 62 pass through a first impregnation die 66 and the secondary first continuous reinforcement materials 64 pass through a second impregnation die 68. The first and second impregnation dies 66, 68 perform a similar function to the impregnation die 16 described herein. Also, the primary and secondary first reinforcement materials 62, 64 may be any of the reinforcement materials described herein. In some exemplary embodiments, the first reinforcement materials 62, 64 are continuous glass fiber rovings. The impregnation die 66 impregnates the primary first reinforcement materials 62 with a resin material and the impregnation die 68 impregnates the secondary first reinforcement materials 64 with a resin material to form inner layers 67, 69, respectively, which are then combined. The resin material injected into the first impregnation die 66 is desirably different from the resin material injected into the second injection die 68 so as to provide differing properties to the two inner layers 67, 69. However, in some exemplary embodiments, the resins could be the same or provide the same property. The interior layers may be further divided into sub-layers (not illustrated). When these sub-layers are present and each of the sub-layers is to be separately impregnated, an equivalent number of impregnation dies may be utilized. In addition, the multiple impregnation dies may be provided in series, such as, for example, the first interior layer may be impregnated in a first impregnation die with a first resin material and then impregnated with a second resin material in a second impregnation die that is located downstream from the first impregnation die.

[0052] The impregnated inner layers 67, 69 are combined and fed into a shaping die 38 where the excess resin is removed and the layers are shaped into a consolidated structure 71. The second reinforcement materials 14 forming the outer layers 24 are unwound from spools 13 and are combined with the consolidated structure 71 to form a reinforcement pack 70. The reinforcement pack 70 is then passed through an injection die 18, which, as discussed herein, provides a second resin material (third in discussion sequence) that includes at least one filler material to impart a desired functionality to the surface of the pultruded part 110. The impregnated reinforcement pack is then passed through a curing die 20 where the impregnated pack is shaped and cured into its final intended shape and form the final pultruded article 110. In one or more exemplary embodiments, the pultruded article 110 may be cut into segmented pieces with a cutting apparatus 60.

[0053] As discussed herein, the filled resin material (e.g., functional filler material in the exterior layers) provides for the inclusion of desired properties to the exterior surface or outer layer of the pultruded article. Thus, the general inventive concepts provide a process for the inclusion of a desired functional filler material in the exterior surface of the pultruded article to the exclusion of the placement of the filler material in the inner layers. Indeed, the filler materials are intentionally placed in the exterior layers as a result of the process. An exemplary advantage provided by the general inventive concepts is that the functional fillers added to the external layers do not displace any structural reinforcement, and as a result, there is no substantial decrease in the structural capability of the external layer, and consequently, the pultruded part. In addition, the filler material on the exterior surface of the pultruded article eliminates the need for a post-finish (such as by painting).

[0054] The general inventive concepts have been described and illustrated herein by way of various exemplary embodiments. Nonetheless, a wide variety of alternatives would be known or otherwise apparent to those of skill in the art based on this disclosure and, thus, are considered to fall within the general inventive concepts.

What is claimed is:

1. A process for forming a pultruded article having a desired functionality in an outer layer, said process comprising:

impregnating a first continuous reinforcement material with a first resin material to form an impregnated inner layer;

contacting said impregnated inner layer with a second continuous reinforcement material to form a reinforcement pack;

impregnating said reinforcement pack with a second resin material containing one or more functional filler materials to form an impregnated reinforcement pack; and

curing said impregnated reinforcement pack to form a pultruded article having an outer layer, wherein said functional filler material becomes impregnated throughout said second continuous reinforcement material to impart a desired functionality to the outer layer of said pultruded article without becoming substantially impregnated in said first continuous reinforcement material.

2. The process of claim 1, wherein impregnating the reinforcement pack comprises passing the reinforcement pack through an injection die; and said curing step comprises passing the reinforcement pack through a curing die.

3. The process of claim 1, wherein said functional filler material is present in said second resin material in an amount from about 2-60% by weight of said second resin material.

4. The process of claim 3, wherein said functional filler material is one or more of a fire retardant, a flame retardant, a smoke suppressor, an electrical conductor, an electrical insulator, a corrosion resistor, a density increasor, a density decreasor, and combinations thereof.

5. The process of claim 4, wherein said functional filler material is a flame retardant including one or more of a water releasing agent, a free radical scavenger, a halogen synergist, a char forming catalyst, a char forming insulator, and combinations thereof.

6. The process of claim 1, wherein said first continuous reinforcement material is a continuous glass fiber roving having a plurality of individual filaments, and said second continuous reinforcement material is a glass mat.

7. The process of claim 6, wherein said one or more functional filler materials has a particle size that is greater than half the diameter of the filaments forming said glass fiber roving.

8. The process of claim 7, wherein said particle size restricts entry of said functional filler material into said roving to retain said functional filler material in said glass mat.

9. The process of claim 6, wherein said functional filler material fills spaces within said glass mat without substantially displacing any structural reinforcement material therein.

10. The process of claim 6, further comprising passing said impregnated inner layer through a shaping die to from a consolidated structure; and contacting said consolidated structure with said at least one second continuous reinforcement material to form said reinforcement pack.

11. The process of claim 1, wherein said one or more functional filler materials has a particle size that restricts entry of said functional filler material into said first continuous reinforcement material to retain said functional filler material in said a second continuous reinforcement material.

12. The process of claim 2, wherein said injection die is distinct from said curing die.

13. The process of claim 1, wherein said step of impregnating at least one first continuous reinforcement material with a first resin material further comprises impregnating at least two continuous reinforcement materials with corresponding resin materials and consolidating them into a combined impregnated inner layer prior to

contacting said impregnated inner layer with the second continuous reinforcement material.

14. The process of claim 13, wherein said functional filler material is present in said second resin material in an amount from about 2-60% by weight of said second resin material.

15. The process of claim 13 further comprising passing said combined impregnated first inner layer through a shaping die to from a consolidated structure; and contacting said consolidated structure with said at least one second continuous reinforcement material to form said reinforcement pack.

16. The process of claim 13, wherein the corresponding resin materials used to impregnate said at least two first continuous reinforcement materials are different from one another.

17. The process of claim 13, wherein said first continuous reinforcement material is a continuous glass fiber roving having a plurality of individual filaments, and said second continuous reinforcement material is a glass mat.

18. The process of claim 17, wherein said one or more functional filler materials has a particle size that is greater than half the diameter of the filaments forming said glass fiber roving.

19. The process of claim 18, wherein said one or more functional filler materials fill spaces within said glass mat without substantially displacing any structural reinforcement material therein.

20. The process of claim 13, wherein said one or more functional filler materials is one or more of a fire retardant, a flame retardant, a smoke suppressor, an electrical conductor, an electrical insulator, a corrosion resistor, a density increasor, a density decreasor, and combinations thereof.

21. A pultruded article comprising:

a first continuous reinforcement material impregnated with a first resin material to form an impregnated inner layer; and

a second continuous reinforcement material adjacent the impregnated inner layer and impregnated with a second resin material containing at least one functional filler material to form an impregnated reinforcement pack,

wherein said impregnated reinforcement pack is shaped and cured by a die to form a pultruded article;

wherein said first and second resins are allowed to intermix at an interface where the second continuous reinforcement material lies adjacent said impregnated inner layer, and

wherein said at least one functional filler material is incorporated into the second continuous reinforcement material but not the first continuous reinforcement material.

22. The pultruded article of claim 21, wherein said first continuous reinforcement material is a continuous glass fiber roving having a plurality of individual filaments, and said second continuous reinforcement material is a glass mat.

23. The pultruded article of claim 22, wherein said at least one functional filler material has a particle size that is greater than half the diameter of the filaments forming said glass fiber roving.

24. The pultruded article of claim 21, wherein said at least one functional filler material is present in said second resin material in an amount from about 2-60% by weight of said second resin material.

25. The pultruded article of claim 24, wherein said at least one functional filler material is one or more of a fire retardant, a flame retardant, a smoke suppressor, an electrical conductor, an electrical insulator, a corrosion resistor, a density increasor, a density decreasor, and combinations thereof.

26. A process for forming a pultruded article having a plurality of different properties across the pultruded article, said process comprising:

providing a primary first continuous reinforcement material from a first spool,

providing a secondary first continuous reinforcement material from a second spool, impregnating said primary first continuous reinforcement material with a first resin material through a first impregnation die to form a first impregnated inner layer;

impregnating said secondary first continuous reinforcement material with a second resin material through a second impregnation die to form a second impregnated inner layer;

feeding said first and second impregnated inner layers into a shaping die to form a consolidated impregnated inner layer;

contacting said consolidated impregnated inner layer with at least one second continuous reinforcement material to form a reinforcement pack;

impregnating said reinforcement pack with at least one third resin material containing one or more functional filler materials to form an impregnated reinforcement pack; and

curing said impregnated reinforcement pack to form a pultruded article having an outer layer including said functional filler material, wherein said one or more functional filler materials impart a desired functionality to the outer layer of said pultruded article.

FIG. 1

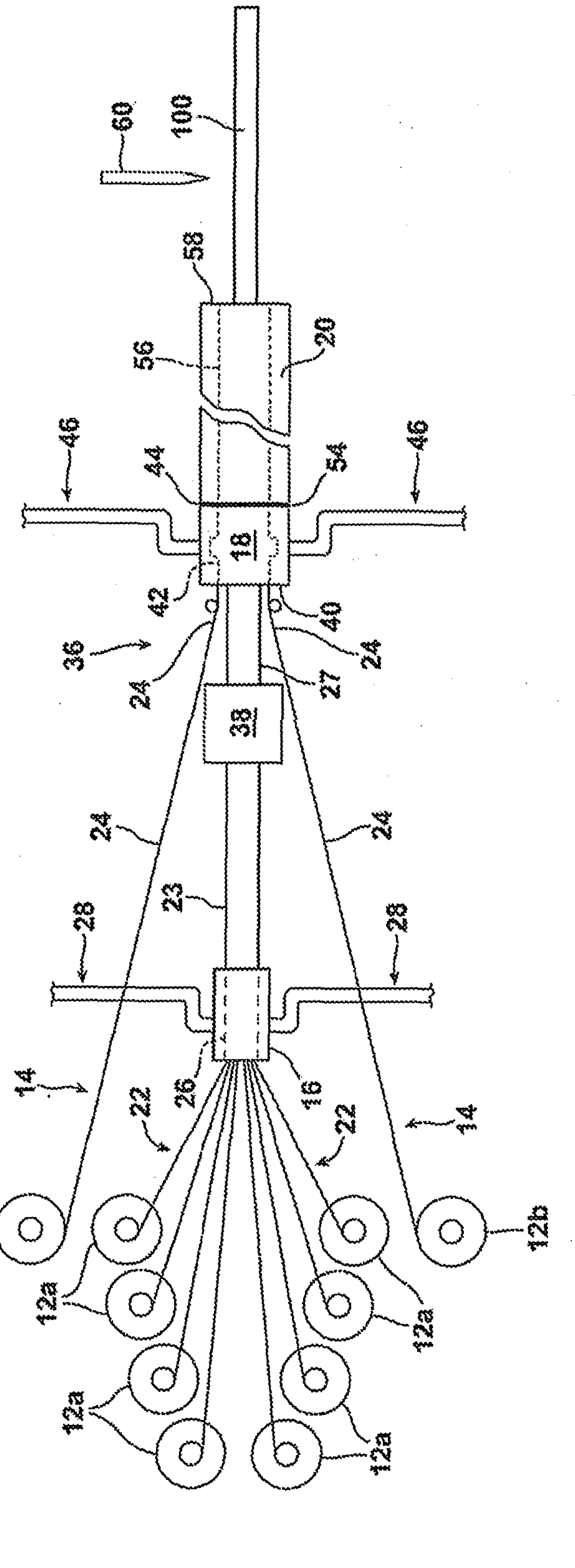
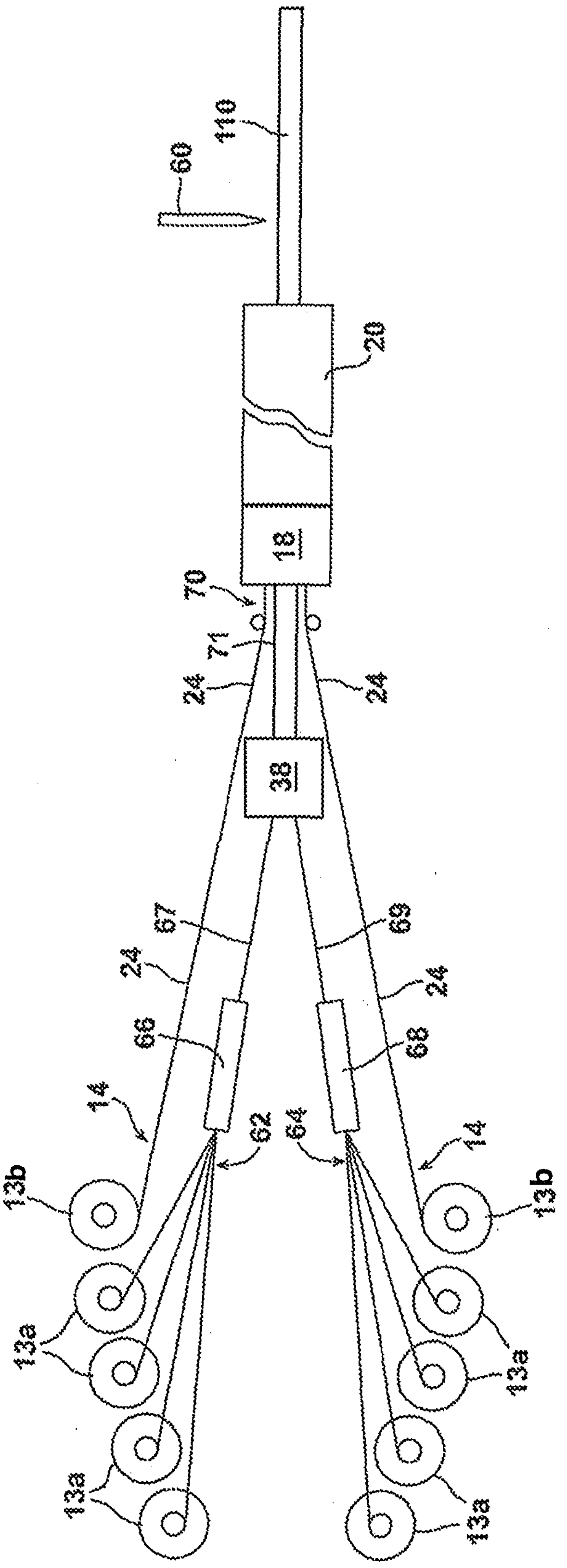

60
100
58
56
20
46
44
54
46
18
42
40
36
24
24
27
38
24
24
23
28
28
14
26
16
22
22
14
12b
12a
12a
12a
12a
12b

FIG. 2


110
60
20
18
70
71
24
24
38
67
69
24
24
66
68
14
62
64
14
13b
13b
13a
13a
13a
13a

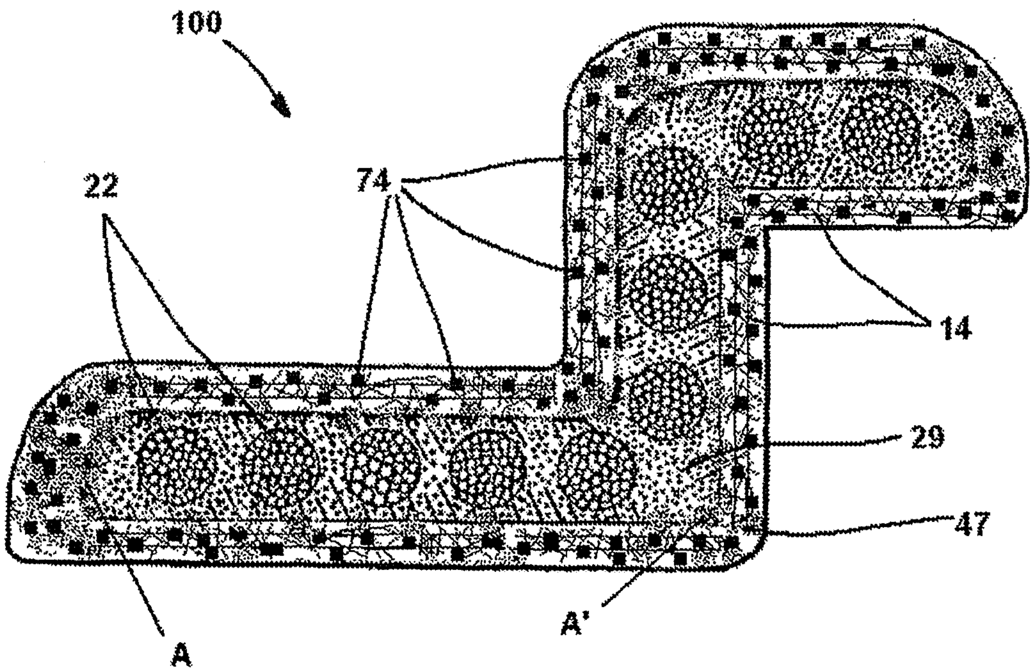


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/046097

A. CLASSIFICATION OF SUBJECT MATTER
INV. B29C70/02 B29C70/52
ADD.

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)
B29C

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.
X	US 2009/023870 A1 (BERKSOY EBISE MUALLA [CA] ET AL) 22 January 2009 (2009-01-22)	1-4,6, 12-17, 20-22, 24-26
Y	paragraph [0065]; figures 1-3 paragraph [0071] paragraph [0083] - paragraph [0089] paragraph [0101] - paragraph [0102] paragraph [0107] - paragraph [0108] -----	5,7-11, 18,19,23
Y	US 5 262 212 A (WATERS WILLIAM D [US]) 16 November 1993 (1993-11-16) abstract column 8, line 32 - column 9, line 41 column 3, line 33 - line 35 ----- -/--	5,7-9, 11,18, 19,23

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

[X] 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 document 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	Date of mailing of the international search report
20 October 2011	03/11/2011

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

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 5 783 013 A (BECKMAN JAY J [US] ET AL) 21 July 1998 (1998-07-21) cited in the application column 1, line 57 - column 2, line 34; figures 1-4 column 5, line 6 - column 6, line 67 -----	1-4,21, 24,25 5,7-10
X A	US 6 221 295 B1 (KAISER MARK A [US] ET AL) 24 April 2001 (2001-04-24) column 7, line 6 - line 33; figure 1 column 12, line 43 - column 14, line 64 -----	21,24,25 1,26
Y	"Advances in ATH benefit composite products", REINFORCED PLASTICS, ELSEVIER ADVANCED TECHNOLOGY, NEW YORK, NY, US, vol. 47, no. 8, 1 September 2003 (2003-09-01), pages 44-46, XP004456309, ISSN: 0034-3617 the whole document -----	5,7-9, 11,18, 19,23
Y	J.M. Huber Corporation: "MoldX Alumina Trihydrate", , 31 December 2008 (2008-12-31), pages 1-6, XP55009925, Online Retrieved from the Internet: URL:http://web.archive.org/web/20100308021 024/http://hubermaterials.com/saleslit/mol dxbrochurehubermaterials.pdf [retrieved on 2011-10-19] the whole document -----	5,7-9, 11,18, 19,23

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2011/046097

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 2009023870	A1	22-01-2009	CA	2641050	A1	16-08-2007
US 5262212	A	16-11-1993	NONE			
US 5783013	A	21-07-1998	CN	1187157	A	08-07-1998
			DE	69626817	D1	24-04-2003
			DE	69626817	T2	24-12-2003
			EP	0831988	A1	01-04-1998
			JP	H11512980	A	09-11-1999
			TW	393394	B	11-06-2000
			WO	9640489	A1	19-12-1996
US 6221295	B1	24-04-2001	US	2002031664	A1	14-03-2002
			US	6316074	B1	13-11-2001