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(54) Title: AROMATIC POLYESTER COATINGS AND LAMINATES

(57) Abstract: A method for coating a non-metallic substrate with a polymer solution that includes an aromatic polyester and a solvent is provided. By selectively controlling the nature of the aromatic polyester, the present inventors have discovered that such polymer solutions can be readily formed, thereby enabling the use of simpler and less complex techniques (e.g., solvent casting) for coating substrates with aromatic polyesters. Moreover, the nature of the polyester and its relative concentration in the solution can also be tailored to achieve coatings that not only adhere well to the substrate, but also possess good thermal and mechanical properties for use in a wide variety of potential applications.

AROMATIC POLYESTER COATINGS AND LAMINATES

Related Applications

[0001] The present application claims priority to U.S. Provisional Application Serial Nos. 61/740,040 (filed on Dec. 20, 2012) and 61/786,884 (filed on March 15, 2013), which are incorporated herein in their entirety by reference thereto.

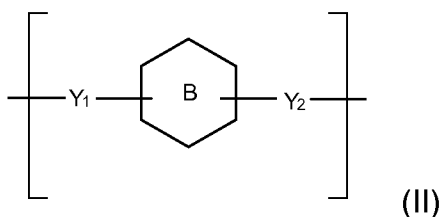
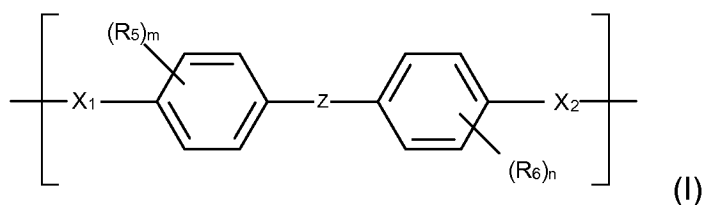
Background of the Invention

[0002] Liquid crystalline polymers ("LCP") are desirable for use in a wide variety of applications due to their high strength, high heat resistance, low coefficient of thermal expansion, and good insulation characteristics. For example, printed circuit boards are sometimes formed from a copper cladding that is reinforced with a fluoropolymer film. Due to the differences in thermal stresses between copper and fluoropolymers, it has been proposed to coat the fluoropolymer film with a pre-extruded liquid crystalline polymer film, which is then positioned adjacent to the copper cladding. While possessing improved heat resistance, one problem with such coatings is that the liquid crystalline polymers can sometimes exhibit poor adhesion to non-metallic substrates, such as fluoropolymer films. Furthermore, the formation of such laminates requires the use of multiple, complex processing steps, which can be costly and inefficient.

[0003] As such, a need exists for an improved process for coating a liquid crystalline polymer onto certain types of substrates, as well as for improved laminates formed therefrom.

Summary of the Invention

[0004] In accordance with one embodiment of the present invention, a method for forming a laminate that contains a coating and a non-metallic substrate is disclosed. The method comprises applying a polymer solution to the non-metallic substrate that comprises a solvent and an aromatic polyester, and thereafter removing the solvent to form the coating on the substrate. The aromatic polyester contains aromatic biphenyl units having the following general Formula I and aromatic ester units having the following general Formula II:



wherein,

R_5 and R_6 are independently halo, haloalkyl, alkyl, alkenyl, aryl, heteroaryl, cycloalkyl, or heterocyclyl;

m and n are independently from 0 to 4;

X_1 and X_2 are independently O, C(O), NH, C(O)HN, or NHC(O);

Z is O or SO₂;

ring B is a substituted or unsubstituted 6-membered aryl group, a substituted or unsubstituted 6-membered aryl group fused to a substituted or unsubstituted 5- or 6-membered aryl group, or a substituted or unsubstituted 6-membered aryl group linked to a substituted or unsubstituted 5- or 6-membered aryl group; and

Y_1 and Y_2 are independently O, C(O), NH, C(O)HN, or NHC(O), wherein at least one of Y_1 and Y_2 are C(O).

[0005] In accordance with another embodiment of the present invention, a laminate is disclosed that comprises a coating disposed on a non-metallic substrate, wherein the coating comprises an aromatic polyester containing aromatic biphenyl units, such as described herein.

[0006] Other features and aspects of the present invention are set forth in greater detail below.

Brief Description of the Figure

[0007] A full and enabling disclosure of the present invention, including the best mode thereof to one skilled in the art, is set forth more particularly in the remainder of the specification, including reference to the accompanying figure, in which:

[0008] Fig. 1 illustrates SEM microphotographs of the paper coated laminate of Example 8.

Detailed Description

[0009] It is to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to limit the scope of the present invention.

[0010] "Alkyl" refers to monovalent saturated aliphatic hydrocarbyl groups having from 1 to 10 carbon atoms and, in some embodiments, from 1 to 6 carbon atoms. "C_{x-y}alkyl" refers to alkyl groups having from x to y carbon atoms. This term includes, by way of example, linear and branched hydrocarbyl groups such as methyl (CH₃), ethyl (CH₃CH₂), *n*-propyl (CH₃CH₂CH₂), isopropyl ((CH₃)₂CH), *n*-butyl (CH₃CH₂CH₂CH₂), isobutyl ((CH₃)₂CHCH₂), *sec*-butyl ((CH₃)(CH₃CH₂)CH), *t*-butyl ((CH₃)₃C), *n*-pentyl (CH₃CH₂CH₂CH₂CH₂), and neopentyl ((CH₃)₃CCH₂).

[0011] "Alkenyl" refers to a linear or branched hydrocarbyl group having from 2 to 10 carbon atoms and in some embodiments from 2 to 6 carbon atoms or 2 to 4 carbon atoms and having at least 1 site of vinyl unsaturation (>C=C<). For example, (C_x-C_y)alkenyl refers to alkenyl groups having from x to y carbon atoms and is meant to include for example, ethenyl, propenyl, 1,3-butadienyl, and so forth.

[0012] "Alkynyl" refers to refers to a linear or branched monovalent hydrocarbon radical containing at least one triple bond. The term "alkynyl" may also include those hydrocarbyl groups having other types of bonds, such as a double bond and a triple bond.

[0013] "Aryl" refers to an aromatic group of from 3 to 14 carbon atoms and no ring heteroatoms and having a single ring (e.g., phenyl) or multiple condensed (fused) rings (e.g., naphthyl or anthryl). For multiple ring systems, including fused, bridged, and spiro ring systems having aromatic and non-aromatic rings that have no ring heteroatoms, the term "Aryl" applies when the point of attachment is at an aromatic carbon atom (e.g., 5,6,7,8 tetrahydronaphthalene-2-yl is an aryl group as its point of attachment is at the 2-position of the aromatic phenyl ring).

[0014] "Cycloalkyl" refers to a saturated or partially saturated cyclic group of from 3 to 14 carbon atoms and no ring heteroatoms and having a single ring or multiple rings including fused, bridged, and spiro ring systems. For multiple ring

systems having aromatic and non-aromatic rings that have no ring heteroatoms, the term “cycloalkyl” applies when the point of attachment is at a non-aromatic carbon atom (e.g., 5,6,7,8,-tetrahydronaphthalene-5-yl). The term “cycloalkyl” includes cycloalkenyl groups, such as adamantyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclooctyl, and cyclohexenyl. The term “cycloalkenyl” is sometimes employed to refer to a partially saturated cycloalkyl ring having at least one site of >C=C< ring unsaturation.

[0015] “Halo” or “halogen” refers to fluoro, chloro, bromo, and iodo.

[0016] “Haloalkyl” refers to substitution of alkyl groups with 1 to 5 or in some embodiments 1 to 3 halo groups.

[0017] “Heteroaryl” refers to an aromatic group of from 1 to 14 carbon atoms and 1 to 6 heteroatoms selected from oxygen, nitrogen, and sulfur and includes single ring (e.g., imidazolyl) and multiple ring systems (e.g., benzimidazol-2-yl and benzimidazol-6-yl). For multiple ring systems, including fused, bridged, and spiro ring systems having aromatic and non-aromatic rings, the term “heteroaryl” applies if there is at least one ring heteroatom and the point of attachment is at an atom of an aromatic ring (e.g., 1,2,3,4-tetrahydroquinolin-6-yl and 5,6,7,8-tetrahydroquinolin-3-yl). In some embodiments, the nitrogen and/or the sulfur ring atom(s) of the heteroaryl group are optionally oxidized to provide for the N oxide (N→O), sulfinyl, or sulfonyl moieties. Examples of heteroaryl groups include, but are not limited to, pyridyl, furanyl, thienyl, thiazolyl, isothiazolyl, triazolyl, imidazolyl, imidazoliny, isoxazolyl, pyrrolyl, pyrazolyl, pyridaziny, pyrimidinyl, purinyl, phthalazyl, naphthylpyridyl, benzofuranyl, tetrahydrobenzofuranyl, isobenzofuranyl, benzothiazolyl, benzoisothiazolyl, benzotriazolyl, indolyl, isoindolyl, indoliziny, dihydroindolyl, indazolyl, indoliny, benzoxazolyl, quinolyl, isoquinolyl, quinolizyl, quianazolyl, quinoxalyl, tetrahydroquinolinyl, isoquinolyl, quinazolinonyl, benzimidazolyl, benzisoxazolyl, benzothienyl, benzopyridaziny, pteridinyl, carbazolyl, carboliny, phenanthridiny, acridiny, phenanthroliny, phenaziny, phenoxaziny, phenothiaziny, and phthalimidyl.

[0018] “Heterocyclic” or “heterocycle” or “heterocycloalkyl” or “heterocyclyl” refers to a saturated or partially saturated cyclic group having from 1 to 14 carbon atoms and from 1 to 6 heteroatoms selected from nitrogen, sulfur, or oxygen and includes single ring and multiple ring systems including fused, bridged, and spiro

ring systems. For multiple ring systems having aromatic and/or non-aromatic rings, the terms “heterocyclic”, “heterocycle”, “heterocycloalkyl”, or “heterocyclyl” apply when there is at least one ring heteroatom and the point of attachment is at an atom of a non-aromatic ring (e.g., decahydroquinolin-6-yl). In some embodiments, the nitrogen and/or sulfur atom(s) of the heterocyclic group are optionally oxidized to provide for the N oxide, sulfinyl, sulfonyl moieties. Examples of heterocyclyl groups include, but are not limited to, azetidiny, tetrahydropyranyl, piperidiny, N-methylpiperidin-3-yl, piperaziny, N-methylpyrrolidin-3-yl, 3-pyrrolidiny, 2-pyrrolidon-1-yl, morpholiny, thiomorpholiny, imidazolidiny, and pyrrolidiny.

[0019] It should be understood that the aforementioned definitions encompass unsubstituted groups, as well as groups substituted with one or more other functional groups as is known in the art. For example, an aryl, heteroaryl, cycloalkyl, or heterocyclyl group may be substituted with from 1 to 8, in some embodiments from 1 to 5, in some embodiments from 1 to 3, and in some embodiments, from 1 to 2 substituents selected from alkyl, alkenyl, alkynyl, alkoxy, acyl, acylamino, acyloxy, amino, quaternary amino, amide, imino, amidino, aminocarbonylamino, amidinocarbonylamino, aminothiocarbonyl, aminocarbonylamino, aminothiocarbonylamino, aminocarbonyloxy, aminosulfonyl, aminosulfonyloxy, aminosulfonylamino, aryl, aryloxy, arylthio, azido, carboxyl, carboxyl ester, (carboxyl ester)amino, (carboxyl ester)oxy, cyano, cycloalkyl, cycloalkyloxy, cycloalkylthio, guanidino, halo, haloalkyl, haloalkoxy, hydroxy, hydroxyamino, alkoxyamino, hydrazino, heteroaryl, heteroaryloxy, heteroarylthio, heterocyclyl, heterocycluloxy, heterocyclylthio, nitro, oxo, oxy, thione, phosphate, phosphonate, phosphinate, phosphonamidate, phosphorodiamidate, phosphoramidate monoester, cyclic phosphoramidate, cyclic phosphorodiamidate, phosphoramidate diester, sulfate, sulfonate, sulfonyl, substituted sulfonyl, sulfonyloxy, thioacyl, thiocyanate, thiol, alkylthio, etc., as well as combinations of such substituents. When incorporated into the polymer of the present invention, such substitutions may be pendant or grafted groups, or may themselves form part of the polymer backbone. For example, in Formula I below, R₁ and/or R₂ may be a sulfonyl- or oxy-substituted aryl group in that the sulfonyl group (-SO₂-) or oxy

group (-O-) is contained within the polymer backbone and links together the phenyl group with the aryl substitution.

[0020] It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention.

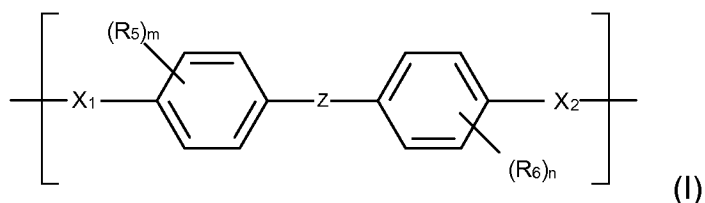
[0021] Generally speaking, the present invention is directed to a method for coating a non-metallic substrate with a polymer solution that includes an aromatic polyester and a solvent. By selectively controlling the nature of the aromatic polyester, the present inventors have discovered that such polymer solutions can be readily formed, thereby enabling the use of simpler and less complex techniques (e.g., solvent casting) for coating substrates with aromatic polyesters. Moreover, the nature of the polyester and its relative concentration in the solution can also be tailored to achieve coatings that not only adhere well to the substrate, but also possess good thermal and mechanical properties for use in a wide variety of potential applications.

[0022] Various embodiments of the present invention will now be described in more detail.

I. Polymer Solution

A. Aromatic Polyester

[0023] The aromatic polyester that is employed in the polymer solution generally contains aromatic biphenyl repeating units of Formula I:



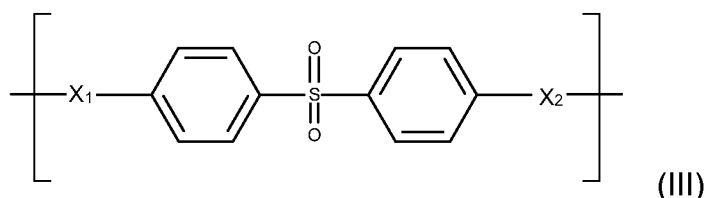
wherein,

R_5 and R_6 are independently halo, haloalkyl, alkyl, alkenyl, aryl, heteroaryl, cycloalkyl, or heterocyclyl;

m and n are independently from 0 to 4, in some embodiments from 0 to 1, and in one particular embodiment, 0;

X_1 and X_2 are independently O, C(O), NH, C(O)HN, or NHC(O); and Z is O or SO₂.

[0024] Without intending to be limited by theory, it is believed that certain types of aromatic biphenyl repeating units can sufficiently disrupt the highly crystalline and linear nature of the polymer backbone without having a significantly adverse impact on other properties of the polymer. Thus, the ability of the resulting polymer to be dissolved or dispersed in various solvents can be enhanced without sacrificing performance. In this regard, the nature and relative concentration of the aromatic biphenyl repeating units are generally selected to achieve the desired solubility without sacrificing other properties. For example, the aromatic biphenyl repeating units of Formula I may constitute from about 5 mol.% to about 50 mol.%, in some embodiments from about 10 mol.% to about 40 mol.%, and in some embodiments, from about 15 mol.% to about 30 mol.% of the polymer. Furthermore, in one particular embodiment, m and n are 0 in Formula I such that the biphenyl repeating unit has the following Formula (III):



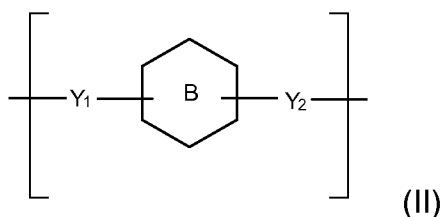
wherein, X_1 and X_2 are independently O, C(O), NH, C(O)HN, or NHC(O). For example, X_1 and/or X_2 may be O and/or NH.

[0025] The repeating units represented in Formula I and/or Formula III above may be derived from a variety of different biphenyl precursor monomers, including, for example, biphenyl alcohols (e.g., 4-(4-hydroxyphenyl)-sulfonylphenol, 4-(4-aminophenyl)sulfonylphenol, 4-(4-aminophenoxy)phenol, 4-(4-hydroxyphenoxy)-phenol, etc.); biphenyl amines (e.g., 4-(4-aminophenyl)sulfonylaniline, 4-(4-aminophenoxy)aniline, etc.); biphenyl acids (e.g., 4-(4-carboxyphenyl)-sulfonylbenzoic acid, 4-(4-formylphenoxy)benzaldehyde, etc.); biphenyl amides (e.g., 4-(4-carbamoylphenyl)sulfonylbenzamide, N-[4-(4-formamidophenyl)sulfonylphenyl]formamide, 4-(4-carbamoylphenoxy)benzamide, etc.); and so forth, as well as combinations thereof.

[0026] In addition to the biphenyl repeating units of Formula I, the aromatic polyester also contains one or more aromatic ester repeating units, typically in an amount of from about 50 mol.% to about 99 mol.%, in some embodiments from

about 55 mol.% to about 98 mol.%, and in some embodiments, from about 60 mol.% to about 95 mol.% of the polymer. The resulting copolymer may have any desired copolymer configuration known in the art, such as a block copolymer, grafted copolymer, random copolymer, etc.

[0027] The aromatic ester repeating units may be generally represented by the following Formula (II):



wherein,

ring B is a substituted or unsubstituted 6-membered aryl group (e.g., 1,4-phenylene or 1,3-phenylene), a substituted or unsubstituted 6-membered aryl group fused to a substituted or unsubstituted 5- or 6-membered aryl group (e.g., 2,6-naphthalene), or a substituted or unsubstituted 6-membered aryl group linked to a substituted or unsubstituted 5- or 6-membered aryl group (e.g., 4,4-biphenylene); and

Y_1 and Y_2 are independently O, C(O), NH, C(O)HN, or NHC(O), wherein at least one of Y_1 and Y_2 are C(O).

[0028] Examples of aromatic ester repeating units that are suitable for use in the present invention may include, for instance, aromatic dicarboxylic repeating units (Y_1 and Y_2 in Formula II are C(O)), aromatic hydroxycarboxylic repeating units (Y_1 is O and Y_2 is C(O) in Formula II), as well as various combinations thereof.

[0029] Aromatic dicarboxylic repeating units, for instance, may be employed that are derived from aromatic dicarboxylic acids, such as terephthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, 1,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, 4,4'-dicarboxybiphenyl, bis(4-carboxyphenyl)ether, bis(4-carboxyphenyl)butane, bis(4-carboxyphenyl)ethane, bis(3-carboxyphenyl)ether, bis(3-carboxyphenyl)ethane, etc., as well as alkyl, alkoxy, aryl and halogen substituents thereof, and combinations thereof. Particularly suitable aromatic dicarboxylic acids may

include, for instance, terephthalic acid ("TA") and isophthalic acid ("IA"). When employed, repeating units derived from aromatic dicarboxylic acids (e.g., IA and/or TA) typically constitute from about 5 mol.% to about 60 mol.%, in some embodiments from about 10 mol.% to about 55 mol.%, and in some embodiments, from about 15 mol.% to about 50% of the polymer.

[0030] Aromatic hydroxycarboxylic repeating units may also be employed that are derived from aromatic hydroxycarboxylic acids, such as, 4-hydroxybenzoic acid; 4-hydroxy-4'-biphenylcarboxylic acid; 2-hydroxy-6-naphthoic acid; 2-hydroxy-5-naphthoic acid; 3-hydroxy-2-naphthoic acid; 2-hydroxy-3-naphthoic acid; 4'-hydroxyphenyl-4-benzoic acid; 3'-hydroxyphenyl-4-benzoic acid; 4'-hydroxyphenyl-3-benzoic acid, etc., as well as alkyl, alkoxy, aryl and halogen substituents thereof, and combination thereof. One particularly suitable aromatic hydroxycarboxylic acid is 4-hydroxybenzoic acid ("HBA"). When employed, repeating units derived from hydroxycarboxylic acids (e.g., HBA) typically constitute from about 1 mol.% to about 70 mol.%, in some embodiments from about 5 mol.% to about 65 mol.%, and in some embodiments, from about 10 mol.% to about 50% of the polymer.

[0031] While a wide variety of aromatic ester repeating units may be employed, the polymer may nevertheless be "low naphthenic" to the extent that it contains a minimal content of repeating units derived from naphthenic hydroxycarboxylic acids and naphthenic dicarboxylic acids, such as naphthalene-2,6-dicarboxylic acid ("NDA"), 6-hydroxy-2-naphthoic acid ("HNA"), or combinations thereof. That is, the total amount of repeating units derived from naphthenic hydroxycarboxylic and/or dicarboxylic acids (e.g., NDA, HNA, or a combination of HNA and NDA) is typically no more than about 60 mol.%, in some embodiments, no more than about 50 mol.%, in some embodiments no more than about 35 mol.%, in some embodiments no more than about 30 mol.%, in some embodiments no more than about 25 mol.%, in some embodiments no more than about 20 mol.%, in some embodiments no more than about 15 mol.%, and in some embodiments, from 0 mol.% to about 10 mol.% of the polymer (e.g., 0 mol.%). Despite the absence of a high level of conventional naphthenic acid repeating units, the present inventors have discovered that selective control over the type and relative concentration of the biphenyl repeating units can lead to "low

naphthenic” polymers that are not only soluble in certain solvents, but also capable of exhibiting good mechanical properties.

[0032] Other repeating units may also be employed in the polymer. In certain embodiments, for instance, repeating units may be employed that are derived from aromatic diols, such as hydroquinone, resorcinol, 2,6-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 4,4'-dihydroxybiphenyl (or 4,4'-biphenol), 3,3'-dihydroxybiphenyl, 3,4'-dihydroxybiphenyl, 4,4'-dihydroxybiphenyl ether, bis(4-hydroxyphenyl)ethane, etc., as well as alkyl, alkoxy, aryl and halogen substituents thereof, and combinations thereof. Particularly suitable aromatic diols may include, for instance, hydroquinone (“HQ”) and 4,4'-biphenol (“BP”). When employed, repeating units derived from aromatic diols (e.g., HQ and/or BP) typically constitute from about 1 mol.% to about 30 mol.%, in some embodiments from about 2 mol.% to about 25 mol.%, and in some embodiments, from about 5 mol.% to about 20% of the polymer. Repeating units may also be employed, such as those derived from aromatic amides (e.g., acetaminophen (“APAP”)) and/or aromatic amines (e.g., 4-aminophenol (“AP”), 3-aminophenol, 1,4-phenylenediamine, 1,3-phenylenediamine, etc.). When employed, repeating units derived from aromatic amides (e.g., APAP) and/or aromatic amines (e.g., AP) typically constitute from about 0.1 mol.% to about 20 mol.%, in some embodiments from about 0.5 mol.% to about 15 mol.%, and in some embodiments, from about 1 mol.% to about 10% of the polymer. It should also be understood that various other monomeric repeating units may be incorporated into the polymer. For instance, in certain embodiments, the polymer may contain one or more repeating units derived from non-aromatic monomers, such as aliphatic or cycloaliphatic hydroxycarboxylic acids, dicarboxylic acids (e.g., cyclohexane dicarboxylic acid), diols, amides, amines, etc. Of course, in other embodiments, the polymer may be “wholly aromatic” in that it lacks repeating units derived from non-aromatic (e.g., aliphatic or cycloaliphatic) monomers.

[0033] In one particular embodiment, for example, the aromatic polyester may be formed from repeating units derived from a biphenyl sulfonyl alcohol and/or biphenyl sulfonyl amine (e.g., 4-(4-hydroxyphenyl)sulfonylphenol, or 4-(4-aminophenyl)-sulfonylaniline), 4-hydroxybenzoic acid (“HBA”), and terephthalic

acid ("TA") and/or isophthalic acid ("IA"), as well as various other optional constituents. The repeating units derived from the sulfonyl compound may constitute from about 5 mol.% to about 50 mol.%, in some embodiments from about 10 mol.% to about 40 mol.%, and in some embodiments, from about 15 mol.% to about 30 mol.%. The repeating units derived from 4-hydroxybenzoic acid ("HBA") may constitute from about 5 mol.% to about 70 mol.%, in some embodiments from about 10 mol.% to about 65 mol.%, and in some embodiments, from about 15 mol.% to about 50% of the polymer. The repeating units derived from terephthalic acid ("TA") and/or isophthalic acid ("IA") may likewise constitute from about 5 mol.% to about 40 mol.%, in some embodiments from about 10 mol.% to about 35 mol.%, and in some embodiments, from about 15 mol.% to about 35% of the polymer. Other possible repeating units may include those derived from 4,4'-biphenol ("BP"), hydroquinone ("HQ"), and/or acetaminophen ("APAP"). In certain embodiments, for example, repeating units derived from BP, HQ, and/or APAP may each constitute from about 1 mol.% to about 30 mol.%, in some embodiments from about 2 mol.% to about 25 mol.%, and in some embodiments, from about 3 mol.% to about 20 mol.% when employed. If desired, the polymer may also contain a relatively low amount of repeating units derived from naphthenic monomers (6-hydroxy-2-naphthoic acid ("HNA") or 2,6-naphthalenedicarboxylic acid ("NDA") within the ranges noted above.

[0034] Although not necessarily a requirement, the resulting aromatic polyester is generally classified as a "thermotropic liquid crystalline" polymer to the extent that it can possess a rod-like structure and exhibit a crystalline behavior in its molten state (e.g., thermotropic nematic state). The polymer may possess a fully crystalline, semi-crystalline, or amorphous-like structure under certain circumstances. For example, when dissolved in a solvent, the polymer may exhibit amorphous-like properties in that it becomes transparent and lacks an identifiable melting point. Yet, after heat treatment and solvent removal, the polymer may exhibit a highly-ordered crystalline structure in which the molecules are aligned. Contrary to many conventional melt processed liquid crystalline polymers, however, these polymers may nevertheless exhibit macroscopically isotropic mechanical properties.

[0035] Regardless of the particular constituents and nature of the polymer, the aromatic polyester may be prepared by initially introducing the aromatic monomer(s) used to form the ester repeating units (e.g., aromatic hydroxycarboxylic acid, aromatic dicarboxylic acid, etc.) and/or other repeating units (e.g., aromatic diol, aromatic amide, aromatic amine, etc.) into a reactor vessel to initiate a polycondensation reaction. The particular conditions and steps employed in such reactions are well known, and may be described in more detail in U.S. Patent No. 4,161,470 to Calundann; U.S. Patent No. 5,616,680 to Linstid, III, et al.; U.S. Patent No. 6,114,492 to Linstid, III, et al.; U.S. Patent No. 6,514,611 to Shepherd, et al.; and WO 2004/058851 to Waggoner. The vessel employed for the reaction is not especially limited, although it is typically desired to employ one that is commonly used in reactions of high viscosity fluids. Examples of such a reaction vessel may include a stirring tank-type apparatus that has an agitator with a variably-shaped stirring blade, such as an anchor type, multistage type, spiral-ribbon type, screw shaft type, etc., or a modified shape thereof. Further examples of such a reaction vessel may include a mixing apparatus commonly used in resin kneading, such as a kneader, a roll mill, a Banbury mixer, etc.

[0036] If desired, the reaction may proceed through the acetylation of the monomers as known the art. This may be accomplished by adding an acetylating agent (e.g., acetic anhydride) to the monomers. Acetylation is generally initiated at temperatures of about 90°C. During the initial stage of the acetylation, reflux may be employed to maintain vapor phase temperature below the point at which acetic acid byproduct and anhydride begin to distill. Temperatures during acetylation typically range from between 90°C to 150°C, and in some embodiments, from about 110°C to about 150°C. If reflux is used, the vapor phase temperature typically exceeds the boiling point of acetic acid, but remains low enough to retain residual acetic anhydride. For example, acetic anhydride vaporizes at temperatures of about 140°C. Thus, providing the reactor with a vapor phase reflux at a temperature of from about 110°C to about 130°C is particularly desirable. To ensure substantially complete reaction, an excess amount of acetic anhydride may be employed. The amount of excess anhydride will vary depending upon the particular acetylation conditions employed, including the presence or absence of reflux. The use of an excess of from about 1 to

about 10 mole percent of acetic anhydride, based on the total moles of reactant hydroxyl groups present is not uncommon.

[0037] Acetylation may occur in a separate reactor vessel, or it may occur *in situ* within the polymerization reactor vessel. When separate reactor vessels are employed, one or more of the monomers may be introduced to the acetylation reactor and subsequently transferred to the polymerization reactor. Likewise, one or more of the monomers may also be directly introduced to the reactor vessel without undergoing pre-acetylation.

[0038] The biphenyl precursor monomer (e.g., biphenyl alcohol, acid, amine, amide, etc.) may also be added to the polymerization apparatus. Although it may be introduced at any time, it is typically desired to apply the biphenyl monomer before melt polymerization has been initiated, and typically in conjunction with the other aromatic precursor monomers for the polymer. The relative amount of the biphenyl monomer added to the reaction mixture may be selected to help achieve a balance between solubility and mechanical properties as described above. In most embodiments, for example, biphenyl monomer(s) constitute from about 0.1 wt.% to about 30 wt.%, in some embodiments from about 0.5 wt.% to about 25 wt.%, and in some embodiments, from about 1 wt.% to about 20 wt.% of the reaction mixture.

[0039] In addition to the monomers and optional acetylating agents, other components may also be included within the reaction mixture to help facilitate polymerization. For instance, a catalyst may be optionally employed, such as metal salt catalysts (e.g., magnesium acetate, tin(II) acetate, tetrabutyl titanate, lead acetate, sodium acetate, potassium acetate, etc.) and organic compound catalysts (e.g., N-methylimidazole). Such catalysts are typically used in amounts of from about 50 to about 500 parts per million based on the total weight of the recurring unit precursors. When separate reactors are employed, it is typically desired to apply the catalyst to the acetylation reactor rather than the polymerization reactor, although this is by no means a requirement.

[0040] The reaction mixture is generally heated to an elevated temperature within the polymerization reactor vessel to initiate melt polycondensation of the reactants. Polycondensation may occur, for instance, within a temperature range of from about 210°C to about 400°C, and in some embodiments, from about

250°C to about 350°C. For instance, one suitable technique for forming the aromatic polyester may include charging precursor monomers and acetic anhydride into the reactor, heating the mixture to a temperature of from about 90°C to about 150°C to acetylate a hydroxyl group of the monomers (e.g., forming acetoxy), and then increasing the temperature to a temperature of from about 210°C to about 400°C to carry out melt polycondensation. As the final polymerization temperatures are approached, volatile byproducts of the reaction (e.g., acetic acid) may also be removed so that the desired molecular weight may be readily achieved. The reaction mixture is generally subjected to agitation during polymerization to ensure good heat and mass transfer, and in turn, good material homogeneity. The rotational velocity of the agitator may vary during the course of the reaction, but typically ranges from about 10 to about 100 revolutions per minute ("rpm"), and in some embodiments, from about 20 to about 80 rpm. To build molecular weight in the melt, the polymerization reaction may also be conducted under vacuum, the application of which facilitates the removal of volatiles formed during the final stages of polycondensation. The vacuum may be created by the application of a suctional pressure, such as within the range of from about 5 to about 30 pounds per square inch ("psi"), and in some embodiments, from about 10 to about 20 psi.

[0041] Following melt polymerization, the molten polymer may be discharged from the reactor, typically through an extrusion orifice fitted with a die of desired configuration, cooled, and collected. Commonly, the melt is discharged through a perforated die to form strands that are taken up in a water bath, pelletized and dried. The resin may also be in the form of a strand, granule, or powder. While unnecessary, it should also be understood that a subsequent solid phase polymerization may be conducted to further increase molecular weight. When carrying out solid-phase polymerization on a polymer obtained by melt polymerization, it is typically desired to select a method in which the polymer obtained by melt polymerization is solidified and then pulverized to form a powdery or flake-like polymer, followed by performing solid polymerization method, such as a heat treatment in a temperature range of 200°C to 350°C under an inert atmosphere (e.g., nitrogen).

[0042] Regardless of the particular method employed, the resulting aromatic polyester may have a relatively high melting temperature. For example, the melting temperature of the polymer may be from about 250°C to about 385°C, in some embodiments from about 280°C to about 380°C, in some embodiments from about 290°C to about 360°C, and in some embodiments, from about 300°C to about 350°C. Of course, in some cases, the polymer may not exhibit a distinct melting temperature when determined according to conventional techniques (e.g., DSC). The polymer may also have a relatively high melt viscosity, such as about 20 Pa-s or more, in some embodiments about 50 Pa-s or more, and in some embodiments, from about 750 to about 500 Pa-s, as determined at a shear rate of 1000 seconds⁻¹ and temperatures at least 20°C above the melting temperature (e.g., 320°C or 350°C) in accordance with ISO Test No. 11443 (equivalent to ASTM Test No. 1238-70). Further, the polymer typically has a number average molecular weight (M_n) of about 2,000 grams per mole or more, in some embodiments from about 4,000 grams per mole or more, and in some embodiments, from about 5,000 to about 50,000 grams per mole. Of course, it is also possible to form polymers having a lower molecular weight, such as less than about 2,000 grams per mole, using the method of the present invention. The intrinsic viscosity of the polymer, which is generally proportional to molecular weight, may also be relatively high. For example, the intrinsic viscosity may be about 1 deciliters per gram ("dL/g") or more, in some embodiments about 2 dL/g or more, in some embodiments from about 3 to about 20 dL/g, and in some embodiments from about 4 to about 15 dL/g. Intrinsic viscosity may be determined in accordance with ISO-1628-5 using a 50/50 (v/v) mixture of pentafluorophenol and hexafluoroisopropanol, as described in more detail below.

[0043] The polymer, as well as coatings containing the polymer, may also exhibit good electrical properties. For instance, the polymer and/or coating may have a relatively low dielectric constant that allows it to be employed as a heat dissipating material in various electronic applications (e.g., flexible printed circuit boards). For example, the average dielectric constant may be about 5.0 or less, in some embodiments from about 0.1 to about 4.5, and in some embodiments, from about 0.2 to about 3.5, as determined by the split post resonator method at a variety of frequencies, such as from about 1 to about 15 GHz (e.g., 1, 2, or 10

GHz). The dissipation factor, a measure of the loss rate of energy, may also be relatively low, such as about 0.0060 or less, in some embodiments about 0.0050 or less, and in some embodiments, from about 0.0010 to about 0.0040, as determined by the split post resonator method at a variety of frequencies, such as from about 1 to about 15 GHz (e.g., 1, 2, or 10 GHz).

B. Solvent

[0044] As indicated above, the aromatic polyester is generally soluble in a wide variety of solvents and can thus be employed to form solutions. Suitable solvents may include, for instance, aprotic solvents, protic solvents, as well as mixtures thereof. Examples of aprotic solvents may include organic solvents, such as halogen-containing solvents (e.g., methylene chloride, 1-chlorobutane, chlorobenzene, 1,1-dichloroethane, 1,2-dichloroethane, chloroform, and 1,1,2,2-tetrachloroethane); ether solvents (e.g., diethyl ether, tetrahydrofuran, and 1,4-dioxane); ketone solvents (e.g., acetone and cyclohexanone); ester solvents (e.g., ethyl acetate); lactone solvents (e.g., butyrolactone); carbonate solvents (e.g., ethylene carbonate and propylene carbonate); amine solvents (e.g., triethylamine and pyridine); nitrile solvents (e.g., acetonitrile and succinonitrile); amide solvents (e.g., N,N'-dimethylformamide, N,N'-dimethylacetamide, tetramethylurea and N-methylpyrrolidone); nitro-containing solvents (e.g., nitromethane and nitrobenzene); sulfide solvents (e.g., dimethylsulfoxide and sulfolane); and so forth. Among the above-listed aprotic solvents, amide solvents (e.g., N-methylpyrrolidone) are particularly suitable. Suitable protic solvents may likewise include, for instance, organic solvents having a phenolic hydroxyl group, such as phenolic compounds substituted with at least one halogen atom (e.g., fluorine or chlorine). Examples of such compounds include pentafluorophenol, tetrafluorophenol, o-chlorophenol, trichlorobenzene, and p-chlorophenol. Mixtures of various aprotic and/or protic solvents may also be employed.

C. Optional Additives

[0045] If desired, the polymer solution and/or coating may also employ one or more additives. Examples of such additives may include, for instance, viscosity modifiers, antimicrobials, pigments, antioxidants, stabilizers, surfactants, waxes, flow promoters, solid solvents, inorganic and organic fillers, and other materials added to enhance properties and processibility. For

example, a filler material may be incorporated with the polymer composition to enhance strength. A filler composition can include a filler material such as a fibrous filler and/or a mineral filler and optionally one or more additional additives as are generally known in the art. Mineral fillers may, for instance, be employed in the polymer composition to help achieve the desired mechanical properties and/or appearance. When employed, mineral fillers typically constitute from about 5 wt.% to about 60 wt.%, in some embodiments from about 10 wt.% to about 55 wt.%, and in some embodiments, from about 20 wt.% to about 50 wt.% of the polymer composition.

[0046] Clay minerals may be particularly suitable for use in the present invention. Examples of such clay minerals include, for instance, talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), illite ($((\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})])$), montmorillonite ($(\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$), vermiculite ($((\text{MgFe},\text{Al})_3(\text{Al},\text{Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O})$), palygorskite ($((\text{Mg},\text{Al})_2\text{Si}_4\text{O}_{10}(\text{OH}) \cdot 4(\text{H}_2\text{O}))$), pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$), etc., as well as combinations thereof. In lieu of, or in addition to, clay minerals, still other mineral fillers may also be employed. For example, other suitable fillers may include boron nitride, calcium silicate, aluminum silicate, mica, diatomaceous earth, wollastonite, alumina, silica, titanium dioxide, calcium carbonate, and so forth. Mica, for instance, may be particularly suitable. There are several chemically distinct mica species with considerable variance in geologic occurrence, but all have essentially the same crystal structure. As used herein, the term “mica” is meant to generically include any of these species, such as muscovite ($\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$), biotite ($\text{K}(\text{Mg},\text{Fe})_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$), phlogopite ($\text{KMg}_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$), lepidolite ($\text{K}(\text{Li},\text{Al})_{2-3}(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$), glauconite ($(\text{K},\text{Na})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$), etc., as well as combinations thereof. Nano-sized inorganic filler particles (e.g., diameter of about 100 nanometers or less) may also be employed in certain embodiments to help improve the flow properties of the composition. Examples of such particles may include, for instance, nanoclays, nanosilica, nanoalumina, etc. In yet another embodiment, inorganic hollow spheres (e.g., hollow glass spheres) may also be employed in the composition to help decrease the dielectric constant of the composition for certain applications.

[0047] Fibers may also be employed as a filler material to further improve the mechanical properties. Such fibers generally have a high degree of tensile strength relative to their mass. For example, the ultimate tensile strength of the fibers (determined in accordance with ASTM D2101) is typically from about 1,000 to about 15,000 Megapascals ("MPa"), in some embodiments from about 2,000 MPa to about 10,000 MPa, and in some embodiments, from about 3,000 MPa to about 6,000 MPa. To help maintain an insulating property, which is often desirable for use in electronic applications, the high strength fibers may be formed from materials that are also generally insulating in nature, such as glass, ceramics (e.g., alumina or silica), aramids (e.g., Kevlar® marketed by E. I. Du Pont de Nemours, Wilmington, Delaware), polyolefins, polyesters, etc., as well as mixtures thereof. Glass fibers are particularly suitable, such as E-glass, A-glass, C-glass, D-glass, AR-glass, R-glass, S1-glass, S2-glass, etc., and mixtures thereof.

[0048] Regardless of the particular ingredients employed, the resulting solution typically contains solvents in an amount of from about 60 wt.% to about 99 wt.%, in some embodiments from about 70 wt.% to about 98 wt.%, and in some embodiments, from about 75 wt.% to about 95 wt.%. Likewise, aromatic polyesters may constitute from about 1 wt.% to about 40 wt.%, in some embodiments from about 2 wt.% to about 30 wt.%, and in some embodiments, from about 5 wt.% to about 25 wt.% of the solution. The "solubility" of the polyester may likewise constitute from about 1% to about 50%, in some embodiments from about 2% to about 40%, and in some embodiments, from about 5% to about 30%. As discussed in more detail below, the "solubility" for a given polyester is calculated by dividing the maximum weight of the polyester that can be added to a solvent without any visible macroscopic phase separation by the weight of the solvent, and then multiplying this value by 100. The resulting solution typically has a solution viscosity within the range of from about 1,000 to about 100,000 centipoise, in some embodiments from about 2,000 to about 50,000 centipoise, and in some embodiments, from about 5,000 to about 20,000 centipoise, as determined at a temperature of 22°C using a Brookfield viscometer (spindle #63 and speed of 3 rpm).

[0049] To help increase the ability of the aromatic polyester to be dispersed in solution, it may be formed into a powder in certain embodiments of the present invention using a variety of different powder formation techniques. Examples of such powder formation techniques may include wet techniques (e.g., solvent evaporation, spray drying, etc.), dry techniques (e.g., grinding, granulation, etc.), and so forth. In one particular embodiment, for example, the polyester may be ground using a jaw crusher, gyratory crusher, cone crusher, roll crusher, impact crusher, hammer crusher, cracking cutter, rod mill, ball mill, vibration rod mill, vibration ball mill, pan mill, roller mill, impact mill, discoid mill, stirring grinding mill, fluid energy mill, jet mill, etc. Jet milling, for instance, typically involves the use of a shear or pulverizing machine in which the polymer composition is accelerated by gas flows and pulverized by collision. Any type of jet mill design may be employed, such as double counterflow (opposing jet) and spiral (pancake) fluid energy mills. Gas and particle flow may simply be in a spiral fashion, or more intricate in flow pattern, but essentially particles collide against each other or against a collision surface. In certain embodiments, it may be desired to mill the polymer composition in the presence of a cryogenic fluid (e.g., dry ice, liquid carbon dioxide, liquid argon, liquid nitrogen, etc.) to produce a low-temperature environment in the system. The low-temperature environment chills the polymer composition below its glass transition point to facilitate grinding in a mill that applies impact or shear, such as a jet-mill.

[0050] The resulting powder generally contains microparticles formed from the aromatic polyester of the present invention. The mean size of the microparticles is generally from about 0.1 to about 200 micrometers, in some embodiments from about 0.1 to about 100 micrometers, in some embodiments from about 0.1 to about 40 micrometers, in some embodiments from about 0.2 to about 30 micrometers, in some embodiments from about 0.5 to about 20 micrometers, and in some embodiments, from about 1 to about 15 micrometers. As used herein, the mean size of a microparticle may refer to its mean length, width, and/or height, and can be determined by optical microscopy as the average size of diameters measured at 2 degree intervals passing through a particle's geometric center. The microparticles may also possess a relatively low "aspect ratio" (mean length and/or width divided by the mean height). For example, the

aspect ratio of the microparticles may be from about 0.4 to about 2.0, in some embodiments from about 0.5 to about 1.5, and in some embodiments, from about 0.8 to about 1.2 (e.g., about 1). In one embodiment, for example, the microparticles may have a shape that is generally spherical in nature. Regardless of the actual size and shape, however, the size distribution of the microparticles may be generally consistent throughout the powder. That is, at least about 50% by volume of the microparticles, in some embodiments at least about 70% by volume of the microparticles, and in some embodiments, at least about 90% by volume of the microparticles (e.g., 100% by volume) may have a mean size within a range of from about 0.1 to about 200 micrometers, in some embodiments from about 0.2 to about 150 micrometers, in some embodiments from about 0.5 to about 100 micrometers, and in some embodiments, from about 1 to about 50 micrometers.

II. Coating

[0051] One benefit of the present invention is that the coating of the present invention can exhibit excellent adhesion to non-metallic substrates. For example, the coating may exhibit an adhesion index of about 3 or more, in some embodiments about 4 or more, and in some embodiments, from about 4.5 to 5, as determined in accordance with ASTM D3359-09e2 (Test Method B). Suitable non-metallic substrates may include, for instance, ceramic materials (e.g., silica, alumina, glass, etc.), polymeric materials, metalloid materials (e.g., silicon, boron, silicon, germanium, arsenic, antimony, tellurium, etc.), and so forth. Suitable polymeric materials may include, for instance, polytetrafluoroalkylenes (e.g., polytetrafluoroethylenes), polyurethanes, polyolefins, polyesters, polyimides, polyamides, etc. The substrate may also be provided in a variety of different forms, such as membranes, films, fibers, fabrics, molds, wafers, tubes, etc. If desired, the substrate may be porous. In certain applications, for instance, the porosity can allow for the passage of vapors, but not liquids, thereby resulting in a barrier material that is vapor-permeable and liquid-impermeable. The porosity may be provided in a variety of ways, such as by a process known as “expansion” in which the density of a polymer is reduced from an initial density, before processing, to a final density, after processing. An “expanded polymer” means a polymer that has been processed by expansion to reduce its density. Suitable expanded polymers may include, for instance, foamed polymers (e.g., polyolefins)

and mechanically expanded polymeric materials. In one particular embodiment of the present invention, for instance, the porous substrate may be formed from an "expanded" fluoropolymer (e.g., polytetrafluoroethylene ("PTFE")), such as described in U.S. Patent Nos. 3,953,566, 3,962,153, 4,096,227, and 4,187,390. For example, as is known in the art, expanded PTFE is generally formed by stretching PTFE in at least one direction so that the resulting structure achieves an open cell, node/fibril configuration, including only slightly expanded structures with short fibrils extending from large nodes of polymeric material to highly expanded structures with very long fibrils interconnected by small nodes.

[0052] The polymer solution may be coated onto the non-metallic substrate using any of a variety of known techniques, such as casting, roller coating, dip coating, spray coating, spinner coating, curtain coating, slot coating, screen printing, bar coating methods etc. In one particular embodiment, the polymer solution may be cast onto the substrate and thereafter the solvent(s) may be removed to form the coating. If desired, the solution may be filtered to remove contaminants prior to casting. The solvent(s) can likewise be removed through a variety of different methods, such as by heating, pressure reduction, ventilation, etc. In one particular embodiment, the solvent(s) are vaporized under ventilation. The vaporization may occur in one or multiple steps. For examples, a drying step may initially be employed at a temperature of from about 50°C to about 200°C for about 10 minutes to about 2 hours, and thereafter a heat treatment step may be employed at a temperature from about 200°C to about 450°C for about 30 minutes to about 6 hours.

[0053] The thickness of the resulting coating may vary, but is typically about 1 millimeter or less, in some embodiments from about 0.5 to about 500 micrometers, in some embodiments from about 1 to about 100 micrometers, and in some embodiments, from about 2 to about 20 micrometers. The majority of the coating is generally formed from aromatic polyesters. That is, aromatic polyesters may constitute about 50 wt.% or more, in some embodiments about 70 wt.% or more, and in some embodiments, from about 80 wt.% to about 99 wt.% of the coating. Of course, the coating may also contain other optional additives as noted above.

[0054] Laminates that contain the coating and substrate may have a variety of different layered configurations. For example, the laminate may have a two-layer structure containing only the coating and substrate. Alternatively, a multi-layered laminate may be formed, such as a three-layer structure in which the coating is positioned between two substrates. Regardless of the number of layers, various conventional processing steps may be employed to provide the laminate with sufficient strength. For example, the laminate may be pressed and/or subjected to heat treatment as is known in the art. Due to the good adhesion properties of the polymer, however, the laminate may be free of an additional adhesive between the coating and the non-metallic substrate. Nevertheless, adhesives can be employed if so desired, such as epoxy, phenol, polyester, nitrile, acryl, polyimide, polyurethane resins, etc.

III. Applications

[0055] The coated substrate or laminate can be employed in a wide variety of possible applications, such as multi-layer print wiring boards for semiconductor package and mother boards, flexible printed circuit board, tape automated bonding, tag tape, packaging for microwave oven, shields for electromagnetic waves, probe cables, communication equipment circuits, barrier products, MEMS devices, etc. In one particular embodiment, for instance, the laminate is employed in a flexible printed circuit board. In such embodiments, a conductive layer may also be applied to the laminate using any known technique, such as ion beam sputtering, high frequency sputtering, direct current magnetron sputtering, glow discharge, etc.

[0056] The present invention may be better understood with reference to the following examples.

Test Methods

Melt Viscosity: The melt viscosity (Pa-s) may be determined in accordance with ISO Test No. 11443 at 320°C or 350°C and at a shear rate of 400 s⁻¹ or 1000 s⁻¹ using a Dynisco 7001 capillary rheometer. The rheometer orifice (die) had a diameter of 1 mm, length of 20 mm, L/D ratio of 20.1, and an entrance angle of 180°. The diameter of the barrel was 9.55 mm ± 0.005 mm and the length of the rod was 233.4 mm.

[0057] *Intrinsic Viscosity:* The intrinsic viscosity (“IV”) may be measured in accordance with ISO-1628-5 using a 50/50 (v/v) mixture of pentafluorophenol and hexafluoroisopropanol. Each sample was prepared in duplicate by weighing about 0.02 grams into a 22 mL vial. 10 mL of pentafluorophenol (“PFP”) was added to each vial and the solvent. The vials were placed in a heating block set to 80°C overnight. The following day 10 mL of hexafluoroisopropanol (“HFIP”) was added to each vial. The final polymer concentration of each sample was about 0.1%. The samples were allowed to cool to room temperature and analyzed using a PolyVisc automatic viscometer.

[0058] *Solubility:* The solubility of a polymer can be determined by adding a predetermined amount of a polymer sample to a solution containing a predetermined amount of a solvent (e.g., N-methylpyrrolidone) and heating the resulting mixture from 150°C to 180°C for 3 hours. The mixture is considered soluble if it forms a clear to stable dispersion that does not undergo phase separation or separate into two layers upon standing at room temperature for a period of seven (7) days. If the mixture is determined to be soluble, additional amounts of the polymer sample are tested to determine the maximum amount of polymer that can be dissolved into the solvent. Likewise, if the mixture is determined to be insoluble, lower amounts of the polymer sample are tested. The “solubility” for a given polymer is calculated by dividing the maximum weight of the polymer that can be added to a solvent without phase separation by the weight of the solvent, and then multiplying this value by 100.

[0059] *Scanning Electron Microscopy (“SEM”):* The coated surfaces are examined by an SEM microscope (JSM 6360LV) at a 1.6 kv voltage.

[0060] *Fourier Transform Infrared Microscopy (“FT-IR”):* The coated surfaces are analyzed by a FT-IR microscope (Bio-rad, UMA-500) in the reflection mode (microATR, 30 degree Ge crystal, 100 scans, and 4 cm⁻¹ resolution).

[0061] *Solution Viscosity:* The solution viscosity is measured at 22°C using a Brookfield viscometer (Model: LVDV-II+ Pro, spindle #63). Viscosity measurements are taken at spindle speeds of 0.3 to 12 rpm until reaching the maximum capacity of the spring.

[0062] *Adhesion Index:* The adhesion properties of a coating are tested in accordance with ASTM D3359-09e2 (Test Method B). The adhesion index is

measured on a scale from 0 to 5, with 0 representing the highest degree of adhesion and 5 representing the lowest degree of adhesion. That is, when a tape is peeled away from the coating during testing, an index of 0 means that greater than 65% of the coating was removed, an index of 1 means that 35-65% was removed, an index of 2 means that 15-35% was removed, an index of 3 means that 5-15% was removed, an index of 4 means that less than 5% was removed, and an index of 5 means that 0% was removed.

EXAMPLE 1

[0063] A 2 L flask is charged with HBA (248.6 g), HNA (338.7 g), TA (99.7 g), IA (99.7 g), 4-aminophenyl sulfone (298 g), and 51 mg of potassium acetate. The flask is equipped with C-shaped stirrer, thermal couple, gas inlet, and distillation head. The flask is placed under a low nitrogen purge and acetic anhydride (99.7% assay, 628.5 g) is added. The milky-white slurry is agitated at 75 rpm and heated to 140°C over the course of 95 minutes using a fluidized sand bath. After this time, the mixture is gradually heated to 320°C steadily over 350 minutes. Reflux is seen once the reaction exceeds 140°C and the overhead temperature is increased to approximately 115°C as acetic acid byproduct was removed from the system. During the heating, the mixture grows yellow and slightly more viscous and the vapor temperature gradually drops to 90°C. Once the mixture reaches 320°C, the nitrogen flow is stopped. The flask is evacuated under vacuum and the agitation is slowed to 30 rpm. As the time under vacuum progresses, the mixture grows viscous. The reaction is stopped by releasing the vacuum and stopping the heat flow to the reactor, when a predetermined torque reading is observed. The flask is cooled and the resulting polymer is recovered as a solid, dense yellow plug. Sample for analytical testing is obtained by mechanical size reduction. The melt viscosity of the sample at 320°C is 103 Pa·s for a shear rate of 1000 s⁻¹ and 134.6 for a shear rate of 400 s⁻¹.

EXAMPLE 2

[0064] A 2 L flask is charged with HBA (310.8 g), HNA (141.1 g), IA (249.2 g), HQ (66.1 g), 4-hydroxyl phenyl sulfone (225.2 g), and 60 mg of potassium acetate. The flask is equipped with C-shaped stirrer, thermal couple, gas inlet, and distillation head. The flask is placed under a low nitrogen purge and acetic anhydride (99.7% assay, 628 g) is added. The milky-white slurry is agitated at 75

rpm and heated to 140°C over the course of 95 minutes using a fluidized sand bath. After this time, the mixture is gradually heated to 320°C steadily over 350 minutes. Reflux is seen once the reaction exceeds 140°C and the overhead temperature is increased to approximately 115°C as acetic acid byproduct was removed from the system. During the heating, the mixture grows yellow and slightly more viscous and the vapor temperature gradually drops to 90°C. Once the mixture reaches 320°C, the nitrogen flow is stopped. The flask is evacuated below 20 psi and the agitation is slowed to 30 rpm over the course of 45 minutes. As the time under vacuum progresses, the mixture grows viscous. After about 70 minutes, in the final vacuum step, a torque value of about 35 in/oz is recorded. The reaction is then stopped by releasing the vacuum and stopping the heat flow to the reactor. The flask is cooled and the resulting polymer is recovered as a solid, dense yellow-brown plug. Sample for analytical testing is obtained by mechanical size reduction. The melt viscosity of the sample at 370°C is 77 Pa-s for a shear rate of 1000 s⁻¹ and 94 Pa-s for a shear rate of 400 s⁻¹.

EXAMPLE 3

[0065] A 2 L flask is charged with HBA (172.7 g), HNA (235.7 g), IA (207.7 g), APAP (75.6 g) and 4-hydroxyl phenyl sulfone (187.7 g). The flask is equipped with a C-shaped stirrer, thermal couple, gas inlet, and distillation head. The flask is placed under a low nitrogen purge and acetic anhydride (99.7% assay, 628.5 g) is added. The milky-white slurry is agitated at 75 rpm and heated to 140°C over the course of 95 minutes using a fluidized sand bath. After this time, the mixture is then gradually heated to 320°C steadily over 350 minutes. Reflux is seen once the reaction exceeds 140°C and the overhead temperature increases to approximately 115°C as acetic acid byproduct is removed from the system. During the heating, the mixture grows yellow and slightly more viscous and the vapor temperature gradually drops to 90°C. Once the mixture has reached 320°C, the nitrogen flow is stopped. The flask is evacuated below 20 psi and the agitation slows to 30 rpm over the course of 45 minutes. As the time under vacuum progresses, the mixture grows viscous. After about 30 minutes, in the final vacuum step, a torque value of about 25 in/oz is recorded. The reaction is then stopped by releasing the vacuum and stopping the heat flow to the reactor. The flask is cooled and the resulting polymer is recovered as a solid, dense yellow-brown plug. Sample for analytical

testing is obtained by mechanical size reduction. The melt viscosity of the sample at 320°C is 99 Pa-s for a shear rate of 1000 s⁻¹ and 145 Pa-s for a shear rate of 400 s⁻¹.

EXAMPLE 4

[0066] A 2 L flask is charged with HBA (241.7 g), IA (270 g), HQ (89.5 g) and 4-hydroxyl phenyl sulfone (203.3 g). The flask is equipped with a C-shaped stirrer, thermal couple, gas inlet, and distillation head. The flask is placed under a low nitrogen purge and acetic anhydride (99.7% assay, 524 g) is added. The milky-white slurry is agitated at 75 rpm and heated to 140°C over the course of 95 minutes using a fluidized sand bath. After this time, the mixture is then gradually heated to 340°C steadily over 280 minutes. Reflux is seen once the reaction exceeds 140°C and the overhead temperature is increased to approximately 115 °C as acetic acid byproduct is removed from the system. During the heating, the mixture grows yellow and slightly more viscous and the vapor temperature gradually drops to 90°C. Once the mixture has reached 340°C, the nitrogen flow is stopped. The flask is evacuated below 20 psi and the agitation slows to 30 rpm over the course of 45 minutes. As the time under vacuum progresses, the mixture grows viscous. After about 15 minutes, in the final vacuum step, a torque value of about 1 in/oz is recorded. The reaction is then stopped by releasing the vacuum and stopping the heat flow to the reactor. The flask is cooled and the resulting polymer is recovered as a solid, dense yellow-brown plug. Sample for analytical testing is obtained by mechanical size reduction. The melt viscosity of the sample at 350°C is 137 Pa-s (shear rate of 1000 s⁻¹) and 152 Pa-s (shear rate of 400 s⁻¹).

EXAMPLE 5

[0067] A 2 L flask is charged with HBA (241.7 g), IA (270 g), HQ (123.9 g) and 4-hydroxyl phenyl sulfone (123.9 g). The flask is equipped with a C-shaped stirrer, thermal couple, gas inlet, and distillation head. The flask is placed under a low nitrogen purge and acetic anhydride (99.7% assay, 524 g) is added. The milky-white slurry is agitated at 75 rpm and heated to 140°C over the course of 95 minutes using a fluidized sand bath. After this time, the mixture is then gradually heated to 340°C steadily over 280 minutes. Reflux is seen once the reaction exceeds 140°C and the overhead temperature is increased to approximately 115 °C as acetic acid byproduct is removed from the system. During the heating, the

mixture grows yellow and slightly more viscous and the vapor temperature gradually drops to 90°C. Once the mixture has reached 340°C, the nitrogen flow is stopped. The flask is evacuated below 20 psi and the agitation slows to 30 rpm over the course of 45 minutes. As the time under vacuum progresses, the mixture grows viscous. After about 40 minutes, in the final vacuum step, a torque value of about 40 in/oz is recorded. The reaction is then stopped by releasing the vacuum and stopping the heat flow to the reactor. The flask is cooled and the resulting polymer is recovered as a solid, dense yellow-brown plug. Sample for analytical testing is obtained by mechanical size reduction. The melt viscosity of the sample at 370°C is 260 Pa-s (shear rate of 1000 s⁻¹) and 353 Pa-s (shear rate of 400 s⁻¹).

EXAMPLE 6

[0068] 45 grams of anhydrous NMP is initially heated at 180°C in a 100 mL beaker in an oil bath with a magnetic stirrer. Gradually, a certain amount of the polymer of the Examples 1, 3, and 5 above are added to the solution to achieve the concentrations noted below. The solution is stirred and is thereafter allowed to equilibrate overnight at room temperature without stirring. Once formed, the viscosity is measured at 22°C using the procedure described above. The results are set forth in the tables below.

Table 1: Viscosity for Example 1 at 17 wt.%, 20 wt.%, 22.5 wt.%, and 25 wt.%

Rpm	Viscosity (cP)			
	17%	20%	22.5%	25%
0.6	-	-	-	42,991
1.5	-	-	-	15,117
3	-	-	-	10,038
6	-	-	-	7,800
12	-	900	1300	6,300
30	-	700	960	-
60	120	585	759	-
100	118	514	660	-

Table 2: Viscosity for Example 3 at 18.2 wt.%

Rpm	Viscosity (cP) at 18.2 wt.%
30	-
60	146
100	146

Table 3: Viscosity for Example 5 at 18.2 wt.%, 25 wt.%, and 30 wt.%

Rpm	Viscosity (cP)		
	18.2%	25%	30%
0.3	-	25,994	41,591
0.6	-	18,796	29,794
1.5	-	9,038	19,756
3	-	6,919	14,077
6	-	4,539	10,598
12	-	3,619	7,558
30	172	-	-
60	170	-	-
100	178	-	-

EXAMPLE 7

[0069] The polymers of Examples 1, 3, and 5 are dissolved in N-methylpyrrolidone (NMP) at the concentrations noted below. The solutions are visually observed for solubility. If macroscopic phase separation is observed, "no" is recorded for the solubility determination. The results are set forth below.

Concentration (%)	Example 1	Example 3	Example 5
10.0	No	No	No
17.0	Yes	-	-
18.2	-	Yes	No
20.0	Yes	-	-
22.5	Yes	-	-
25.0	Yes	-	No
30.0	-	-	No

EXAMPLE 8

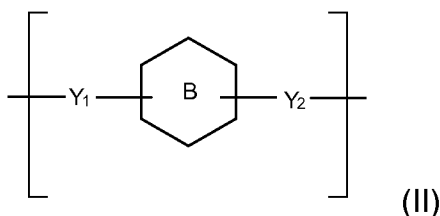
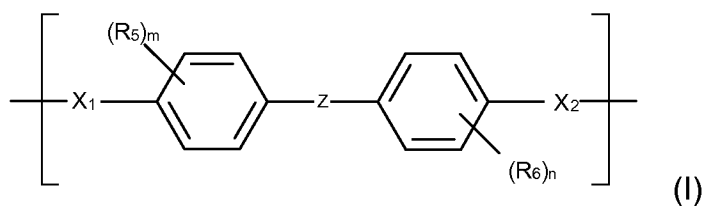
[0070] The ability to form a coating on paper is demonstrated. More particularly, the polymer of Example 5 is dissolved in N-methylpyrrolidone (NMP) at a concentration of 18.2 wt.%. The solution is applied to a paper web, dried at room temperature overnight, and then put in a convection oven at 200°C overnight. The resulting coating has a thickness of 114 μm.

[0071] These and other modifications and variations of the present invention may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present invention. In addition, it should be understood that aspects of the various embodiments may be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing

description is by way of example only, and is not intended to limit the invention so further described in such appended claims.

WHAT IS CLAIMED IS:

1. A laminate comprising a coating that is disposed on a non-metallic substrate, wherein the coating comprises an aromatic polyester containing aromatic biphenyl units having the following general Formula I and aromatic ester units having the following general Formula II:



wherein,

R_5 and R_6 are independently halo, haloalkyl, alkyl, alkenyl, aryl, heteroaryl, cycloalkyl, or heterocyclyl;

m and n are independently from 0 to 4;

X_1 and X_2 are independently O, C(O), NH, C(O)HN, or NHC(O);

Z is O or SO₂;

ring B is a substituted or unsubstituted 6-membered aryl group, a substituted or unsubstituted 6-membered aryl group fused to a substituted or unsubstituted 5- or 6-membered aryl group, or a substituted or unsubstituted 6-membered aryl group linked to a substituted or unsubstituted 5- or 6-membered aryl group; and

Y_1 and Y_2 are independently O, C(O), NH, C(O)HN, or NHC(O), wherein at least one of Y_1 and Y_2 are C(O).

2. The laminate of claim 1, wherein aromatic polyesters constitute about 70 wt.% or more of the coating.

3. The laminate of claim 1 or 2, wherein Z is SO₂.

4. The laminate of claim 3, wherein the biphenyl repeating units are derived from 4-(4-hydroxyphenyl)-sulfonylphenol, 4-(4-

aminophenyl)sulfonylphenol, 4-(4-aminophenyl)sulfonylaniline, or a combination thereof.

5. The laminate of claim 1 or 2, wherein Z is SO₂.

6. The laminate of any of the foregoing claims, wherein biphenyl repeating units constitute from about 5 mol.% to about 50 mol.% of the aromatic polyester and the aromatic ester repeating units constitute from about 50 mol.% to about 99 mol.% of the aromatic polyester.

7. The laminate of any of the foregoing claims, wherein m and n in Formula I are 0.

8. The laminate of any of the foregoing claims, wherein X₁, X₂, or both are O or NH.

9. The laminate of any of the foregoing claims, wherein ring B is 1,4-phenylene, 2,6-naphthalene, 4,4-biphenylene, or a combination thereof.

10. The laminate of any of the foregoing claims, wherein the aromatic polyester contains from about 5 mol.% to about 60 mol.% of aromatic ester repeating units derived from an aromatic dicarboxylic acid and from about 1 mol.% to about 70 mol.% of aromatic ester repeating units derived from an aromatic hydroxycarboxylic acid.

11. The laminate of any of the foregoing claims, wherein the aromatic polyester further comprises repeating units derived from an aromatic diol, aromatic amide, aromatic amine, or a combination thereof.

12. The laminate of any of the foregoing claims, wherein the aromatic polyester is wholly aromatic.

13. The laminate of any of the foregoing claims, wherein the non-metallic substrate includes a ceramic material, such as glass; a metalloid, such as silicon; a polymeric material, such as polytetrafluoroalkylene; or a combination thereof.

14. The laminate of any of the foregoing claims, wherein the coating exhibits an adhesion index of about 3 or more, as determined in accordance with ASTM D3359-09e2 (Test Method B).

15. A method for forming the laminate of any of the foregoing claims, the method comprising applying a polymer solution to the non-metallic substrate, wherein the polymer solution comprises a solvent and the aromatic polyester, and thereafter, removing the solvent to form the coating on the substrate.

16. The method of claim 15, wherein solvents constitute from about 60 wt.% to about 99 wt.% of the solution.

17. The method of claim 15 or 16, wherein the solution includes an aprotic solvent, such as a halogen-containing solvent, ether solvent, ketone solvent, ester solvent, lactone solvent, carbonate solvent, amine solvent, nitrile solvent, amide solvent, nitro-containing solvent, sulfide solvent, or a combination thereof.

18. The method of any of claims 15 to 17, further comprising dissolving a plurality of microparticles into the solvent to form the polymer solution, the microparticles including the aromatic polyester.

19. The method of any of claims 15 to 18, wherein the solution has a solution viscosity within the range of from about 1,000 to about 100,000 centipoise, as determined at a temperature of 22°C using a Brookfield viscometer (spindle #63 and speed of 3 rpm).

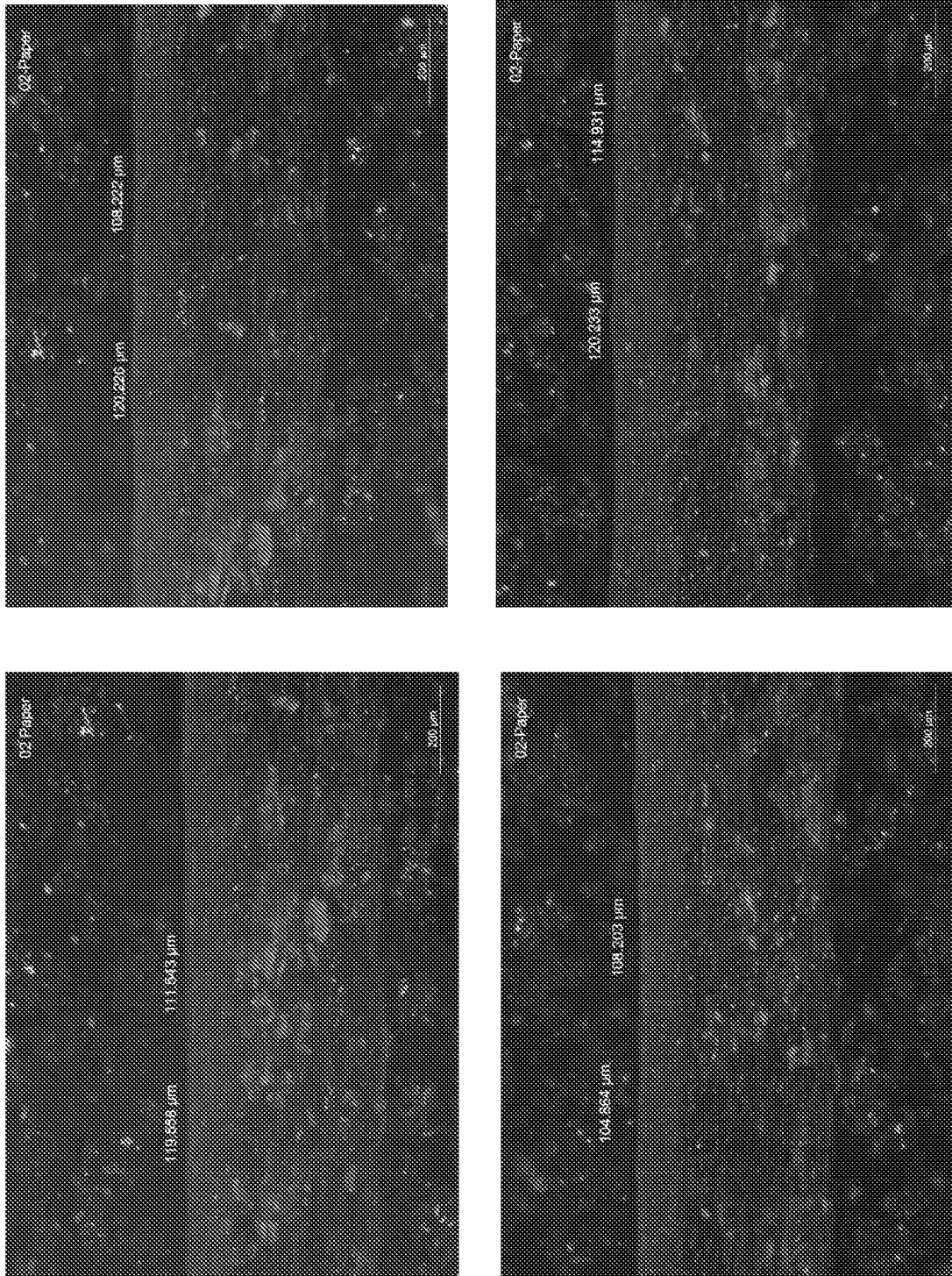


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/059855

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08L69/00 C08G63/60 C08G63/668 C09D167/00 C09D177/12
 C08J7/04 C08G63/688
 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)
 C08L C08K C08G C09D 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)
 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	EP 1 178 072 A2 (SUMITOMO CHEMICAL CO [JP]) 6 February 2002 (2002-02-06) claims 1,8 paragraphs [0046] - [0052] paragraphs [0009] - [0016] formula (e); paragraph [0020]	1-19
X	EP 0 196 528 A2 (KANEKAFUCHI CHEMICAL IND [JP]) 8 October 1986 (1986-10-08) claims 1,2,9 column 4, lines 7-10 example 1	1-19
X	US 4 797 465 A (PORTUGALL MICHAEL [DE] ET AL) 10 January 1989 (1989-01-10) claims 1,7 example 1	1-14
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 5 December 2013	Date of mailing of the international search report 12/12/2013
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Schlicke, Benedikt
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/059855

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 619 975 A (MATZNER MARKUS [US] ET AL) 28 October 1986 (1986-10-28) claims 1-3 column 12, lines 15-20 -----	1-14
X	US 2009/111949 A1 (CHO CHUNG KUN [KR] ET AL CHO CHUNG-KUN [KR] ET AL) 30 April 2009 (2009-04-30) claims 1-3,8-13 paragraphs [0053] - [0055] -----	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/059855

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1178072	A2	06-02-2002	CN 1336394 A 20-02-2002
			DE 60126872 T2 08-11-2007
			EP 1178072 A2 06-02-2002
			KR 20020011086 A 07-02-2002
			TW I256959 B 21-06-2006
			US 2002049270 A1 25-04-2002
			US 2004091686 A1 13-05-2004

EP 0196528	A2	08-10-1986	DE 3673202 D1 13-09-1990
			EP 0196528 A2 08-10-1986
			JP S61213147 A 22-09-1986
			US 4738880 A 19-04-1988

US 4797465	A	10-01-1989	CA 1266946 A1 20-03-1990
			DE 3542778 A1 11-06-1987
			EP 0226847 A1 01-07-1987
			JP S62132921 A 16-06-1987
			US 4797465 A 10-01-1989

US 4619975	A	28-10-1986	CA 1267779 A1 17-04-1990
			DE 3661315 D1 05-01-1989
			EP 0214612 A2 18-03-1987
			JP S62116626 A 28-05-1987
			US 4619975 A 28-10-1986

US 2009111949	A1	30-04-2009	KR 20090041914 A 29-04-2009
			US 2009111949 A1 30-04-2009
