



- (51) International Patent Classification:
C08K 3/00 (2006.01) C08J 3/20 (2006.01)
C08K 3/38 (2006.01)
- (21) International Application Number: PCT/US2013/060617
- (22) International Filing Date: 19 September 2013 (19.09.2013)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
61/702,776 19 September 2012 (19.09.2012) US
13/828,742 14 March 2013 (14.03.2013) US
- (71) Applicants: MOMENTIVE PERFORMANCE MATERIALS INC. [US/US]; 260 Hudson River Road, Waterford, NY 12188 (US). LIN, Kang, Yi [—/US]; 7659 Normandie Boulevard, Apt. 612, Middleburg Heights, OH 44130 (US).
- (72) Inventors: RAMAN, Chandrashekar; 5523 Waterford Circle, Sheffield Village, OH 44035 (US). XIANG, Bei; 14579 Polo Club Drive, Strongsville, OH 44136 (US). MURUGAIAH, Anand; 16075 Fox Hunt Drive, Strongsville, OH 44136 (US).
- (74) Agent: SLABY, Scott, M.; McDonald Hopkins LLC, 600 Superior Avenue, East, Suite 2100, 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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, 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, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: COMPOSITIONS COMPRISING EXFOLIATED BORON NITRIDE AND METHOD FOR FORMING SUCH COMPOSITIONS

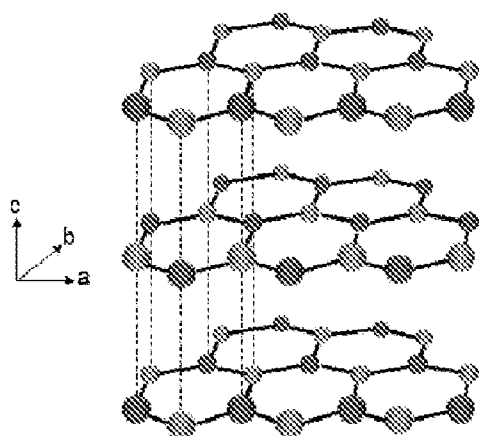


FIGURE 1

(57) Abstract: A composition comprising exfoliated boron nitride crystals dispersed in a resin matrix and a method of forming such compositions comprises the in situ exfoliation of boron nitride crystals by compounding boron nitride crystals in a resin material with a hard filler material having a hardness greater than the hardness of the boron nitride crystals.



Published:

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

— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

COMPOSITIONS COMPRISING EXFOLIATED BORON NITRIDE AND METHOD FOR
FORMING SUCH COMPOSITIONS**CROSS REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 61/702,776 entitled "Composition Comprising Exfoliated Boron Nitride And Method For Forming Such Compositions" filed on September 19, 2012, and U.S. Application No. 13/828,742 entitled "Composition Comprising Exfoliated Boron Nitride And Method For Forming Such Compositions" filed on March 14, 2013, each of which is hereby incorporated in its entirety by reference.

FIELD

[0002] The present invention relates to compositions comprising boron nitride, in particular compositions comprising exfoliated boron nitride, and methods for making such compositions. The present invention also relates to a method for forming a thermally conductive composition comprising boron nitride via the in situ exfoliation of boron nitride in a resin material.

BACKGROUND

[0003] Thermal management of various electronic and opto-electronic devices is increasingly gaining attention due to the severe challenges faced in such devices. The trend of shrinking sizes and increased functionality continues in personal hand-held electronic devices. The power density, and hence the density of heat that needs to be dissipated have significantly increased, which poses significant challenges to providing good thermal management in those devices. Similarly, in opto-electronic devices, also known as light emitting diodes (LEDs), the power consumption and lumen output is ever increasing. Thermal management problems are also widely prevalent in other applications such as electronic components in automobiles, rechargeable battery systems and power invertors for hybrid vehicles, etc. Insufficient or ineffective thermal management can have a strong and deleterious effect on the performance and long-term reliability of devices.

[0004] Currently, LED-based bulbs are being used to replace older bulbs and are designed to fit into conventional “Edison” sockets. Fitting LED bulbs into Edison sockets only exacerbates the thermal management challenges since the heat dissipation is limited by natural convection. LED bulbs therefore require well-designed heat sinks to efficiently and adequately dissipate the waste heat. Inefficient thermal management leads to higher operating temperatures of the LEDs, which is indicated by the junction temperature (T_j) of the LED. The lifetime of an LED (defined as time taken to lose 30% light output, i.e., to reach B30) can possibly decrease from 80,000 hours to 20,000 hours when the junction temperature is increased from 115 °C to 135 °C.

[0005] Aluminum heat sinks are a natural choice for LED applications based on similarities to heat sinks used for other electronic devices. However the use of aluminum heat sinks for LED bulbs presents several challenges. One challenge is electrically insulating the heat sink from the Edison socket. Any electrical connectivity or leak between a metal heat sink and the socket can be extremely dangerous during installation. Another challenge is providing heat sinks with complex shapes because die-casting heat fin shapes can be difficult and may require costly secondary machining operations. Aluminum heat sinks can also be quite heavy and can add significantly to the weight, and consequently the cost of transportation, of the bulb. Finally, aluminum heat sinks will need a finish step of painting to smooth surface finish and impart colors desired by the consumers.

[0006] Plastic heat sinks are an alternative to aluminum heat sinks. Plastics are electrically insulating, more amenable to complex heat sink structures via injection molding, light in weight, and can be colored freely to meet aesthetic or branding requirements. Plastics also offer the possibility of integrating several parts, which can lead to a simpler overall bulb assembly. Plastics, however, have very poor thermal conductivity – generally only around 0.2 W/mK – which is nearly two orders of magnitude lower than aluminum (around 200 W/mK). Therefore, plastics are generally not sufficient to meet thermal management challenges.

[0007] Fillers are often added to plastics to make unique composite materials. For example, reinforcing fillers like glass fibers are added to improve the mechanical properties of plastics. Similarly graphite, carbon black or other carbon forms, including even carbon nanotubes recently are added to plastics to make electrically conductive plastic-based materials. Graphite and metal powders are also used sometimes to enhance thermal conductivity, but this usually leads to increased electrical conductivity as well since these properties are usually concomitant. However, some ceramic materials such as silica, alumina, zinc oxide, magnesium oxide, aluminum nitride, boron nitride (hexagonal or cubic forms), etc., present the opportunity to make thermally conductive yet electrically insulating formulations with plastics since they are good thermal conductors and electrical insulators.

[0008] While boron nitride/plastic composites have been proposed, boron nitride/plastic composites have several drawbacks. Boron nitride is a relatively expensive material that can cost from 10 to 40 times more than the plastic resins that it is compounded with and as compared to aluminum alloys. From a performance standpoint, the in-plane thermal conductivity of the boron nitride/plastic composite is only around 2-10 W/mK even at high loadings of boron nitride, e.g., above 25-60 wt.% (15-45 vol %). Boron nitride is also very inert and not easily wetted by resins. This leads to imperfect interfaces and large thermal resistances between the filler and matrix, effectively lowering the thermal conductivity of the composite thus leading to higher BN loadings required to achieve the required thermal conductivity. The higher filler loadings drives up the cost of these composites significantly making it less cost competitive in thermal management applications. The poor interfaces between the filler and resin also results in poor physical properties of the composites. It therefore becomes imperative to address the problems of wetting to achieve high thermal conductivity and optimum physical properties.

[0009] It is important to note however that even though thermal conductivity of thermally conductive plastics is not as high as aluminum metal, it is sufficient for thermal management applications in LED bulbs, and other convection limited applications. Boron nitride/plastics composites are

anisotropic, which can also be an issue that may limit the applicability of boron nitride/plastic composites.

[0010] The crystal structure of hexagonal BN is shown in FIGURE 1. The a-b crystal planes are made of tight, covalently-bonded boron and nitrogen atoms. The a-b planes are repeated along the c-direction held together by weak van der Waal's forces. Due to this crystal structure, the natural particle shape of hexagonal BN particles are platelets and typically have aspect ratios (~10-50).

[0011] Where anisotropy is acceptable, the high aspect ratio of BN can be an advantage. Typically, all else being equal, the higher the aspect ratio, the higher the thermal conductivity.

[0012] The crystal structure of hexagonal BN shown in FIGURE 1 is very similar to graphite. Exfoliation of graphite has been used as a way to increase the aspect ratio of graphite particles and increase thermal conductivity performance. In contrast to graphite, the exfoliation of hexagonal BN is extremely difficult due to the partially ionic or polar character of the boron and nitrogen atoms. Intercalation and exfoliation of BN crystals has been demonstrated in the lab, but by exceptionally difficult means that pose several challenges to scale-up and commercialization. (Shen et al. "Intercalation of Hexagonal Boron Nitride by Strong Oxidizers and Evidence for the Metallic Nature of the Products", Journal of Solid State Chemistry, v147, pp74-81 (1999).) Even if BN crystals are successfully exfoliated, compounding these nano-scale high surface area materials into resins, achieving good dispersion and wetting of the fillers by the matrix will also be extremely challenging.

SUMMARY

[0013] In one aspect, the present invention provides compositions comprising exfoliated boron nitride. In another aspect, the present invention provides a method for making a composition comprising exfoliated boron nitride. The compositions can exhibit high thermal conductivities

[0014] In one embodiment, the present invention provides composition comprising a resin material, exfoliated boron nitride, an optional functionalization additive, and a hard filler material having a hardness greater than the hardness of hexagonal boron nitride, wherein the exfoliated boron

nitride is produced in situ by mixing boron nitride crystals with the resin material in the presence of the hard filler.

[0015] In another embodiment, the present invention provides a method of forming a thermally conductive composition comprising exfoliated boron nitride, the method comprising exfoliating boron nitride crystals in situ by mixing boron nitride crystals and a hard filler material having a hardness greater than the boron nitride crystals in a resin material.

[0016] The in situ exfoliation of boron nitride crystals in a resin matrix allows for forming a composition that exhibits relatively high thermal conductivities without having to exfoliate the boron nitride in a separate step prior to compounding with the resin material.

[0017] In one aspect, the present invention provides, a composition comprising a resin material, exfoliated boron nitride, an optional functionalization additive, and a hard filler material having a hardness greater than the hardness of hexagonal boron nitride, wherein the exfoliated boron nitride is produced in situ by mixing boron nitride crystals with the resin material in the presence of the hard filler.

[0018] In one embodiment, the composition comprises from about 15 weight percent to about 60 weight percent of boron nitride; from about 1 weight percent to about 55 weight percent of the hard filler material; from about 0 to about 15 weight percent of the functionalization additive; and from about 20 weight percent to about 75 weight percent of the resin material.

[0019] In one embodiment, the composition comprises from about 10 weight percent to about 50 weight percent of boron nitride; from about 20 weight percent to about 50 weight percent of the hard filler material; from about 0.1 to about 7 weight percent of the functionalization additive; and from about 20 weight percent to about 75 weight percent of the resin material.

[0020] In one embodiment, the composition comprises from about 15 volume percent to about 50 volume percent of boron nitride.

[0021] In one embodiment, the composition comprising the exfoliated boron nitride has a greater number of boron nitride particles than the volume of boron nitride in a composition that is devoid of the hard filler material.

[0022] In one embodiment, the exfoliated boron nitride has an average thickness of about 1 micron or less; about 0.5 micron or less; even about 0.2 micron or less.

[0023] In one embodiment, the ratio of hard filler material to boron nitride is at least from about 20:1 to about 1:20 by volume; from about 15:1 to about 1:15 by volume; from about 10:1 to about 1:10 by volume; from about 3:1 to 1:3 by volume. The composition of any of claims 1-8, wherein the ratio of hard filler material to boron nitride is at least from about 2:1 to about 1:2 by volume; even about 1:1 by volume.

[0024] In one embodiment, the boron nitride crystal diameter is greater than 0.5 microns. In one embodiment, the boron nitride crystal diameter is greater than 1 micron. In one embodiment, the boron nitride crystal diameter is greater than 3 microns. In one embodiment, the boron nitride crystal diameter is greater than 8 microns. In one embodiment, the boron nitride crystal diameter is greater than 12 microns. In one embodiment, the boron nitride crystal diameter is greater than 25 microns. In one embodiment, the boron nitride crystal diameter is greater than 40 microns.

[0025] In one embodiment, the boron nitride crystal surface area is less than 50 m²/g. In one embodiment, the boron nitride crystal surface area is less than 20 m²/g. In one embodiment, the boron nitride crystal surface area is less than 15 m²/g. In one embodiment, the boron nitride crystal surface area is less than 10 m²/g. In one embodiment, the boron nitride crystal surface area is less than 5 m²/g. In one embodiment, the BN crystal surface area is less than 1.5 m²/g.

[0026] In one embodiment, the boron nitride graphitization index is less than 4; less than 2; less than 1.5; less than 1.0.

[0027] In one embodiment, the hard filler material is chosen from zinc oxide, magnesium oxide, silica, alumina, aluminum nitride, silicon nitride, silicon carbide, titania, tungsten carbide, titanium nitride, cubic boron nitride, diamond, or a combination of two or more thereof.

[0028] In one embodiment, hard filler material has a Mohs hardness of about 4.5 or greater. In one embodiment, the hard filler material has a Mohs hardness of from about 2 to about 9.5.

[0029] In one embodiment, the functionalization additive is a silane. In one embodiment, the silane is chosen from a mercaptosilane, an alkacryloxy silane, a vinyl silane, a halo silane, a thiocarboxylate silane, a blocked mercapto silane, or a combination of two or more thereof.

[0030] In one embodiment, the functionalization additive is present in an amount of from about 1 weight percent to about 10 weight percent.

[0031] In one embodiment, the composition has a thermal conductivity of about 5 W/mK or greater. In one embodiment, the composition has a thermal conductivity of from about 5 W/mK to about 15 W/mK.

[0032] In one embodiment, the present invention provides a method of forming a thermally conductive composition comprising exfoliated boron nitride, the method comprising exfoliating boron nitride crystals in situ by mixing boron nitride crystals and a hard filler material having a hardness greater than the boron nitride crystals in a resin material.

[0033] These and other aspects are further understood with reference to the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0034] FIGURE 1 illustrates the crystal structure of hexagonal boron nitride;

[0035] FIGURE 2 is an SEM image of a nylon composition comprising 40% boron nitride that is not exfoliated;

[0036] FIGURE 3 is a SEM image showing a highly crystalline boron nitride that has not been compounded or dispersed in a resin;

[0037] FIGURE 4 is a SEM image of a nylon composition comprising exfoliated boron nitride prepared in accordance with one embodiment of the invention; and

[0038] FIGURE 5 is a SEM image of a nylon composition comprising exfoliated boron nitride prepared in accordance with one embodiment of the invention.

DETAILED DESCRIPTION

[0039] The present invention provides a composition comprising exfoliated boron nitride disposed in a resin matrix. The compositions comprise a resin matrix, exfoliated boron nitride, and a filler material dispersed in the resin matrix, the filler material having a hardness greater than the hardness of hexagonal boron nitride crystals. The present invention also provides a method for forming the composition comprising the in situ exfoliation of boron nitride in a resin matrix.

[0040] The method of forming a composition comprising exfoliated boron nitride comprises mixing crystalline boron nitride into a resin material in the presence of a material having a hardness greater than the hardness of (non-exfoliated) crystalline boron nitride material. The inventors have found that mixing crystalline boron nitride into a resin matrix in the presence of a material having a hardness greater than the crystalline boron nitride results in exfoliation of the boron nitride crystals. The exfoliation of the boron nitride crystals occurs in situ. The resulting material has a thermal conductivity higher than a similar composition that is devoid of any hard filler material. The in-situ exfoliation of the boron nitride crystals allows for a high thermal conductivity to be formed without a separate step of exfoliating boron nitride and subsequently compounding the exfoliated boron nitride into a resin material.

[0041] Mixing the crystalline boron nitride and the resin material can be accomplished using any suitable mixing method. Mixing can be accomplished by any type of mixing equipment or device suitable for mixing resin materials. Examples of suitable mixing equipment includes, but is not limited to, Brabender mixers, Banbury mixers, a roll or a set of rollers, a kneader, a co-kneader, a single screw extruder, a twin screw extruder, etc.

[0042] The boron nitride component comprises crystalline or partially crystalline boron nitride particles made by processes known in the art. These

include spherical BN particles in the micron size range produced in a process utilizing a plasma gas as disclosed in U.S. Pat. No. 6,652,822; hBN powder comprising spherical boron nitride agglomerates is formed from irregular non-spherical BN particles bound together by a binder and subsequently spray-dried, as disclosed in US Patent Publication No. US2001/0021740; BN powder produced from a pressing process as disclosed in U.S. Pat. Nos. 5,898,009 and 6,048,511; BN agglomerated powder as disclosed in US Patent Publication No. 2005/0041373; BN powder having high thermal diffusivity as disclosed in US Patent Publication No. US2004/0208812A1; and highly delaminated BN powder as disclosed in U.S. Pat. No. 6,951,583. These also include BN particles of the platelet morphology.

[0043] In one embodiment, the BN powder has an average particle size of at least 50 microns (μm). In another embodiment, the BN powder has an average particle size of about 1 μm to about 500 μm ; from about 5 μm to about 100 μm ; even from about 10 μm to about 30 μm . In one embodiment, the BN powder comprises irregularly shaped agglomerates of hBN platelets, having an average particle size of above 10 μm . Here, as elsewhere in the specification and claims, numerical values can be combined to form new and non-disclosed ranges. Particle size can be measured using a Horiba LA300 particle size distribution analyzer where the particle to be analyzed (e.g., BN) is introduced in an amount adjusted to meet the required transmission. A few drops of 2% Rhodapex CO-436 can be added to improve the dispersion of the powder, and the particle size can be measured using laser diffraction after a 3 second sonication. The particle size distribution resulting from the measurement can be plotted on a volume basis and the D90 represents the 90th percentile of the distribution.

[0044] In another embodiment, the BN powder is in the form of spherical agglomerates of hBN platelets. In one embodiment of spherical BN powder, the agglomerates have an average agglomerate size distribution (ASD) or diameter from about 10 μm to about 500 μm . In another embodiment, the BN powder is in the form of spherical agglomerates having an ASD in the range of about 30 μm to about 125 μm . In one embodiment, the ASD is about 74 to about 100 microns. In another embodiment, about 10 μm to about 40 μm . Here, as elsewhere in the

specification and claims, numerical values can be combined to form new and non-disclosed ranges.

[0045] In one embodiment, the BN powder is in the form of platelets having an average length along the b-axis of at least about 1 micron, and typically between about 1 μm and 20 μm , and a thickness of no more than about 5 microns. In another embodiment, the powder is in the form of platelets having an average aspect ratio of from about 20 to about 300.

[0046] In one embodiment, the boron nitride crystal diameter is greater than 0.5 microns. In one embodiment, the boron nitride crystal diameter is greater than 1 micron. In one embodiment, the boron nitride crystal diameter is greater than 3 microns. In one embodiment, the boron nitride crystal diameter is greater than 8 microns. In one embodiment, the boron nitride crystal diameter is greater than 12 microns. In one embodiment, the boron nitride crystal diameter is greater than 25 microns. In one embodiment, the boron nitride crystal diameter is greater than 40 microns.

[0047] In one embodiment, the boron nitride crystal surface area is less than 50 m^2/g . In one embodiment, the boron nitride crystal surface area is less than 20 m^2/g . In one embodiment, the boron nitride crystal surface area is less than 15 m^2/g . In one embodiment, the boron nitride crystal surface area is less than 10 m^2/g . In one embodiment, the boron nitride crystal surface area is less than 5 m^2/g . In one embodiment, the BN crystal surface area is less than 3 m^2/g . In one embodiment, the BN crystal surface area is less than 1.5 m^2/g .

[0048] In one embodiment, the BN is an h-BN powder having a highly ordered hexagonal structure with a crystallization index of at least 0.12; at least 0.20; at least 0.30; at least 0.45; even at least 0.55. In another embodiment, the BN powder has a crystallization index of about 0.20 to about 0.55; from about 0.30 to about 0.55; even from about 0.40 to about 0.55. Here, as elsewhere in the specification and claims, numerical values can be combined to form new and non-disclosed ranges.

[0049] In one embodiment, the boron nitride has a graphitization index is less than 4; less than 2; less than 1.5, even less than 1. In another embodiment, the boron nitride has a graphitization index from about 0.1 to about 4; from

about 0.5 to about 3; even from about 1 to about 2. Here, as elsewhere in the specification and claims, numerical values can be combined to form new and non-disclosed ranges.

[0050] In one embodiment, the exfoliated boron nitride has an average thickness of about 1 micron or less; about 0.5 micron or less; even about 0.2 micron or less.

[0051] The crystalline boron nitride is mixed with a hard filler material having a hardness greater than the hardness of the (non-exfoliated) crystalline boron nitride. The hardness value can be chosen from a measure of hardness such as Mohs hardness, Knoop hardness, Vickers hardness, Rockwell hardness, etc. In one embodiment, the hardness value is based on the Mohs hardness value. In one embodiment, the hard filler material has a Mohs hardness of 2 or greater; 3 or greater; 4 or greater; 5 or greater; 6 or greater; even 8 or greater. In one embodiment, the hard material has a Mohs hardness of from about 2 to about 9; from about 3 to about 8; from about 4.0 to about 7.5; even from about 4.5 to about 6.5. Here as elsewhere in the specification and claims, numerical values can be combined to form new and non-disclosed ranges.

[0052] The hard filler material can be selected as desired for a particular purpose or intended use. Examples of suitable hard materials include, but are not limited to, a metal oxide such as, e.g., zinc oxide, magnesium oxide, aluminum oxide, beryllium oxide, yttrium oxide, hafnium oxide, etc.; a nitride such as, e.g., aluminum nitride, silicon nitride, cubic boron nitride, etc.; silica; a carbide, e.g., silicon carbide, titanium carbide, tantalum carbide, beryllium carbide, boron carbide, etc.; a boride, e.g., zirconium boride, titanium diboride, aluminum boride, other oxides, nitrides, oxy-nitrides, carbides, borides, silicides, or a combination of two or more thereof, etc. Particles or metals or pure elements may also be suitable for use including, but not limited to, powders, particles, or flakes of aluminum, silver, copper, bronze, brass, boron, silicon, nickel, nickel alloys, tungsten, tungsten alloys, etc. Minerals such as apatite, feldspar, topaz, garnet, andalusite, asbestos, barite, flint fluorite, hematite, pyrite, quartz, etc. Other polyatomic molecules of sufficient hardness such as perovskites, titanates,

silicates, chalcogenides, etc. can also be suitable hard filler materials. It will be appreciated that the composition can comprise two or more hard filler materials.

[0053] The hard filler material can have an average particle size of less than 100 microns; less than 50 microns; less than 30 microns; less than 20 microns; less than 15 microns; less than 10 microns; less than 3 microns; less than 1 micron; even less than 100 nanometers. In one embodiment the hard filler material has an average particle size of from about 50 nanometers to about 100 microns; from about 100 nanometers to about 50 micron; from about 250 nanometers to about 30 micron; from about 500 nanometers to about 25 micron; even from about 1 to about 15 micron. Here as elsewhere in the specification and claims, numerical values can be combined to form new and non-disclosed ranges.

[0054] In one embodiment, the thermally conductive compositions comprise a functionalization additive such as, for example, a silane additive. In one embodiment, the silane additive can be chosen from an acryloxy silane, a vinyl silane, a halo silane (e.g., a chlorosilane), a mercapto silane, a thiocarboxylate silane, a blocked mercapto silane, or a combination of two or more thereof. In one embodiment, the thermally conductive compositions can comprise from about 0.1 to about 6 wt. % of a functionalization additive; from about 1.5 to about 4 wt.%; even from about 2.7 to about 3.7 wt. %. Here as elsewhere in the specification and claims, numerical values can be combined to form new and non-disclosed ranges.

[0055] The silane additive can be added at any point in processing of the composition. In one embodiment, the silane additive can be added in-situ at any point in the mixing process. In another embodiment, the silane is added to a filler or filler composition prior to introduction into the mixing or processing equipment.

[0056] In addition to silanes various other classes of functionalization additives can be added to improve the interface between the fillers and the resin matrix. Other examples of functionalization additives include organometallic compounds such as titanates & zirconates (e.g., Ken-react by Kenrich), aluminates, hyperdispersants (e.g., Solsperse by Lubrizol), maleated oligomers such as maleated polybutadiene resin or styrene maleic anhydride copolymer

(e.g., those from Cray Valley), fatty acids or waxes and their derivatives, and ionic or non-ionic surfactants. These functionalization additives may be used at 1 wt. % to about 15 wt%; or from about 3 wt. % to about 12 wt. %; even from about 5 wt. % to 10 wt. %. Here as elsewhere in the specification and claims, numerical values can be combined to form new and non-disclosed ranges.

[0057] The filler materials and optional functionalization additive (e.g., a silane) can be added separately to the resin or as a blend. In one aspect, the filler material is provided as a blend of boron nitride, hard filler material, and a silane.

[0058] In one embodiment, the thermally conductive filler is provided as a blend or composite of boron nitride, hard filler material, a functionalization additive (e.g., a silane additive), and optionally other filler materials. In one embodiment, the thermally conductive filler composition comprises a blended composition comprising boron nitride in an amount of from about 15 weight percent to about 70 weight percent; a hard filler in an amount of from about 1 weight percent to about 75 weight percent; and a functionalization additive in an amount of from about 0.1 weight percent to about 6 weight percent. In one embodiment, the thermally conductive filler composition comprises a blended composition comprising boron nitride in an amount of from about 25 weight percent to about 60 weight percent; a hard filler material in an amount of from about 15 weight percent to about 60 weight percent; and a functionalization additive in an amount of from about 0.5 weight percent to about 5 weight percent. In one embodiment, the thermally conductive filler composition comprises a blended composition comprising boron nitride in an amount of from about 30 weight percent to about 50 weight percent; a hard filler material in an amount of from about 20 weight percent to about 50 weight percent; and a functionalization additive in an amount of from about 1 weight percent to about 3.5 weight percent. In one embodiment, the thermally conductive filler composition comprises a blended composition comprising boron nitride in an amount of from about 35 weight percent to about 45 weight percent; a hard filler material in an amount of from about 30 weight percent to about 40 weight percent; and a functionalization additive in an amount of from about 1.5 weight

percent to about 2.5 weight percent. In still another embodiment, the thermally conductive filler comprises a blended composition comprising boron nitride in an amount of from about 15 weight percent to about 40 weight percent; a hard filler material in an amount of from about 5 weight percent to about 50 weight percent; and a silane additive in an amount of from about 1 weight percent to about 4 weight percent. In one embodiment, the composition comprises from about 15 weight percent to about 60 weight percent of boron nitride; from about 1 weight percent to about 55 weight percent of the hard filler material; from about 0 to about 15 weight percent of the functionalization additive; and from about 20 weight percent to about 75 weight percent of the resin material. In one embodiment, the composition comprises from about 10 weight percent to about 50 weight percent of boron nitride; from about 20 weight percent to about 50 weight percent of the hard filler material; from about 0.1 to about 7 weight percent of the functionalization additive; and from about 20 weight percent to about 75 weight percent of the resin material. Here as elsewhere in the specification and claims, numerical values can be combined to form new and non-disclosed ranges.

[0059] In one embodiment, the blended filler composition comprises boron nitride, hard filler material, a silane additive, and glass fiber or glass flake. As used herein "glass fiber" can also refer to and will encompass glass flake.

[0060] The composite or blended filler compositions can be prepared by any suitable method to mix the various components in the filler composition. In one embodiment, the boron nitride, hard filler material, and optional additional filler are mixed together in a blender and the silane additive is introduced into the blender. The composite or blended filler composition can be a substantially homogeneous mixture or blend of the component materials.

[0061] The blend of the boron nitride, hard filler material, and the silane (and the optional other filler materials, e.g., a metal oxide) can be blended and treated prior to introduction into the resin composition to covalently bind the silane to the blend of the boron nitride and the hard filler material. Suitable blending methods are v-blender with various intensifier bars, paddle blenders, ribbon blenders etc. This can be accomplished by subjecting the blend of the

boron nitride, hard filler material, and the silane to conditions to hydrolyze the silane and allow the hydrolyzed silane to react with the filler surface. In one embodiment, treating the blended filler can be carried out by exposing the material to moisture and heat. While not being bound to any particular theory, heat treating the filler comprising the blend of the boron nitride and the silane can cause condensation of the silane on the filler and chemically react and bind the silane to the filler surface. The inventors have found that heat treating the blended filler compositions prior to use in the resin composition can improve the thermal conductivity of the composition. While the blended filler can be exposed to temperatures during processing of the resin composition that are capable of binding the silane to the filler materials, silane material that is not bonded to the filler material can potentially evaporate at the high processing temperatures.

[0062] In one embodiment, the blend of the boron nitride, hard filler material, and the silane can be treated by heating at 50 °C for seventy two hours in a convection oven. In another embodiment, the filler blend comprising boron nitride, a metal oxide and an optional glass fiber and the silane can be heat treated at 60 °C for four hours. In one embodiment the heat treatment is at 80 °C for two hours. In one embodiment the heat treatment is carried out under controlled moisture conditions. In one embodiment the heat treatment is carried out at 50 °C and 50% relative humidity for twenty four hours.

[0063] The polymer matrix material can include any polymer or resin material as desired for a particular purpose or intended application. In one embodiment, the resin material can be a thermoplastic material. In another embodiment, the resin material can be a thermoset material. Examples of suitable resin materials include, but are not limited to, polycarbonate; acrylonitrile butadiene styrene (ABS) ($C_8H_8C_4H_6C_3H_3N$); polycarbonate/acrylonitrile butadiene styrene alloys (PC-ABS); polybutylene terephthalate (PBT); polyethylene terephthalate (PET); polyphenylene oxide (PPO); polyphenylene sulfide (PPS); polyphenylene ether; modified polyphenylene ether containing polystyrene; liquid crystal polymers; polystyrene; styrene-acrylonitrile copolymer; rubber-reinforced polystyrene; poly ether ketone (PEEK); acrylic resins such as polymers and copolymers of alkyl esters of acrylic

and methacrylic acid styrene-methyl methacrylate copolymer; styrene-methyl methacrylate-butadiene copolymer; polymethyl methacrylate; methyl methacrylate-styrene copolymer; polyvinyl acetate; polysulfone; polyether sulfone; polyether imide; polyarylate; polyamideimide; polyvinyl chloride; vinyl chloride-ethylene copolymer; vinyl chloride-vinyl acetate copolymer; polyimides, polyamides; polyolefins such as polyethylene; ultra high molecular weight polyethylene; high density polyethylene; linear low density polyethylene; polyethylene naphthalate; polyethylene terephthalate; polypropylene; chlorinated polyethylene; ethylene acrylic acid copolymers; polyamides, for example, nylon 6, nylon 6,6, and the like; phenylene oxide resins; phenylene sulfide resins; polyoxymethylenes; polyesters; polyvinyl chloride; vinylidene chloride/vinyl chloride resins; and vinyl aromatic resins such as polystyrene; poly(vinylnaphthalene); poly(vinyltoluene); polyimides; polyaryletheretherketone; polyphthalamide; polyetheretherketones; polyaryletherketone, and combinations of two or more thereof.

[0064] The choice of resin matrix material may depend on the particular requirements of the application for which the boron nitride/resin composite material is to be used. For example, properties such as impact resistance, tensile strength, operating temperature, heat distortion temperature, barrier characteristics, etc., are all affected by the choice of polymer matrix material.

[0065] In some embodiments, the resin matrix material can include one or more polyamide thermoplastic polymer matrices. A polyamide polymer is a polymer containing an amide bond (--NHCO--) in the main chain and capable of being heat-melted at temperatures less than about 300 degrees Celsius. Specific examples of suitable polyamide resins include, but are not limited to, polycaproamide (nylon 6), polytetramethylene adipamide (nylon 46), polyhexamethylene adipamide (nylon 66), polyhexamethylene sebacamide (nylon 610), polyhexamethylene dodecamide (nylon 612), polyundecamethylene adipamide (nylon 116), polyundecanamide (nylon 11), polydodecanamide (nylon 12), polytrimethylhexamethylene terephthalamide (nylon TMHT), polyhexamethylene isophthalamide (nylon 61), polyhexamethylene terephthal/isophthalamide (nylon 6T/61), polynonamethylene terephthalamide

(nylon 9T), polybis(4-aminocyclohexyl)methane dodecamide (nylon PACM12), polybis(3-methyl-4-aminocyclohexyl)methane dodecamide (nylon dimethyl PACM12), polymethaxylylene adipamide (nylon MXD6), polyundecamethylene terephthalamide (nylon 11T), polyundecamethylene hexahydroterephthalamide (nylon 11T(H)) and their copolymerized polyamides and mixed polyamides. Among these, nylon 6, nylon 46, nylon 66, nylon 11, nylon 12, nylon 9T, nylon MXD6, and their copolymerized polyamides and mixed polyamides are exemplary in terms of availability, handleability and the like.

[0066] Examples of thermoset resins include, but not limited to, silicones, epoxies, acrylics, phenolics, etc.

[0067] It will be appreciated that the base polymer resin material can be modified or provided with other fillers or additives, other than the boron nitride or hard filler material, to modify other properties such as impact resistance, UV stability, fire retardancy, etc.

[0068] The compositions (prior to or after mixing of the resin, boron nitride, and hard filler material components) can comprise from about 20 wt. % to about 80 wt. % of the polymer matrix; from about 20 wt. % to about 70 wt. % of the polymer matrix; from about 35 wt. % to about 65 wt. % of the polymer matrix; even from about from about 42 wt. % to about 58 wt. % of the polymer matrix. The composition can comprise from about 15 wt. % to about 70 wt. % of boron nitride; from about 20 wt. % to about 50 wt. %; from about 25 wt. % to about 40 wt. % of boron nitride; even from about 30 wt. % to about 35 wt. % of boron nitride. The composition can comprise from about 10 wt. % to about 70 wt. % of the hard filler material; from about 15 wt. % to about 50 wt. % of the hard material; from about 17 wt. % to about 30 wt. % of the hard material; even from about 20 wt. % to about 25 wt. % of the hard material. In one embodiment, the boron nitride is present in an amount of from about 5 weight percent to about 60 weight percent of the total composition weight; the hard filler material is present in an amount of from about 10 weight percent to about 55 weight percent of the total composition weight; and the resin material is present in an amount of from about 20 weight percent to about 75 weight percent of the total composition

weight. Here as elsewhere in the specification and claims, numerical values can be combined to form new and non-disclosed ranges.

[0069] The inventors have found that mixing crystalline boron nitride with a resin material in the presence of a hard filler material provides for the in situ exfoliation of the boron nitride in the resin matrix and provides a composition comprising exfoliated boron nitride. The composition comprising exfoliated boron nitride can have higher aspect boron nitride particles compared to a composition that does not comprise the exfoliated boron nitride. In one embodiment, the composition comprising exfoliated boron nitride has a ratio of hard filler to boron nitride material (HM:BN) by volume of from about 20:1 to about 1:20; from about 15:1 to about 1: 15; from about 10:1 to about 1:10; from about 8:1 to 1:8; from about 5:1 to about 1:5; from about 3:1 to about 1:3; from about 2:1 to about 1:2; even about 1:1. In one embodiment, the HM:BN ratio in the composition comprising the exfoliated boron nitride is from about 1:20 to about 1:1; from about 1:10 to about 1:8; from about 1:5 to about 1:3; even from about 1:2 to about 1:1. Here as elsewhere in the specification and claims, numerical values can be combined to form new and non-disclosed ranges.

[0070] The compositions comprising the exfoliated boron nitride generally have a thermal conductivity higher than that of a composition comprising the same weight percentage of boron nitride but that is devoid of any hard filler material over and above any contribution to the thermal conductivity from the hard filler material. In one embodiment, the compositions comprising the exfoliated boron nitride have a thermal conductivity that is higher than the predicted thermal conductivity based on the Lewis Nielsen model for boron nitride and the hard filler material(s). In one embodiment the composition comprising the exfoliated boron nitride has a thermal conductivity of about 5 W/mK or greater; about 6 W/mK or greater; about 7.5 W/mK or greater: about 10 W/mK or greater; even about 12 W/mK or greater. In one embodiment, the composition comprising exfoliated boron nitride has a thermal conductivity of from about 5 W/mK to about 15 W/mK; from about 6 W/mK to about 12 W/mK; from about 7.5 W/mK to about 10 W/mK. Here as elsewhere in the specification

and claims, numerical values can be combined to form new and non-disclosed ranges.

[0071] The present invention has been described with respect to various aspects and embodiments of the compositions comprising exfoliated boron nitride and a process for forming such compositions by the in situ exfoliation of boron nitride in a resin matrix. The invention can be further understood with respect to the following examples. The examples are merely for the purpose of illustrating aspects and additional embodiments of the invention and are not intended to limit the invention to the specific embodiments described therein.

Examples

Examples 1-21

[0072] Boron nitride powder (PT110 available from Momentive Performance Materials) is compounded with zinc oxide (AZO66XL available from U.S. Zinc) into Nylon 6 (from Sigma Aldrich) in a Brabender Plasti-corder batch mixer at 245 C° for eight minutes with a silane additive (NXT silane available from Momentive Performance Materials). The compounded sample is compression molded into a 4" x 4" sheet with a thickness of about 0.3 mm. The concentrations of boron nitride, zinc oxide, Nylon 6, and silane are shown in Table 1. Comparative Example 1 is prepared in a similar manner to the Examples except that zinc oxide is excluded from composition.

Table 1

Example	BN (wt%)	ZnO (wt%)	Silane (wt%)	Resin (wt%)	BN (vol%)	ZnO (vol%)	ZnO/BN Vol	TC (W/mK)	Pred. TC (W/mK)	Δ TC (%)	Density (g/cc)	Theo. Dens.
Comparative Ex. 1	40%	0%	1.2%	58.8%	24.7%	0.0%	0.000	3.66	3.66	0.0	1.42	1.41
Comparative Ex. 2	54.8%	0%	1.6%	43.6%	37.3%	0%	0.000	6.94	6.71	3.3	1.54	1.55
Comparative Ex. 3	67.7%	0%	2.0%	30.3%	50.7%	0%	0.000	15.06	12.37	17.9		
1	40%	30%	2.1%	27.9%	35.4%	10.6%	0.299	9.99	9.71	2.9	1.99	2.01
2	20%	50%	2.1%	27.9%	19.8%	19.8%	1.000	6.58	5.75	12.6	2.24	2.25
3	45%	25%	2.1%	27.9%	38.8%	8.6%	0.222	11.8	10.5	10.5	1.97	1.96
4	50%	20%	2.1%	27.9%	42.0%	6.7%	0.161	12.5	11.3	9.4	1.90	1.91
5	30%	30%	1.8%	38.2%	24.3%	9.8%	0.403	5.52	5.21	5.6	1.84	1.85
6	40%	20%	1.8%	38.2%	30.9%	6.2%	0.201	6.89	6.43	6.7	1.76	1.76
7	45%	15%	1.8%	38.2%	34.0%	4.5%	0.132	7.86	6.98	11.2	1.78	1.72
8	40%	20%	1.8%	38.2%	34.0%	4.5%	0.132	6.51	6.43	1.2	1.71	1.76
9	40%	20%	1.8%	38.2%	34.0%	4.5%	0.132	6.73	6.43	4.4	1.71	1.76
10	40%	20%	3.6%	36.4%	30.9%	6.2%	0.201	7.52	6.43	14.5	1.76	1.76
11	40%	20%	1.8%	38.2%	30.9%	6.2%	0.201	6.90	6.43	6.7	1.76	1.76
12	40%	20%	0.0%	40.0%	30.9%	6.2%	0.201	6.64	6.43	3.1	1.74	1.76
13	40%	20%	1.8%	38.2%	30.9%	6.2%	0.201	6.53	6.43	1.5	1.73	1.76
14	50%	20%	4.2%	25.8%	42.0%	6.7%	0.161	12.5	11.3	9.2	1.94	1.91
15	30%	40%	4.2%	25.8%	28.0%	15.0%	0.535	8.42	7.85	6.7	2.12	2.13
16	40%	20%	3.6%	36.4%	30.9%	6.2%	0.201	7.46	6.43	13.8	1.81	1.76
17	53%	19%	2.2%	25.8%	45.1%	6.5%	0.144	14.0	13.04	6.8	1.96	1.96
18	55%	20%	4.5%	20.5%	48.3%	7.0%	0.146	15.6	15.8	-1.0	2.06	2.00
19	40%	20%	0.0%	40.0%	30.9%	6.2%	0.201	5.67	6.43	-11.8	1.76	1.76
20	40%	20%	1.8%	38.2%	30.9%	6.2%	0.201	7.06	6.43	8.9	1.79	1.76
21	50%	20%	2.1%	27.9%	42.0%	6.7%	0.161	13.2	11.3	14.1	1.97	1.91
22	30%	30%	3.6%	36.4%	24.3%	9.8%	0.401	5.36	5.21	2.7	1.87	1.85
23	35%	25%	3.6%	36.4%	27.7%	7.9%	0.287	5.58	5.85	-4.8	1.82	1.80
24	20%	40%	3.6%	36.4%	17.0%	13.7%	0.803	4.09	3.82	6.6	1.99	1.94
25	25%	35%	3.6%	36.4%	20.8%	11.7%	0.562	4.76	4.54	4.7	1.90	1.89

26	15%	45%	3.6%	36.4%	13.1%	15.8%	1.204	3.23	3.06	5.4	2.00	1.99
27	45%	15%	3.6%	36.4%	34.0%	4.5%	0.134	7.29	6.98	4.2	1.74	1.72
28	50%	10%	3.6%	36.4%	36.9%	3.0%	0.080	7.91	7.49	5.4	1.62	1.75
29	55%	5%	3.6%	36.4%	39.7%	1.4%	0.036	-	7.94	-	-	1.65
Comparative Ex. 4	60%	0	3.6%	36.4%	42.4%	0	0	-	8.34	-	-	1.61
30	40%	20%	0	40.0%	30.9%	6.2%	0.201	5.67	6.43		1.76	1.76
31	40%	20%	1.8%	38.2%	30.9%	6.2%	0.201	7.06	6.43	8.9	1.79	1.76

Example 32

[0073] Example 32 is prepared in a manner similar to Examples 1-24 except that magnesium oxide (RF-10CS available from Ube Industries (Japan)) is used instead of zinc oxide as the hard material. The specifics of Example 32 are shown in Table 2.

Table 2

Example	BN (wt%)	MgO (wt%)	Silane (wt%)	Resin	BN (vol%)	MgO (vol%)	MgO/BN Vol	TC (W/mK)	Pred. TC (Wm/K)	Difference in TC
32	40%	20%	0.036	36.4%	29.8%	9.5%	0.318	6.44	7.22	-12.1%

[0074] As shown in Tables 1 and 2, the compositions comprising the hard filler material (e.g., zinc oxide or magnesium oxide) have higher thermal conductivities than Comparative Example 1 that does not include any hard material. Significantly, the compositions comprising the hard filler material exhibited thermal conductivities above the predicted thermal conductivity. The Lewis Nielsen model can be used to predict thermal conductivity of composites and is given by the following equations:

$$K_c = K_m \left(\frac{1+AB\phi}{1-B\psi\phi} \right) \quad (1)$$

$$B = \frac{\lambda-1}{\lambda+A} \quad \lambda = \frac{K_f}{K_m} \quad A = 2 \frac{L}{D} \quad (2)$$

$$\psi = 1 + \left(\frac{1-\phi_m}{\phi_m^2} \right) \phi \quad (3)$$

In the above equations, K_f is the thermal conductivity of the filler, K_m is matrix's and K_c is final composite thermal conductivity. ϕ is the volume fraction of the filler in the system and ϕ_m is the maximum packing fraction for the filler system. For high aspect ratio fillers, A is related to the aspect ratio of the fillers as shown above, but is also dependent on the extent of orientation of the fillers. If the fillers are perfectly aligned, A is set to twice the aspect ratio as shown above. As can be seen

from Equation 1, higher the aspect ratio of the fillers, higher the value of A , and hence higher the thermal conductivity. This model was extended to predict the thermal conductivity with multiple fillers to discount any direct contribution to the thermal conductivity of the composites by the hard material. Exceeding the thermal conductivity predicted by this model can be indicative of the observed exfoliation. The data of comparative examples 2 and 3 could be indicative of exfoliated BN albeit at very high loadings, which would make those formulations cost prohibitive. The present process provides exfoliated BN at lower BN loadings.

[0075] Additionally, at similar boron nitride loadings, the compositions comprising the hard material have a higher number of boron nitride particles than Comparative Example 1 (See Examples 1, 6, 8-13, 16, and 20-21), which suggests that the boron nitride has been exfoliated. SEM images illustrate the exfoliation of the boron nitride in the samples compounded with the hard material. FIGURE 2 is a back-scatter SEM image of the cross section of Comparative Example 1. In FIGURE 2, the boron nitride particles are fairly well dispersed in the matrix and have a thickness of about 2.5 microns. This is consistent with the SEM analysis of PT110 crystals that are not dispersed in a resin material (See FIGURE 3). FIGURES 4 and 5 are SEM images of Examples 1 and 5, respectively, and illustrate that the compositions compounded with a hard material resulted in the exfoliation of the boron nitride. In Example 1, the exfoliated boron nitride sheets have a thickness of about 0.15 microns and an aspect ratio from about 13 to about 50. In Example 5, the exfoliated boron nitride sheets have a thickness of about 0.2 microns and an aspect ratio of from about 8 to about 58.

Examples 33-38

[0076] Blended filler compositions are prepared with boron nitride, zinc oxide, an optional glass fiber, and a silane. The silane is NXT. The blended fillers are prepared and introduced into a Nylon 6 resin in a Brabender Plasti-corder. The fillers introduced into the resins are either introduced with or without prior heat treatment of the blended filler. Filler compositions that are heat treated prior to

introduction into the resin are heat treated at 50 °C for 72 hours in a convection oven. Table 3 shows the thermal conductivities of the compositions.

Table 3

Example	BN Grade	BN wt. %	ZnO wt. %	Glass Fiber wt. %	Silane	Filler Heat Treated	Resin wt. %	TC (W/mK)
33	CF600	36.8	7.8	10.4	1.7	No	43.4	4.7
34	CF600	36.8	7.8	10.4	1.7	Yes	43.4	4.9
35	CF600	20	50	---	2.1	No	27.9	4.7
36	CF600	20	50	---	2.1	Yes	27.9	5.4
37	PT110	40	30	---	3.5	No	26.5	9.5
38	PT110	40	30	---	3.5	Yes	26.5	11.2

[0077] The foregoing description identifies various, non-limiting embodiments of compositions comprising exfoliated boron nitride and methods of forming such compositions via the in situ exfoliation of boron nitride in a resin matrix. Modifications may occur to those skilled in the art and to those who may make and use the invention. The disclosed embodiments are merely for illustrative purposes and not intended to limit the scope of the invention or the subject matter set forth in the following claims.

CLAIMS

What is claimed is:

1. A composition comprising a resin material, exfoliated boron nitride, an optional functionalization additive, and a hard filler material having a hardness greater than the hardness of hexagonal boron nitride, wherein the exfoliated boron nitride is produced in situ by mixing boron nitride crystals with the resin material in the presence of the hard filler.
2. The composition of claim 1, wherein the composition comprises from about 5 weight percent to about 60 weight percent of boron nitride; from about 1 weight percent to about 55 weight percent of the hard filler material; from about 0 to about 15 weight percent of the functionalization additive; and from about 20 weight percent to about 75 weight percent of the resin material.
3. The composition of claim 1, wherein the composition comprises from about 20 weight percent to about 50 weight percent of boron nitride; from about 10 weight percent to about 50 weight percent of the hard filler material; from about 0.1 to about 7 weight percent of the functionalization additive; and from about 20 weight percent to about 75 weight percent of the resin material.
4. The composition of claim 1, comprising from about 15 volume percent to about 50 volume percent of boron nitride.
5. The composition of any of claims 1-4, wherein the composition comprising the exfoliated boron nitride has a greater number of boron nitride particles than the volume of boron nitride in a composition that is devoid of the hard filler material.
6. The composition of any of claims 1-5, wherein the exfoliated boron nitride has an average thickness of about 1 micron or less.

7. The composition of any of claims 1-6, wherein the ratio of hard filler material to boron nitride is at least from about 20:1 to about 1:20 by volume.

8. The composition of any of claims 1-6, wherein the ratio of hard filler material to boron nitride is at least from about 10:1 to about 1:10 by volume.

9. The composition of any of claims 1-8, where the boron nitride crystal diameter is greater than 3 microns.

10. The composition of any of claims 1-9, where the boron nitride graphitization index is less than 4.

11. The composition of any of claims 1-9, where the boron nitride graphitization index is from about 0.1 to about 4.

12. The composition of any of claims 1-11, wherein the hard filler material is chosen from zinc oxide, magnesium oxide, silica, alumina, aluminum nitride, silicon nitride, silicon carbide, titania, tungsten carbide, titanium nitride or a combination of two or more thereof; a metal oxide chosen from zinc oxide, magnesium oxide, aluminum oxide, beryllium oxide, yttrium oxide, hafnium oxide, or a combination of two or more thereof; a nitride chosen from aluminum nitride, silicon nitride, cubic boron nitride, or a combination thereof; silica; a carbide chosen from silicon carbide, titanium carbide, tantalum carbide, beryllium carbide, boron carbide, or a combination of two or more thereof; a boride chosen from zirconium boride, titanium diboride, aluminum boride, or a combination of two or more thereof; particles or metals or pure elements chosen from powders, particles, or flakes of aluminum, copper, bronze, brass, boron, silicon, nickel, nickel alloys, tungsten, tungsten alloys, or a combination of two or more thereof; apatite, feldspar, topaz, garnet, andalusite, asbestos, barite, flint fluorite, hematite, pyrite, quartz,

perovskite, titanates, silicates, chalcogenide, or a combination of two or more thereof; or a combination of two or more of any of these materials.

13. The composition of any of claims 1-12, wherein the hard filler material has a Mohs hardness of about 4.5 or greater.

14. The composition of any of claims 1-12, wherein the hard filler material has a Mohs hardness of from about 2 to about 9.5.

15. The composition of any of claims 1-14, wherein the functionalization additive is a silane.

16. The composition of claim 15, wherein the silane is chosen from a mercaptosilane, an alkacryloxy silane, a vinyl silane, a halo silane, a thicarbonylate silane, a blocked mercapto silane, or a combination of two or more thereof.

17. The composition of any of claims 1-16, wherein the functionalization additive is present in an amount of from about 1 weight percent to about 10 weight percent.

18. The composition of any of claims 1-17, comprising a silane as the functionalization additive, wherein the boron nitride, hard filler material, and silane are provided as a blended filler composition comprising a blend of the boron nitride, hard filler material, and the silane.

19. The composition of claim 18, wherein the blended composition comprises the silane condensed onto the surface of the blend of the boron nitride and the hard filler material.

20. The composition of any of claims 1-19, having a thermal conductivity of about 5 W/mK or greater.

21. The composition of any of claims 1-19, having a thermal conductivity of from about 5 W/mK to about 15 W/mK.

22. The composition of any of claims 1-21, wherein the polymer material is chosen from polycarbonate; acrylonitrile butadiene styrene (ABS) ($C_8H_8C_4H_6C_3H_3N$); polycarbonate/acrylonitrile butadiene styrene alloys (PC-ABS); polybutylene terephthalate (PBT); polyethylene terephthalate (PET); polyphenylene oxide (PPO); polyphenylene sulfide (PPS); polyphenylene ether; modified polyphenylene ether containing polystyrene; liquid crystal polymers; polystyrene; styrene-acrylonitrile copolymer; rubber-reinforced polystyrene; poly ether ketone (PEEK); acrylic resins such as polymers and copolymers of alkyl esters of acrylic and methacrylic acid styrene-methyl methacrylate copolymer; styrene-methyl methacrylate-butadiene copolymer; polymethyl methacrylate; methyl methacrylate-styrene copolymer; polyvinyl acetate; polysulfone; polyether sulfone; polyether imide; polyarylate; polyamideimide; polyvinyl chloride; vinyl chloride-ethylene copolymer; vinyl chloride-vinyl acetate copolymer; polyimides, polyamides; polyolefins such as polyethylene; ultra-high molecular weight polyethylene; high density polyethylene; linear low density polyethylene; polyethylene naphthalate; polyethylene terephthalate; polypropylene; chlorinated polyethylene; ethylene acrylic acid copolymers; polyamides, for example, nylon 6, nylon 6,6, and the like; phenylene oxide resins; phenylene sulfide resins; polyoxymethylenes; polyesters; polyvinyl chloride; vinylidene chloride/vinyl chloride resins; and vinyl aromatic resins such as polystyrene; poly(vinylnaphthalene); poly(vinyltoluene); polyimides; polyaryletheretherketone; polyphthalamide; polyetheretherketones; polyaryletherketone, and combinations of two or more thereof.

23. A method of forming a thermally conductive composition comprising exfoliated boron nitride, the method comprising exfoliating boron nitride crystals in situ by mixing boron nitride crystals and a hard filler material having a hardness greater than the boron nitride crystals in a resin material.

24. The method of claim 23, wherein the hard filler material has a Mohs hardness of from about 2 to about 9.5.

25. The method of claims 23 or 24, wherein the hard filler material is chosen from zinc oxide, magnesium oxide, silica, alumina, aluminum nitride, silicon nitride, silicon carbide, titania, tungsten carbide, titanium nitride or a combination of two or more thereof; a metal oxide chosen from zinc oxide, magnesium oxide, aluminum oxide, beryllium oxide, yttrium oxide, hafnium oxide, or a combination of two or more thereof; a nitride chosen from aluminum nitride, silicon nitride, cubic boron nitride, or a combination thereof; silica; a carbide chosen from silicon carbide, titanium carbide, tantalum carbide, beryllium carbide, boron carbide, or a combination of two or more thereof; a boride chosen from zirconium boride, titanium diboride, aluminum boride, or a combination of two or more thereof; particles or metals or pure elements chosen from powders, particles, or flakes of aluminum, copper, bronze, brass, boron, silicon, nickel, nickel alloys, tungsten, tungsten alloys, or a combination of two or more thereof; apatite, feldspar, topaz, garnet, andalusite, asbestos, barite, flint fluorite, hematite, pyrite, quartz, perovskite, titanates, silicates, chalcogenide, or a combination of two or more thereof; or a combination of two or more of any of these materials.

26. The method of any of claims 23-25, wherein the hard filler material has a particle size of from about 50 nanometers to about 100 micron.

27. The method of any of claims 23-26, wherein the boron nitride is present in an amount of from about 5 weight percent to about 60 weight percent of the total composition weight; the hard filler material is present in an amount of from about 1 weight percent to about 55 weight percent of the total composition weight; and the resin material is present in an amount of from about 20 weight percent to about 75 weight percent of the total composition weight.

28. The method of claim 27, further comprising adding from about 0.1 to about 7 weight percent of a functionalization additive.

29. The method of any of claims 23-28, wherein mixing is accomplished using a mixer, a roll, a set of rolls, a kneader, a co-kneader, a Banbury mixer, a single screw extruder, a twin screw extruder, or a combination of two or more thereof.

30. The method of any of claims 23-29, wherein the boron nitride and hard filler material are provided as a blended filler composition comprising a blend of the boron nitride and the hard filler material.

31. The method of claim 30, wherein the blended filler composition further comprises a silane.

32. The method of claim 31, wherein the silane is condensed on the surface of the blended filler composition.

33. The method of claim 31, wherein the silane is chosen from a mercaptosilane, an alkacryloxy silane, a vinyl silane, a halo silane, a thicarboxylate silane, a blocked mercapto silane, or a combination of two or more thereof.

34. The method of claim 30, wherein the silane is present in an amount of from about 0.1 weight percent to about 6 weight percent.

1/5

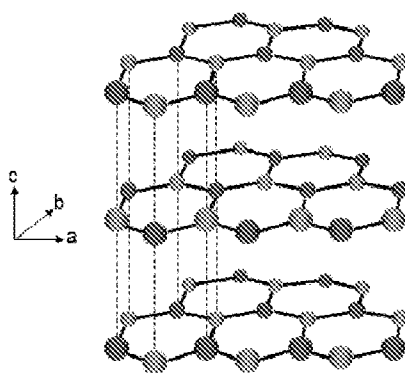


FIGURE 1

2/5

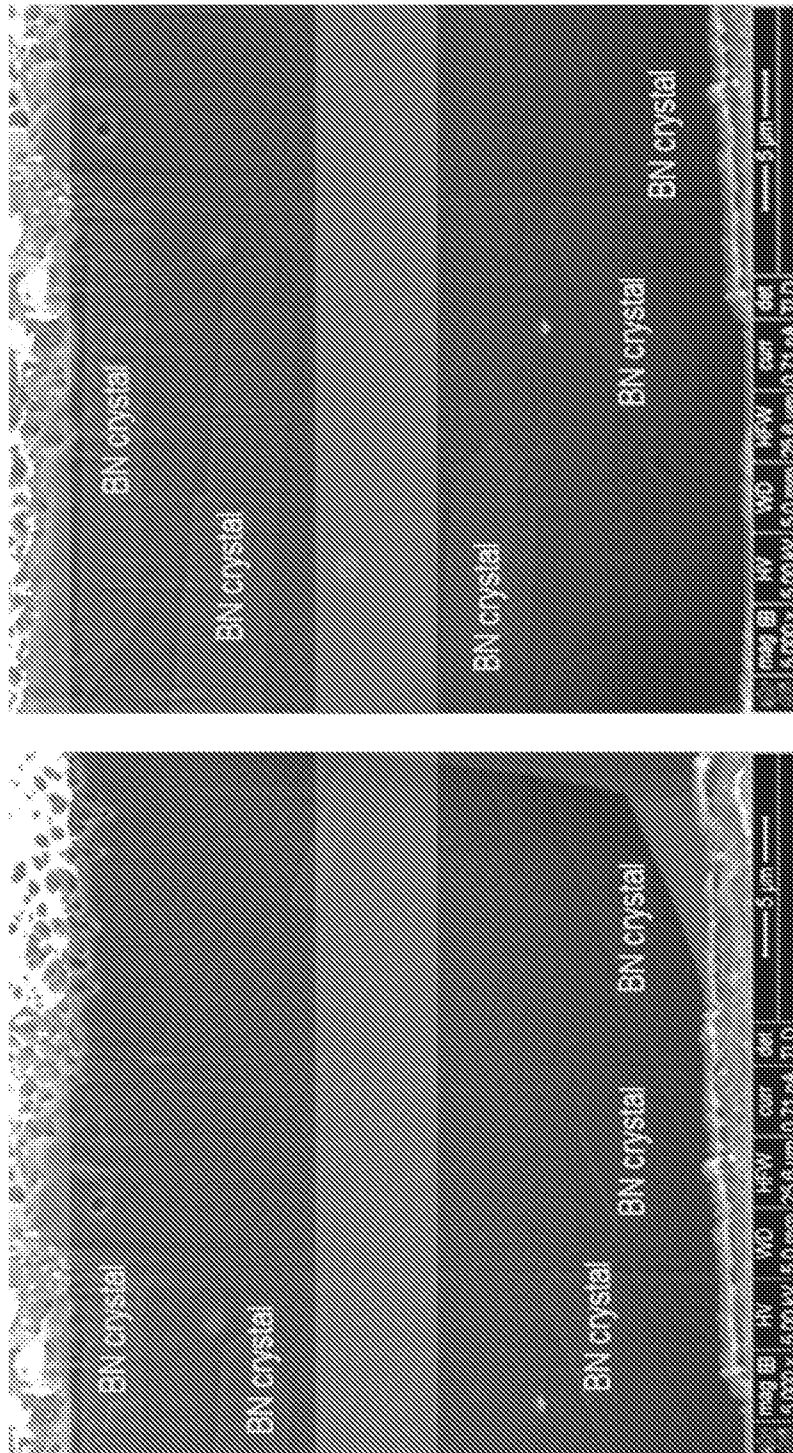


FIGURE 2

3/5

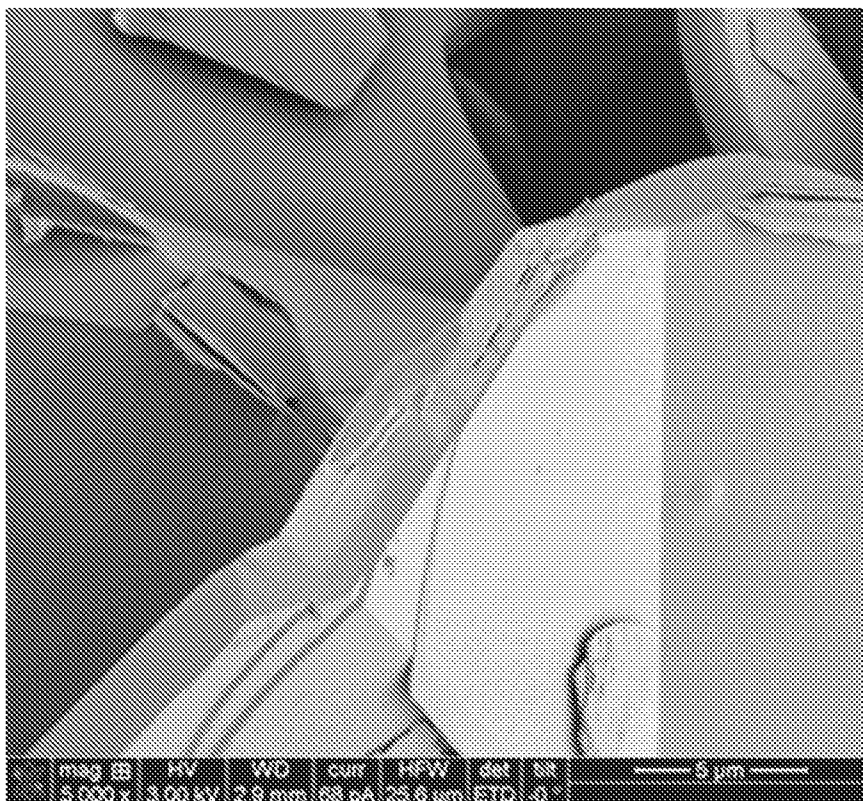


FIGURE 3

4/5

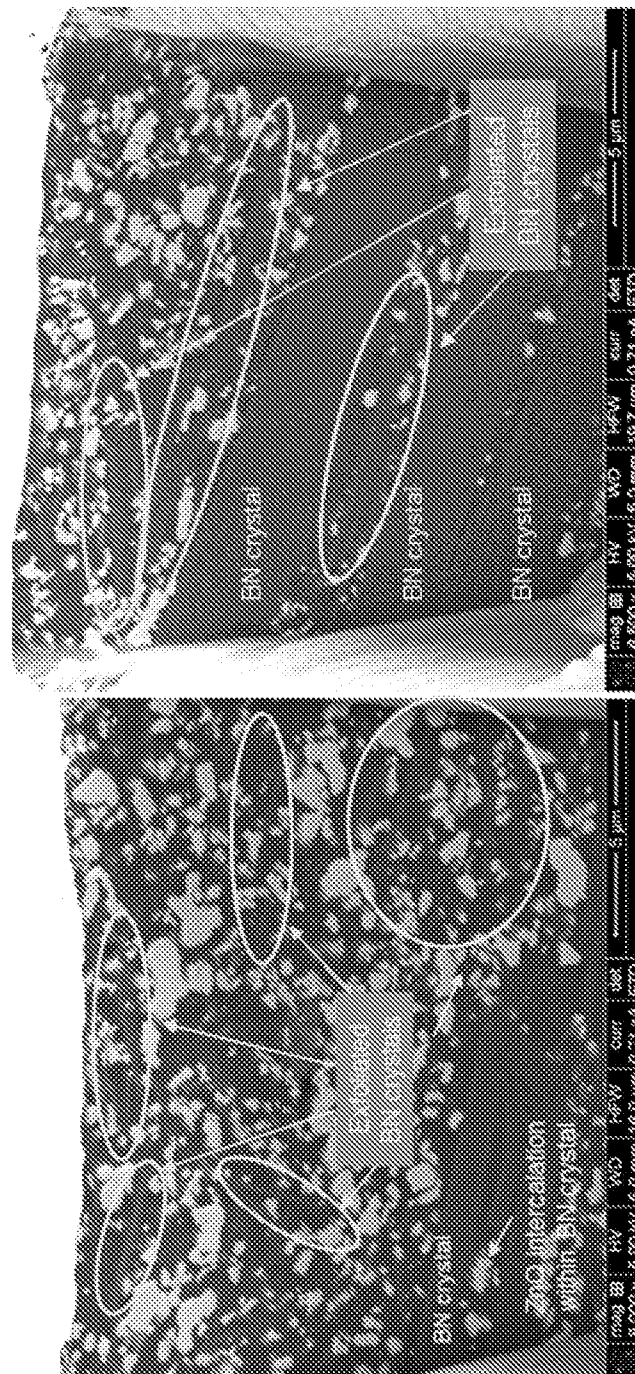


FIGURE 4

5/5

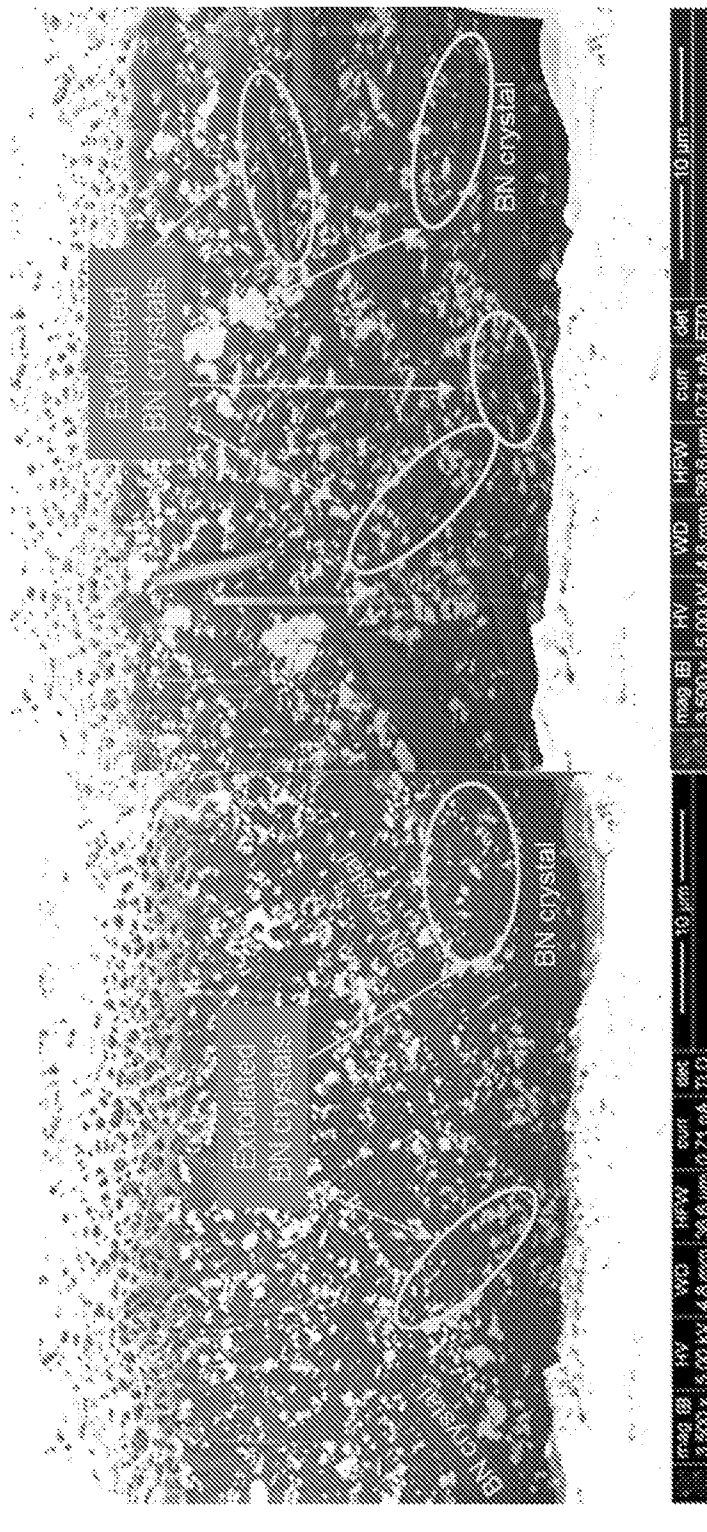


FIGURE 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/060617

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08K3/00 C08K3/38 C08J3/20
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)

C08K C08J

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

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

EP0-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	<p>DATABASE WPI Week 201201 Thomson Scientific, London, GB; AN 2011-P52468 XP002715472, -& KR 2011 0124127 A (SHIN KOBE ELECTRIC MACHINERY) 16 November 2011 (2011-11-16) abstract; examples</p> <p style="text-align: center;">-----</p>	1-34
A	<p>DATABASE WPI Week 201247 Thomson Scientific, London, GB; AN 2012-H93034 XP002715473, & WO 2012/093895 A2 (DOOSAN CORP) 12 July 2012 (2012-07-12) abstract</p> <p style="text-align: center;">-----</p> <p style="text-align: right;">-/--</p>	1-34



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

7 January 2014

Date of mailing of the international search report

30/01/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Masson, Patrick

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/060617

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Week 201233 Thomson Scientific, London, GB; AN 2012-B89323 XP002715474, & CN 102 321 364 A (DONGGUAN PUQIANG HIGH POLYMER MATERIAL) 18 January 2012 (2012-01-18) abstract</p>	1-34
A	<p>----- US 2007/026221 A1 (STEVENS GARY [GB] ET AL) 1 February 2007 (2007-02-01) page 3, paragraph 22 page 9, paragraph 85-88</p>	1-34
A	<p>----- US 6 951 583 B2 (CLERE THOMAS M [US] ET AL) 4 October 2005 (2005-10-04) cited in the application column 6, line 52 - column 7, line 30; claims</p>	1-34
A	<p>----- US 2011/045223 A1 (LIN YI [US] ET AL) 24 February 2011 (2011-02-24) page 2, paragraph 26-28; example 17</p>	1-34
A	<p>----- US 5 900 447 A (ISHIDA HATSUO [US]) 4 May 1999 (1999-05-04) column 2; claims; examples</p>	1-34
A	<p>----- US 2006/293427 A1 (MARTENS MARVIN M [US] ET AL) 28 December 2006 (2006-12-28) page 1, paragraph 8-11 page 3, paragraph 35; claims</p>	1-34
A	<p>----- US 2011/165410 A1 (AOYAGI EIJIRO [JP] ET AL) 7 July 2011 (2011-07-07) example 1</p>	1-34
A	<p>----- US 2005/041373 A1 (PRUSS EUGENE A [US] ET AL) 24 February 2005 (2005-02-24) cited in the application the whole document</p> <p>-----</p>	1-34

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/060617

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 20110124127 A	16-11-2011	NONE	
WO 2012093895 A2	12-07-2012	KR 20120079986 A WO 2012093895 A2	16-07-2012 12-07-2012
CN 102321364 A	18-01-2012	NONE	
US 2007026221 A1	01-02-2007	EP 2069430 A1 JP 2010505027 A KR 20090084835 A US 2007026221 A1 WO 2008039279 A1	17-06-2009 18-02-2010 05-08-2009 01-02-2007 03-04-2008
US 6951583 B2	04-10-2005	AT 402119 T AU 5747201 A EP 1278701 A2 ES 2311015 T3 JP 2003531802 A JP 2008280243 A US 2002006511 A1 US 2004076572 A1 WO 0183371 A2	15-08-2008 12-11-2001 29-01-2003 01-02-2009 28-10-2003 20-11-2008 17-01-2002 22-04-2004 08-11-2001
US 2011045223 A1	24-02-2011	NONE	
US 5900447 A	04-05-1999	CA 2250511 A1 DE 69818900 D1 EP 0875531 A2 JP 4070870 B2 JP H1171498 A US 5900447 A	15-04-2000 20-11-2003 04-11-1998 02-04-2008 16-03-1999 04-05-1999
US 2006293427 A1	28-12-2006	CA 2611270 A1 EP 1888688 A1 JP 2008543991 A US 2006293427 A1 WO 2006135840 A1	21-12-2006 20-02-2008 04-12-2008 28-12-2006 21-12-2006
US 2011165410 A1	07-07-2011	CN 102149542 A EP 2325000 A1 JP 5330396 B2 KR 20110051263 A TW 201014707 A US 2011165410 A1 WO 2010027070 A1	10-08-2011 25-05-2011 30-10-2013 17-05-2011 16-04-2010 07-07-2011 11-03-2010
US 2005041373 A1	24-02-2005	CA 2534787 A1 CN 1839096 A CN 103086719 A EP 1656323 A1 JP 4662933 B2 JP 2007502770 A JP 2011040788 A TW 1276603 B US 2005041373 A1 US 2009071695 A1 US 2011147064 A1 WO 2005021428 A1	10-03-2005 27-09-2006 08-05-2013 17-05-2006 30-03-2011 15-02-2007 24-02-2011 21-03-2007 24-02-2005 19-03-2009 23-06-2011 10-03-2005

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/060617

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
<div></div>			