

PRODUCTION OF SUBSTITUTED PHENYLENE AROMATIC DIESTERS

PRIORITY CLAIM

[0001] This application claims priority to U.S. provisional patent application serial no. 61/141,959 filed on December 31, 2008, the entire content of which is incorporated by reference herein.

BACKGROUND

[0002] The present disclosure relates to substituted 1,2-phenylene aromatic diesters.

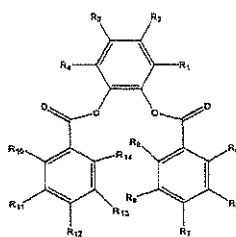
[0003] A known synthesis for unsubstituted phenylene dibenzoate is esterification of catechol with benzoyl chloride in a liquid medium. Substituted phenylene dibenzoate shows promise as a component in improved catalyst systems for the production of olefin-based polymers having improved properties. Consequently, the art recognizes the need for improved processes for the production of substituted phenylene aromatic diesters and the resultant compositions.

SUMMARY

[0004] The present disclosure is directed to substituted 1,2-phenylene aromatic diesters.

[0005] In an embodiment, a process for producing a diester is provided. The process includes reacting a substituted aromatic diol with an aromatic carboxylic acid or derivative thereof under reaction conditions. The reaction forms a substituted 1,2-phenylene dibenzoate of the structure (II):

(II)



wherein R₁-R₁₄ are the same or different. At least one of R₁-R₄ is selected from an unsubstituted hydrocarbyl group having 2 to 20 carbon atoms and a substituted hydrocarbyl group having 2 to 20 carbon atoms. Each of the other R groups of R₁-R₄ is hydrogen. Each of R₅-R₁₄ is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20

carbon atoms, a substituted hydrocarbyl group having 1 to 20 atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof.

[0006] In an embodiment, the process includes selecting a substituted catechol wherein neither R_1 nor R_2 is a methyl group when each of the other R groups of R_1 - R_{14} groups is hydrogen.

[0007] The disclosure provides another process for producing a diester. In an embodiment, a process for producing a diester includes reacting a substituted aromatic diol with a substituted aromatic acyl halide under reaction conditions. The reaction forms a substituted 1,2-phenylene dibenzoate of the structure (II) wherein R_1 - R_{14} are the same or different. At least one of R_1 - R_4 , at least one of R_5 - R_9 , and at least one of R_{10} - R_{14} is selected from an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof.

[0008] The disclosure provides another process for producing a diester. In an embodiment, a process for producing a diester includes reacting an aromatic diol with a disubstituted carboxylic acid or derivative thereof under reaction conditions. The reaction forms a substituted 1,2-phenylene dibenzoate of the structure (II) wherein R_1 - R_{14} are the same or different. At least two of R_5 - R_9 , and at least two of R_{10} - R_{14} are selected from an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof.

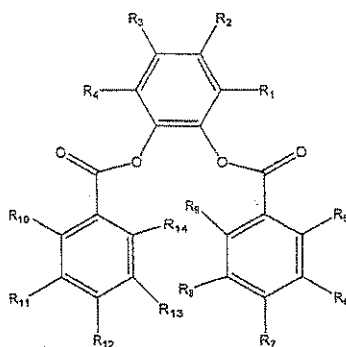
[0009] The disclosure provides another process for producing a diester. In an embodiment, a process for producing a diester includes reacting an aromatic diol with a first aromatic carboxylic acid or derivative thereof and a second aromatic carboxylic acid or derivative thereof under reaction conditions. The reaction forms a substituted 1,2-phenylene dibenzoate of the structure (II) wherein R_1 - R_{14} are the same or different. Each of R_1 - R_{14} is selected from hydrogen, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof. At least one of R_5 - R_9 is different than its respective R_{10} - R_{14} mate.

[0010] The disclosure provides another process for producing a diester. In an embodiment, a process for producing a diester includes reacting a dihydroxynaphthalene with a carboxylic acid or derivative thereof under reaction conditions. The reaction forms a substituted 1,2-phenylene dibenzoate wherein R_1 - R_{14} are the same or different. In an embodiment, R_2 and R_3 are members of a C_6 aromatic ring. In a further embodiment, at least one R group of R_1 - R_{14} is not hydrogen.

[0011] The disclosure provides another process for producing a diester. In an embodiment, a process for producing a diester includes reacting an aromatic diol with a naphthoyl halide under reaction conditions. The reaction forms a substituted 1,2-phenylene dibenzoate (II) wherein any two consecutive R groups in R_5 - R_9 and/or any two consecutive R groups in R_{10} - R_{14} are members of a C_6 aromatic ring.

[0012] The disclosure provides a composition. In an embodiment, a substituted phenylene aromatic diester is provided having the structure (II):

(II)



wherein R_1 - R_{14} are the same or different. R_1 is not an isopropyl group or a tertiary alkyl group. Each of R_1 and R_3 is selected from an unsubstituted alkyl group having 1 to 20 carbon atoms, an alkenyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. Each of R_2 , R_4 , and R_5 - R_{14} is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, and combinations thereof.

[0013] The present disclosure provides another composition. In an embodiment, a substituted phenylene aromatic diester of the structure (II) is provided. R_1 - R_{14} are the same or different. R_1 is an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms. Each of R_2 - R_4 is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon

atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. Each of R₅-R₁₄ is selected from an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

[0014] The present disclosure provides another composition. In an embodiment, a substituted phenylene aromatic diester of the structure (II) is provided. R₁-R₁₄ are the same or different. R₂ is an alkyl group having 2 to 20 carbon atoms. Each other R group of R₁-R₄ is hydrogen. Each of R₅-R₁₄ is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. The R groups R₂, R₇, and R₁₂ are simultaneously not a t-butyl group.

[0015] The present disclosure provides another composition. In an embodiment, a substituted phenylene aromatic diester with the structure (II) is provided. R₁-R₁₄ are the same or different. Each of R₁, R₃, R₄ is hydrogen. R₂ is a hydrocarbyl group having 1 to 20 carbon atoms. At least one of R₇ and R₁₂ is a halogen. Each of R₅-R₆, R₈-R₁₁ and R₁₃-R₁₄ is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

[0016] The disclosure provides another composition. In an embodiment, a substituted phenylene aromatic diester is provided having the structure (II). R₁-R₁₄ are the same or different. Each of R₁, R₃, R₄ is hydrogen. R₂ is a hydrocarbyl group having 1 to 20 carbon atoms. Each of R₅-R₁₄ is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. At least one of R₅-R₆, R₈-R₁₁ and R₁₃-R₁₄ is selected from a C₁-C₆ alkyl group, a halogen, and combinations thereof.

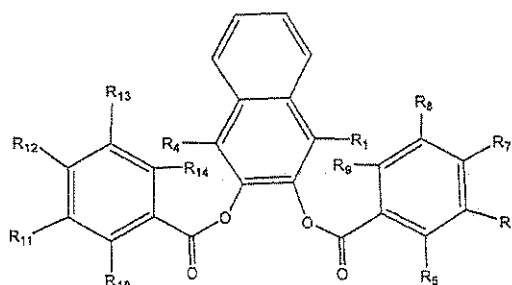
[0017] The disclosure provides another composition. In an embodiment, a substituted 1,2-phenylene aromatic diester of the structure (II) is provided. R₁-R₁₄ are the same or different. R₁ is not a secondary alkyl group or a tertiary alkyl group. Each of R₁ and R₄ is selected from an unsubstituted alkyl group having 1 to 20 carbon atoms, an alkenyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. Each of R₂-R₃ and each of R₅-R₁₄ is selected

from hydrogen, unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

[0018] Another composition is provided. In an embodiment, a substituted phenylene aromatic diester of the structure (II) is provided. R_1 - R_{14} are the same or different. Each of R_1 - R_{14} is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. At least one of R_5 - R_9 is different than its respective R_{10} - R_{14} mate.

[0019] Another composition is provided. In an embodiment, a substituted phenylene aromatic diester is provided with the structure (IV) below.

(IV)



[0020] R_1 , R_4 and R_{5-14} are the same or different. Each of R_1 and R_4 is hydrogen. At least one of R_5 - R_{14} is selected from an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. R_7 and R_{12} are simultaneously not a methyl group.

[0021] An advantage of the present disclosure is the provision of substituted phenylene aromatic diester compounds with improved properties.

[0022] An advantage of the present disclosure is the provision of improved substituted phenylene aromatic diester suitable for use in procatalyst and/or catalyst compositions for the production of olefin-based polymers.

DETAILED DESCRIPTION

[0023] The present disclosure is directed to the production of substituted 1,2-phenylene aromatic diesters.

[0024] In an embodiment, a process for producing a diester is provided. The process includes reacting a substituted aromatic diol with an aromatic carboxylic acid or derivative thereof. The reaction forms a substituted phenylene aromatic diester.

[0025] As used herein, an "aromatic diol" is a compound containing at least one benzene ring with at least two adjacent hydroxyl groups. It is understood that the aromatic diol may be a monocyclic structure or a polycyclic structure. Nonlimiting examples of suitable aromatic diols include benzenediols such as 1,2-benzenediol (catechol), 1,2-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, and 1,8-dihydroxynaphthalene.

[0026] The term "substituted aromatic diol," as used herein, refers to an aromatic diol whereby at least one (or two, or three, or four) of the benzene-ring substituents (other than the two hydroxyl groups) is a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof. As used herein, the term "hydrocarbyl" and "hydrocarbon" refer to substituents containing only hydrogen and carbon atoms, including branched or unbranched, saturated or unsaturated, cyclic, polycyclic, fused, or acyclic species, and combinations thereof. Nonlimiting examples of hydrocarbyl groups include alkyl-, cycloalkyl-, alkenyl-, alkadienyl-, cycloalkenyl-, cycloalkadienyl-, aryl-, aralkyl, alkylaryl, and alkynyl- groups.

[0027] As used herein, the terms "substituted hydrocarbyl" and "substituted hydrocarbon" refer to a hydrocarbyl group that is substituted with one or more nonhydrocarbyl substituent groups. A nonlimiting example of a nonhydrocarbyl substituent group is a heteroatom. As used herein, a "heteroatom" refers to an atom other than carbon or hydrogen. The heteroatom can be a non-carbon atom from Groups IV, V, VI, and VII of the Periodic Table. Nonlimiting examples of heteroatoms include: halogens (F, Cl, Br, I), N, O, P, B, S, and Si. A substituted hydrocarbyl group also includes a halohydrocarbyl group and/or a silicon-containing hydrocarbyl group. As used herein, the term "halohydrocarbyl group" refers to a hydrocarbyl group that is substituted with one or more halogen atoms. As used herein, the term "silicon-containing hydrocarbyl group" is a hydrocarbyl group that is substituted with one or more silicon atoms. The silicon atom(s) may or may not be in the carbon chain.

[0028] An aromatic carboxylic acid, or a derivative of an aromatic carboxylic acid, is another reactant in the present process. As used herein, an "aromatic carboxylic acid" is a compound containing at least one benzene ring with at least one carboxyl group directly bonded to the benzene ring. It is understood that the aromatic carboxylic acid may be a monocyclic structure or a polycyclic structure. The aromatic carboxylic acid may be a mono- or a poly-carboxylic acid. Nonlimiting examples of suitable aromatic carboxylic acids include benzoic acid, 1-naphthoic acid, 2-naphthoic acid, 6H-phenalene-2-carboxylic acid, anthracene-2-carboxylic acid, phenanthrene-2-carboxylic acid, and phenanthrene-3-carboxylic acid.

[0029] A "derivative of an aromatic carboxylic acid" or "an aromatic carboxylic acid derivative," as used herein, refers to an aromatic acyl halide, an aromatic anhydride, an aromatic carboxylate salt, or any combination thereof. It is understood that the derivative of the aromatic carboxylic acid may be a monocyclic structure or a polycyclic structure. Nonlimiting examples of suitable aromatic acyl halides include halides of any of the aromatic carboxylic acids disclosed above (*i.e.*, a halide of one or more of the following: benzoic acid, 1-naphthoic acid, 2-naphthoic acid, 6H-phenalene-2-carboxylic acid, anthracene-2-carboxylic acid, phenanthrene-2-carboxylic acid, and/or phenanthrene-3-carboxylic acid). Further nonlimiting examples of suitable aromatic acyl halides include benzoyl chloride, benzoyl fluoride, benzoyl bromide, and benzoyl iodide, naphthoyl chloride, naphthoyl fluoride, naphthoyl bromide, naphthoyl iodide, and any combination of the foregoing aromatic acyl halides.

[0030] Nonlimiting examples of suitable aromatic anhydrides include anhydride of the aromatic carboxylic acids disclosed above (*i.e.*, an anhydride of one or more of the following: benzoic acid, 1-naphthoic acid, 2-naphthoic acid, 6H-phenalene-2-carboxylic acid, anthracene-2-carboxylic acid, phenanthrene-2-carboxylic acid, and/or phenanthrene-3-carboxylic acid). Further nonlimiting examples of suitable aromatic anhydrides include benzoic anhydride and any combination of the foregoing aromatic anhydrides.

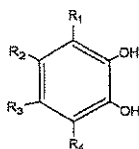
[0031] Nonlimiting examples of suitable aromatic carboxylate salts include potassium, sodium, or lithium salt of the aromatic carboxylic acids disclosed above (*i.e.*, salts of one or more of the following: benzoic acid, 1-naphthoic acid, 2-naphthoic acid, 6H-phenalene-2-carboxylic acid, anthracene-2-carboxylic acid, phenanthrene-2-carboxylic acid,

and/or phenanthrene-3-carboxylic acid). Further nonlimiting examples of suitable aromatic carboxylate salts include potassium benzoate, sodium benzoate, lithium benzoate, potassium 2-naphthoate, sodium 2-naphthoate, and any combination of the foregoing aromatic carboxylate salts.

[0032] The aromatic carboxylic acid, or derivative thereof may be substituted. The term "substituted aromatic carboxylic acid or derivative thereof," as used herein, refers to an aromatic carboxylic acid, or derivative thereof, whereby at least one of the benzene-ring substituents (other than the carboxyl group) is a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof. Thus, the term "substituted aromatic carboxylic acid or derivative thereof" includes substituted aromatic carboxylic acid, substituted aromatic acyl halide, substituted aromatic anhydride, and/or substituted aromatic carboxylate salt.

[0033] In an embodiment, the present process includes reacting the substituted aromatic diol with the aromatic carboxylic acid (or derivative thereof) under reaction conditions to form a substituted phenylene aromatic diester. "Reaction conditions," as used herein, refer to temperature, pressure, reactant concentrations, solvent concentrations, reactant mixing/addition parameters, and/or other conditions that influence the properties of the resulting product.

[0034] The characteristics of the phenylene moiety are determined by the substituted aromatic diol. For example, a substituted 1,2-benzenediol yields a substituted 1,2-phenylene aromatic diester. In an embodiment, the substituted aromatic diol is a substituted catechol. The substituted catechol has the structure (I):

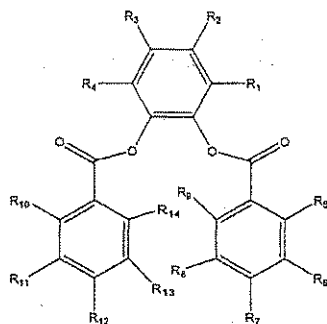


(I)

wherein at least one, or two, or three, or four R group(s) of R₁-R₄ is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof. Each of R₁-R₄ may or may not be hydrogen. The

process includes reacting the substituted catechol with an aromatic acyl halide, such as a benzoyl halide. This reaction forms a substituted 1,2-phenylene dibenzoate of the structure (II):

(II)



wherein R₁-R₄ are the same or different. At least one of R₁-R₄ is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof. Any of R₁-R₄ may also be hydrogen.

[0035] In an embodiment, each R group of R₁-R₄ that is not hydrogen is an alkyl group having 1 to 20 carbon atoms.

[0036] In an embodiment, the process includes reacting a substituted aromatic diol, such as a substituted catechol, with an unsubstituted or substituted aromatic acyl halide under reaction conditions. At least one of R₁-R₄ of the substituted catechol is selected from an unsubstituted hydrocarbyl group having 2 to 20 carbon atoms or a substituted hydrocarbyl group having 2 to 20 carbon atoms. Each of the other R groups of R₁-R₄ is hydrogen. The process includes forming a substituted phenylene aromatic diester of structure (II) wherein R₁-R₁₄ are the same or different. One of R₁-R₄ of structure (II) is a substituted hydrocarbyl group having 2 to 20 carbon atoms or an unsubstituted hydrocarbyl group having 2 to 20 carbon atoms. Each of the other R₁-R₄ substituents is hydrogen. Each of R₅-R₁₄ is hydrogen. In another embodiment, each R₁-R₄ group(s) that is not hydrogen is an alkyl group having 2 to 20 carbon atoms.

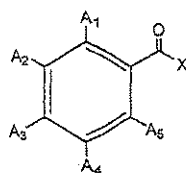
[0037] In an embodiment, only one of R₁-R₄ is substituted with the remaining R₁-R₄ being hydrogen.

[0038] In an embodiment, the process includes selecting a substituted catechol such that neither R_1 nor R_2 is a methyl group when each of the other R groups of R_1 - R_{14} is hydrogen.

[0039] In an embodiment, the process includes reacting the substituted catechol with a substituted aromatic acyl halide under reaction conditions. The substituted catechol includes one (or two, or three, or four) R groups of R_1 - R_4 selected from an unsubstituted/substituted hydrocarbyl group having 2 to 20 carbon atoms and the remaining R groups of R_1 - R_4 being hydrogen.

[0040] In an embodiment, the substituted aromatic acyl halide is a substituted benzoyl halide of the structure (III):

(III)



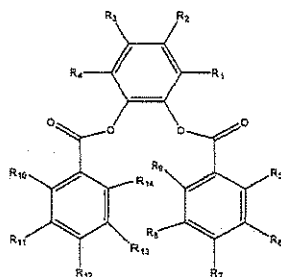
wherein X is a halogen atom (F, Cl, Br, I). At least one (or two, or three, or four, or five) A group(s) of A_1 - A_5 is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof. Any of A_1 - A_5 may also be hydrogen. A nonlimiting example of a suitable substituted aromatic acyl halide is a substituted benzoyl chloride.

[0041] The reaction between the substituted catechol and the substituted aromatic acyl halide (III) forms a substituted 1,2-phenylene dibenzoate of the structure (II) wherein R_1 - R_{14} are the same or different. One of R_1 - R_4 is selected from an unsubstituted or a substituted hydrocarbyl group having 1 to 20 carbon atoms. Each of the other of R_1 - R_4 is hydrogen. R_5 - R_{14} are the same or different. Each of R_5 - R_{14} is selected from hydrogen, a substituted or unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof. In a further embodiment, each R group of R_1 - R_{14} that is not hydrogen is an alkyl group having 1 to 20 carbon atoms.

[0042] The disclosure provides another process. In an embodiment, a process for producing a diester is provided which includes reacting a substituted aromatic diol with a

substituted aromatic acyl halide under reaction conditions and forming a substituted 1,2-phenylene dibenzoate of structure (II):

(II)

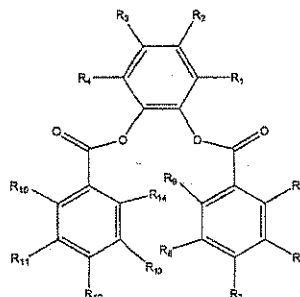


wherein R_1 - R_{14} are the same or different. At least one (or two, or three, or four) R group(s) of R_1 - R_4 , at least one (or two, or three, or four, or five) R group(s) of R_5 - R_9 , and at least one (or two, or three, or four, or five) R group(s) of R_{10} - R_{14} is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof. Each of R_1 - R_{14} may or may not be hydrogen. In a further embodiment, each R_1 - R_{14} group(s) that is not hydrogen is an alkyl group having 1 to 20 carbon atoms.

[0043] In an embodiment, the process includes reacting a substituted catechol with a substituted benzoyl halide to form the substituted 1,2-phenylene dibenzoate of structure (II) wherein at least one of R_1 - R_4 , at least one of R_5 - R_9 , and at least one of R_{10} - R_{14} is substituted (*i.e.*, not hydrogen) as disclosed above. In a further embodiment, each R_1 - R_{14} group(s) that is not hydrogen is an alkyl group having 1 to 20 carbon atoms.

[0044] The disclosure provides another process. In an embodiment, a process is provided which includes reacting an aromatic diol with a di-substituted (or tri-, or tetra-, or penta-substituted) aromatic carboxylic acid or derivative thereof under reaction conditions. The aromatic diol may be substituted or unsubstituted. The process includes forming a substituted 1,2-phenylene dibenzoate of the structure (II):

(II)



wherein R_1 - R_{14} are the same or different. At least two of R_5 - R_9 and at least two of R_{10} - R_{14} is selected from an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof. In a further embodiment, each R_1 - R_{14} group(s) that is not hydrogen is an alkyl group having 1 to 20 carbon atoms.

[0045] In an embodiment, the process includes reacting a catechol with a di-substituted (or tri-, or tetra-, or penta-substituted) aromatic acyl halide and forming a substituted 1,2-phenylene dibenzoate of the structure (II) wherein each of R_1 - R_4 is hydrogen, and at least two of R_5 - R_9 and at least two of R_{10} - R_{14} are substituted as disclosed above. In a further embodiment, each R_1 - R_{14} group(s) that is not hydrogen is an alkyl group having 1 to 20 carbon atoms.

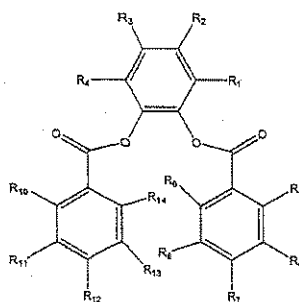
[0046] In an embodiment, the process includes reacting a substituted aromatic diol with a di-substituted (or tri-, or tetra-, or penta-substituted) aromatic acyl halide to form a substituted phenylene dibenzoate of structure (II) wherein at least one of R_1 - R_4 is selected from an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen. At least two of R_5 - R_9 and at least two of R_{10} - R_{14} are substituted as disclosed above. In a further embodiment, each R group of R_1 - R_{14} that is not hydrogen is an alkyl group having 1 to 20 carbon atoms.

[0047] The ester groups extending from the phenylene moiety of structure (II) may be considered mirror images of each other. In this sense, a symmetry may exist between the ester groups such that the individual substituents R_5 - R_9 correspond to or otherwise mirror respective individual substituents R_{10} - R_{14} . As used herein, the term "mated" or "a respective

mate” or similar term(s) refers to the following relationships or pairings between substituents R₅-R₉ and substituents R₁₀-R₁₄: R₅ is mated/paired with R₁₀, R₆ is mated/paired with R₁₁, R₇ is mated/paired with R₁₂, R₈ is mated/paired with R₁₃, and R₉ is mated/paired with R₁₄.

[0048] The disclosure provides another process. In an embodiment, a process for producing a diester is provided which includes reacting an aromatic diol with a first aromatic carboxylic acid or derivative thereof and a second aromatic carboxylic acid or derivative thereof under reaction conditions. The aromatic diol may be substituted or may be unsubstituted. The second aromatic carboxylic acid or derivative thereof is different than the first aromatic carboxylic acid or derivative thereof. The process forms a substituted 1,2-phenylene dibenzoate of the structure (II):

(II)



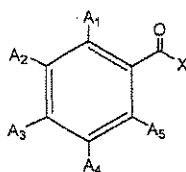
wherein R₁-R₁₄ are the same or different. Each of R₁-R₁₄ is selected from hydrogen, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof. At least one of R₅-R₉ is different than its respective R₁₀-R₁₄ mate. In a further embodiment, each R group of R₁-R₁₄ that is not hydrogen is an alkyl group having 1 to 20 carbon atoms.

[0049] The reaction between the aromatic diol and the first aromatic carboxylic acid (or derivative thereof) and the second aromatic carboxylic acid (or derivative thereof) may be reacted in any order as desired. In one embodiment, the aromatic diol is reacted with a first aromatic acyl halide. Then a second aromatic acyl halide is added to this diol/acyl halide mixture under reaction conditions. The reaction proceeds to form a substituted 1,2-phenylene dibenzoate wherein at least one of R₅-R₉ is different than its respective R₁₀-R₁₄ mate.

[0050] In an embodiment, the process includes reacting the aromatic diol with the first aromatic acyl halide and the second aromatic acyl halide different than the first aromatic acyl halide simultaneously, or substantially simultaneously. The process forms a mixture which contains a substituted 1,2-phenylene diester of structure (II) wherein at least one of R_5 - R_9 is different than its respective R_{10} - R_{14} mate. The mixture may or may not be separated and used in a catalyst synthesis procedure.

[0051] In another nonlimiting example, the first aromatic acyl halide may be a benzoyl halide of structure (III) wherein one substituent, such as substituent A_1 is substituted.

(III)

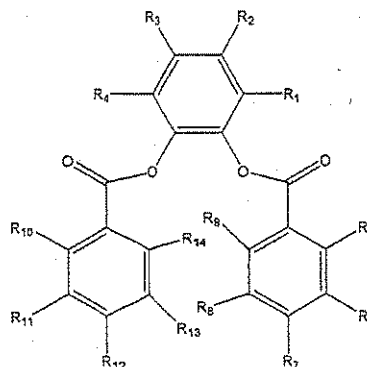


[0052] The second aromatic acyl halide may be a benzoyl halide of structure (III) wherein a substituent other than A_1 (A_3 for example) is substituted. The process includes reacting the aromatic diol with the first aromatic acyl halide and the second aromatic acyl halide to form a substituted 1,2-phenylene dibenzoate wherein at least one of R_5 - R_9 is different than its respective R_{10} - R_{14} mate. For example, the reaction may yield a substituted 1,2-phenylene dibenzoate wherein R_5 is not the same substituent as R_{10} and/or R_7 is not the same substituent as R_{12} .

[0053] In any of the foregoing processes the aromatic diol may be a dihydroxynaphthalene. The dihydroxynaphthalene may be substituted or unsubstituted. Similarly, the carboxylic acid derivative of any of the foregoing processes may be a naphthoyl halide. The naphthoyl halide may be substituted or unsubstituted.

[0054] The present disclosure provides another process for producing a diester. In an embodiment, a process for producing a diester is provided which includes reacting a dihydroxynaphthalene with a carboxylic acid or derivative thereof under reaction conditions. The dihydroxynaphthalene may be 1,2-dihydroxynaphthalene and/or 2,3-dihydroxynaphthalene. The reaction forms or otherwise produces a 1,2-phenylene dibenzoate of the structure (II):

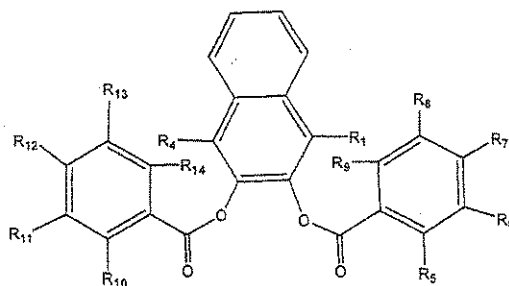
(II)



wherein R_1 - R_{14} are the same or different. Any consecutive R groups in R_1 - R_4 are members of a C_6 aromatic ring. Each of R_1 - R_{14} may or may not be hydrogen. In a further embodiment, the dihydroxynaphthalene is an unsubstituted or a substituted 2,3-dihydroxynaphthalene. Each of R_5 - R_{14} is hydrogen. In another embodiment, the dihydroxynaphthalene is a substituted 1,2-dihydroxynaphthalene. Each of R_5 - R_{14} is hydrogen. In an embodiment, at least one R group of R_1 - R_{14} that is not a part of a C_6 aromatic ring is not hydrogen.

[0055] In an embodiment, the process includes reacting an unsubstituted or a substituted 2,3-dihydroxynaphthalene with an aromatic acyl halide and forming a 1,2-phenylene dibenzoate of the structure (IV) below.

(IV)

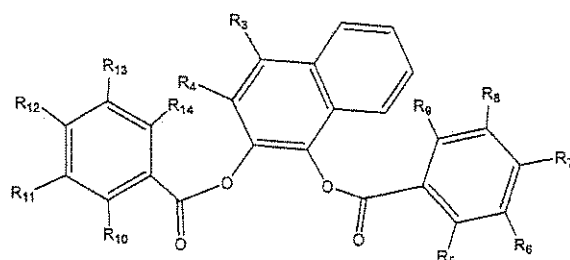


[0056] The aromatic acyl halide may be substituted or unsubstituted. R_1 and R_4 are the same or different and each is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof. In a further embodiment, the aromatic acyl halide is substituted and at least one of R_5 - R_{14} is selected from an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a substituted

hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof.

[0057] In an embodiment, the process includes reacting an unsubstituted or substituted 1,2-dihydroxynaphthalene with an aromatic acyl halide and forming a 1,2-phenylene dibenzoate of the structure (V) below.

(V)

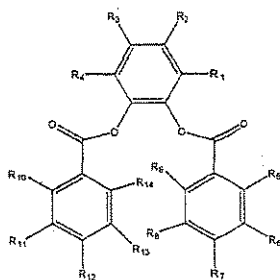


[0058] In an embodiment, the 1,2 dihydroxynaphthalene may be selected such that R₃ and R₄ are the same or different and each is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof. The aromatic acyl halide may be substituted such that at least one of R₅-R₁₄ is selected from an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof.

[0059] In an embodiment, the process includes reacting a dihydroxynaphthalene with a naphthoyl halide. The dihydroxynaphthalene may be any dihydroxynaphthalene disclosed herein and may be substituted or unsubstituted. The naphthoyl halide may be any naphthoyl halide disclosed herein and may be substituted or unsubstituted. The reaction forms or otherwise produces a naphthalene dinaphthoate.

[0060] The present disclosure provides another process for producing a diester. In an embodiment, a process for producing a diester is provided which includes reacting an aromatic diol with a naphthoyl halide under reaction conditions. The aromatic diol and/or the naphthoyl halide may or may not be substituted. The naphthoyl halide may be a 1-naphthoyl halide and/or a 2-naphthoyl halide. The reaction forms or otherwise produces a 1,2-phenylene dibenzoate of the structure (II):

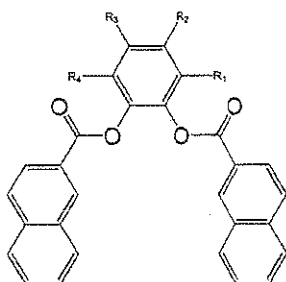
(II)



wherein each of R_1 - R_{14} may be hydrogen. Any consecutive R groups in R_5 - R_9 and/or in R_{10} - R_{14} are members of a C_6 aromatic ring.

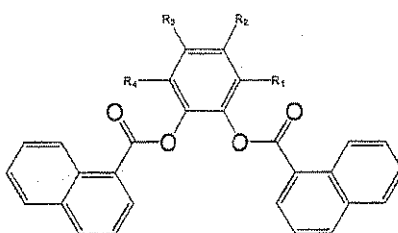
[0061] In an embodiment, the process includes reacting an aromatic diol with a 2-naphthoyl halide under reaction conditions and forming a 1,2-phenylene dibenzoate of the structure (VI).

(VI)



[0062] In an embodiment, the process includes reacting an aromatic diol with a 1-naphthoyl halide and forming a 1,2-phenylene dibenzoate of the structure (VII).

(VII)



[0063] In an embodiment, R_1 - R_4 are the same or different and each is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof.

[0064] In another embodiment, the process includes reacting a dihydroxynaphthalene with a naphthoyl halide to form a naphthalene dinaphthoate.

[0065] In an embodiment, any process disclosed herein may include introducing a catalyst into the reaction (or reaction mixture) to assist the reaction between the aromatic diol and the aromatic carboxylic acid or derivative thereof. In one embodiment, the process includes reacting (i) an aromatic diol (substituted or unsubstituted), (ii) an aromatic acyl halide (substituted or unsubstituted), and (iii) the catalyst, and forming or otherwise producing a phenylene aromatic diester. Not wishing to be bound by any particular theory, it is believed that the catalyst promotes esterification between the aromatic diol and the aromatic carboxylic acid (or derivative thereof). Nonlimiting examples of suitable catalysts are metal triflates (trifluoromethanesulfonate) such as bismuth triflate and/or inorganic acids such as sulfuric acid.

[0066] In an embodiment, the reaction between the substituted/unsubstituted aromatic carboxylic acid (or derivative thereof) and the substituted/unsubstituted aromatic diol as described above is performed in the presence of a base such as an amine and/or a nitrogen-containing heterocyclic aromatic compound. In one embodiment, the base is triethylamine. In another embodiment, the base is pyridine.

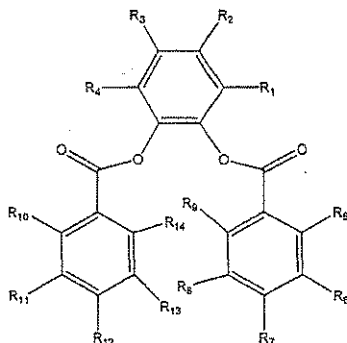
[0067] In an embodiment, any of the reactions disclosed herein are performed in a liquid medium. Nonlimiting examples of suitable solvents for the liquid medium may be selected from pyridine, tetrahydrofuran, a halohydrocarbon (aliphatic and/or aromatic), hydrocarbon, alcohol, ether, and any combination thereof. In a further embodiment, the liquid reaction medium is a non-aqueous liquid.

[0068] In an embodiment, any of the processes disclosed herein may include removing a reaction product from the liquid medium. The reaction product includes any of the substituted phenylene aromatic diesters disclosed herein. Removal of the reaction product from the liquid medium may include one or more of the following procedures: extracting with a different solvent, precipitating, filtrating, concentrating the filtrate, evaporating the liquid medium, crystallizing the substituted phenylene aromatic diester, recrystallizing the substituted phenylene aromatic diester, complexing with a metal salt, and any combination of the foregoing.

[0069] Any process may comprise two or more embodiments disclosed herein.

[0070] The disclosure provides a composition. In an embodiment, a substituted phenylene aromatic diester of the structure (II) is provided:

(II)



[0071] wherein R_1 - R_{14} are the same or different. R_1 is not an isopropyl group or a tertiary alkyl group. Each of R_1 and R_3 is selected from an unsubstituted alkyl group having 1 to 20 carbon atoms, an unsubstituted alkenyl group having 1 to 20 atoms, halohydrocarbonyl group, a halogen, a silicon-containing hydrocarbonyl group, and combinations thereof. Each of R_2 , R_4 , and R_5 - R_{14} is selected from hydrogen, an unsubstituted hydrocarbonyl group having 1 to 20 carbon atoms, a halohydrocarbonyl group, a halogen, and combinations thereof.

[0072] The term "primary alkyl group," as used herein, refers to an alkyl group having 1 to 20 carbon atoms with a carbon atom bonded to a phenyl ring (*i.e.*, a "C—Ph bond"), the carbon atom bonded to one other carbon atom other than the C—Ph bond. A "secondary alkyl group," as used herein, refers to an alkyl group having 1 to 20 carbon atoms with a carbon atom bonded to a phenyl ring, the carbon atom bonded to two other carbon atoms, other than the C—Ph bond. A "tertiary alkyl group," as used herein, refers to an alkyl group having 1 to 20 carbon atoms with a carbon atom bonded to a phenyl ring, the carbon atom bonded to three other carbon atoms, other than the C—Ph bond.

[0073] In an embodiment, only atoms selected from C, H, Si, and/or a halogen are bonded to the phenyl moieties at substituent points R_1 - R_{14} of structure (II).

[0074] In an embodiment, each of R_2 and R_4 is hydrogen. In another embodiment, each of R_2 , R_4 , and R_5 - R_{14} is hydrogen.

[0075] In an embodiment, R_1 is a methyl group and R_3 is a branched alkyl group.

[0076] In an embodiment, each of R_1 and R_3 is selected from a hydrocarbonyl group having 2 to 20 carbon atoms.

[0077] In an embodiment, any R group of R₁-R₁₄ that is not a hydrogen is an alkyl group having 1 to 20 carbon atoms.

[0078] In an embodiment, each of R₁ and R₃ is selected from a C₁-C₈ alkyl group. R₅-R₁₄ are the same or different and each of R₅-R₁₄ is selected from hydrogen, a C₁-C₈ alkyl group, and a halogen. Nonlimiting examples of suitable C₁-C₈ alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, i-butyl, and t-butyl, n-pentyl, i-pentyl, neopentyl, t-pentyl, n-hexyl, and 2,4,4-trimethylpentan-2-yl. In a further embodiment, at least one of R₅-R₁₄ is a C₁-C₈ alkyl group or a halogen.

[0079] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ that is a t-butyl group. Each of R₂, R₄ and R₅-R₁₄ is hydrogen.

[0080] In an embodiment, structure (II) includes R₁ and R₃, each being an isopropyl group. Each of R₂, R₄ and R₅-R₁₄ is hydrogen.

[0081] In an embodiment, structure (II) includes each of R₁, R₅, and R₁₀ as a methyl group and R₃ is a t-butyl group. Each of R₂, R₄, R₆-R₉ and R₁₁-R₁₄ is hydrogen.

[0082] In an embodiment, structure (II) includes each of R₁, R₇, and R₁₂ as a methyl group and R₃ is a t-butyl group. Each of R₂, R₄, R₅, R₆, R₈, R₉, R₁₀, R₁₁, R₁₃, and R₁₄ is hydrogen.

[0083] In an embodiment, structure (II) includes R₁ as a methyl group and R₃ is a t-butyl group. Each of R₇ and R₁₂ is an ethyl group. Each of R₂, R₄, R₅, R₆, R₈, R₉, R₁₀, R₁₁, R₁₃, and R₁₄ is hydrogen.

[0084] In an embodiment, structure (II) includes each of R₁, R₅, R₇, R₉, R₁₀, R₁₂, and R₁₄ as a methyl group and R₃ is a t-butyl group. Each of R₂, R₄, R₆, R₈, R₁₁, and R₁₃ is hydrogen.

[0085] In an embodiment, structure (II) includes R₁ as a methyl group and R₃ is a t-butyl group. Each of R₅, R₇, R₉, R₁₀, R₁₂, and R₁₄ is an i-propyl group. Each of R₂, R₄, R₆, R₈, R₁₁, and R₁₃ is hydrogen.

[0086] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ is a t-butyl group. Each of R₇ and R₁₂ is an ethoxy group. Each of R₂, R₄, R₅, R₆, R₈, R₉, R₁₀, R₁₁, R₁₃, and R₁₄ is hydrogen.

[0087] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ is a t-butyl group. Each of R₇ and R₁₂ is a fluorine atom. Each of R₂, R₄, R₅, R₆, R₈, R₉, R₁₀, R₁₁, R₁₃, and R₁₄ is hydrogen.

[0088] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ is a t-butyl group. Each of R₇ and R₁₂ is a chlorine atom. Each of R₂, R₄, R₅, R₆, R₈, R₉, R₁₀, R₁₁, R₁₃, and R₁₄ is hydrogen.

[0089] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ is a t-butyl group. Each of R₇ and R₁₂ is a bromine atom. Each of R₂, R₄, R₅, R₆, R₈, R₉, R₁₀, R₁₁, R₁₃, and R₁₄ is hydrogen.

[0090] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ is a t-butyl group. Each of R₇ and R₁₂ is an iodine atom. Each of R₂, R₄, R₅, R₆, R₈, R₉, R₁₀, R₁₁, R₁₃, and R₁₄ is hydrogen.

[0091] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ is a t-butyl group. Each of R₆, R₇, R₁₁, and R₁₂ is a chlorine atom. Each of R₂, R₄, R₅, R₈, R₉, R₁₀, R₁₃, and R₁₄ is hydrogen.

[0092] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ is a t-butyl group. Each of R₆, R₈, R₁₁, and R₁₃ is a chlorine atom. Each of R₂, R₄, R₅, R₇, R₉, R₁₀, R₁₂, and R₁₄ is hydrogen.

[0093] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ is a t-butyl group. Each of R₂ and R₄ is hydrogen. Each of R₅-R₁₄ is a fluorine atom.

[0094] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ is a t-butyl group. Each of R₇ and R₁₂ is a trifluoromethyl group. Each of R₂, R₄, R₅, R₆, R₈, R₉, R₁₀, R₁₁, R₁₃, and R₁₄ is hydrogen.

[0095] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ is a t-butyl group. Each of R₇ and R₁₂ is an ethoxycarbonyl group. Each of R₂, R₄, R₅, R₆, R₈, R₉, R₁₀, R₁₁, R₁₃, and R₁₄ is hydrogen.

[0096] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ is a t-butyl group. Each of R₇ and R₁₂ is a diethylamino group. Each of R₂, R₄, R₅, R₆, R₈, R₉, R₁₀, R₁₁, R₁₃, and R₁₄ is hydrogen.

[0097] In an embodiment, structure (II) includes R₁ that is a methyl group and R₃ is a 2,4,4-trimethylpentan-2-yl group. Each of R₂, R₄ and R₅-R₁₄ is hydrogen.

[0098] In an embodiment, structure (II) includes R₁ and R₃, each of which is a sec-butyl group. Each of R₂, R₄ and R₅-R₁₄ is hydrogen.

[0099] In an embodiment, structure (II) includes R₃ is that a 2,4,4-trimethylpentan-2-yl group.

[00100] In an embodiment, structure (II) includes one of R₇ and R₁₂ is an alkyl group having 1 to 6 carbon atoms or a halogen atom.

[00101] In an embodiment, structure (II) includes each of R₇ and R₁₂ is a methyl group and each of R₅ - R₆, R₈ - R₁₁, and R₁₃ - R₁₄ is hydrogen.

[00102] In an embodiment, structure (II) includes each of R₇ and R₁₂ is a fluorine atom or a chlorine atom and each of R₅ - R₆, R₈ - R₁₁, and R₁₃ - R₁₄ is hydrogen.

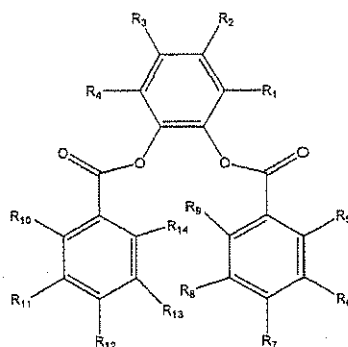
[00103] Nonlimiting examples of suitable substituted 1,2-phenylene dibenzoate include the following compounds as well as their derivatives with R₅-R₁₄ substitution(s) as defined above: 3,5-dimethyl-1,2-phenylene dibenzoate; 5-ethyl-3-methyl-1,2-phenylene dibenzoate; 3-methyl-5-propyl-1,2-phenylene dibenzoate; 5-isopropyl-3-methyl-1,2-phenylene dibenzoate; 5-butyl-3-methyl-1,2-phenylene dibenzoate; 5-isobutyl-3-methyl-1,2-phenylene dibenzoate; 5-tert-butyl-3-methyl-1,2-phenylene dibenzoate; 5-cyclopentyl-3-methyl-1,2-phenylene dibenzoate; 5-cyclohexyl-3-methyl-1,2-phenylene dibenzoate; 3-methyl-5-(2,4,4-trimethylpentan-2-yl)-1,2-phenylene dibenzoate; 5-methylbiphenyl-3,4-diyl dibenzoate; 3-ethyl-5-methyl-1,2-phenylene dibenzoate; 3,5-diethyl-1,2-phenylene dibenzoate; 3-ethyl-5-propyl-1,2-phenylene dibenzoate; 3-ethyl-5-isopropyl-1,2-phenylene dibenzoate; 5-butyl-3-ethyl-1,2-phenylene dibenzoate; 3-ethyl-5-isobutyl-1,2-phenylene dibenzoate; 5-tert-butyl-3-ethyl-1,2-phenylene dibenzoate; 5-cyclopentyl-3-ethyl-1,2-phenylene dibenzoate; 5-cyclohexyl-3-ethyl-1,2-phenylene dibenzoate; 3-ethyl-5-(2,4,4-trimethylpentan-2-yl)-1,2-phenylene dibenzoate; 5-ethylbiphenyl-3,4-diyl dibenzoate; 5-methyl-3-propyl-1,2-phenylene dibenzoate; 5-ethyl-3-propyl-1,2-phenylene dibenzoate; 3,5-dipropyl-1,2-phenylene dibenzoate; 5-isopropyl-3-propyl-1,2-phenylene dibenzoate; 5-butyl-3-propyl-1,2-phenylene dibenzoate; 5-isobutyl-3-propyl-1,2-phenylene dibenzoate; 5-tert-butyl-3-propyl-1,2-phenylene dibenzoate; 5-cyclopentyl-3-propyl-1,2-phenylene dibenzoate; 5-cyclohexyl-3-propyl-1,2-phenylene dibenzoate; 3-propyl-5-(2,4,4-trimethylpentan-2-yl)-1,2-phenylene dibenzoate; 5-propylbiphenyl-3,4-diyl dibenzoate; 3-isopropyl-5-methyl-1,2-phenylene dibenzoate; 5-ethyl-3-isopropyl-1,2-phenylene dibenzoate; 3-isopropyl-5-propyl-

1,2-phenylene dibenzoate; 3,5-diisopropyl-1,2-phenylene dibenzoate; and/or 5-butyl-3-isopropyl-1,2-phenylene dibenzoate; 5-isobutyl-3-isopropyl-1,2-phenylene dibenzoate; 5-tert-butyl-3-isopropyl-1,2-phenylene dibenzoate; 5-cyclopentyl-3-isopropyl-1,2-phenylene dibenzoate; 5-cyclohexyl-3-isopropyl-1,2-phenylene dibenzoate; 3-isopropyl-5-(2,4,4-trimethylpentan-2-yl)-1,2-phenylene dibenzoate; 5-isopropylbiphenyl-3,4-diyl dibenzoate; 3-butyl-5-methyl-1,2-phenylene dibenzoate; 3-butyl-5-ethyl-1,2-phenylene dibenzoate; 3-butyl-5-propyl-1,2-phenylene dibenzoate; 3-butyl-5-isopropyl-1,2-phenylene dibenzoate; 3,5-dibutyl-1,2-phenylene dibenzoate; 3-butyl-5-isobutyl-1,2-phenylene dibenzoate; 5-tert-butyl-3-butyl-1,2-phenylene dibenzoate; 3-butyl-5-cyclopentyl-1,2-phenylene dibenzoate; 3-butyl-5-cyclohexyl-1,2-phenylene dibenzoate; 3-butyl-5-(2,4,4-trimethylpentan-2-yl)-1,2-phenylene dibenzoate; 5-butylbiphenyl-3,4-diyl dibenzoate; 3-isobutyl-5-methyl-1,2-phenylene dibenzoate; 5-ethyl-3-isobutyl-1,2-phenylene dibenzoate; 3-isobutyl-5-propyl-1,2-phenylene dibenzoate; 3-isobutyl-5-isopropyl-1,2-phenylene dibenzoate; 5-butyl-3-isobutyl-1,2-phenylene dibenzoate; 3,5-diisobutyl-1,2-phenylene dibenzoate; 5-tert-butyl-3-isobutyl-1,2-phenylene dibenzoate; 5-cyclopentyl-3-isobutyl-1,2-phenylene dibenzoate; 5-cyclohexyl-3-isobutyl-1,2-phenylene dibenzoate; 3-isobutyl-5-(2,4,4-trimethylpentan-2-yl)-1,2-phenylene dibenzoate; 5-isobutylbiphenyl-3,4-diyl dibenzoate; 3-cyclopentyl-5-methyl-1,2-phenylene dibenzoate; 3-cyclopentyl-5-ethyl-1,2-phenylene dibenzoate; 3-cyclopentyl-5-propyl-1,2-phenylene dibenzoate; 3-cyclopentyl-5-isopropyl-1,2-phenylene dibenzoate; 5-butyl-3-cyclopentyl-1,2-phenylene dibenzoate; 3-cyclopentyl-5-isobutyl-1,2-phenylene dibenzoate; 5-tert-butyl-3-cyclopentyl-1,2-phenylene dibenzoate; 3,5-dicyclopentyl-1,2-phenylene dibenzoate; 5-cyclohexyl-3-cyclopentyl-1,2-phenylene dibenzoate; 3-cyclopentyl-5-(2,4,4-trimethylpentan-2-yl)-1,2-phenylene dibenzoate; 5-cyclopentylbiphenyl-3,4-diyl dibenzoate; 3-cyclohexyl-5-methyl-1,2-phenylene dibenzoate; 3-cyclohexyl-5-ethyl-1,2-phenylene dibenzoate; 3-cyclohexyl-5-propyl-1,2-phenylene dibenzoate; 3-cyclohexyl-5-isopropyl-1,2-phenylene dibenzoate; 5-butyl-3-cyclohexyl-1,2-phenylene dibenzoate; 3-cyclohexyl-5-isobutyl-1,2-phenylene dibenzoate; 5-tert-butyl-3-cyclohexyl-1,2-phenylene dibenzoate; 3-cyclohexyl-5-cyclopentyl-1,2-phenylene dibenzoate; 3,5-dicyclohexyl-1,2-phenylene dibenzoate; 3-cyclohexyl-5-(2,4,4-trimethylpentan-2-yl)-1,2-phenylene dibenzoate; 5-cyclohexylbiphenyl-3,4-diyl dibenzoate; 5-methylbiphenyl-2,3-diyl dibenzoate; 5-ethylbiphenyl-2,3-diyl dibenzoate; 5-propylbiphenyl-2,3-diyl dibenzoate; 5-

isopropylbiphenyl-2,3-diyl dibenzoate; 5-butylbiphenyl-2,3-diyl dibenzoate; 5-isobutylbiphenyl-2,3-diyl dibenzoate; 5-tert-butylbiphenyl-2,3-diyl dibenzoate; 5-cyclopentylbiphenyl-2,3-diyl dibenzoate; 5-cyclohexylbiphenyl-2,3-diyl dibenzoate; 5-(2,4,4-trimethylpentan-2-yl)biphenyl-2,3-diyl dibenzoate; and/or 3,5-diphenyl-1,2-phenylene dibenzoate.

[00104] The present disclosure provides another composition. In an embodiment, a substituted phenylene aromatic diester of the structure (II) is provided :

(II)



wherein R_1 - R_{14} are the same or different, R_2 is an alkyl group having 2 to 20 carbon atoms and each of the other R groups of R_1 - R_4 is hydrogen. Each of R_5 - R_{14} is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. Each of R_2 , R_7 , and R_{12} is simultaneously not a t-butyl group.

[00105] In an embodiment, R_2 is selected from of a t-butyl group and a 2,4,4-trimethylpentan-2-yl group.

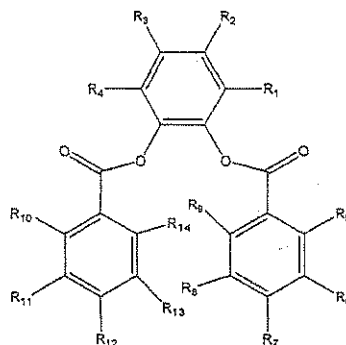
[00106] In an embodiment, one of R_7 and R_{12} is an alkyl group having 1 to 6 carbon atoms or a halogen atom.

[00107] In an embodiment, each of R_7 and R_{12} is methyl group and each of R_5 - R_6 , R_8 - R_{11} , and R_{13} - R_{14} is hydrogen.

[00108] In an embodiment, each of R_7 and R_{12} is fluorine or chlorine. Each of R_5 - R_6 , R_8 - R_{11} , and R_{13} - R_{14} is hydrogen.

[00109] The present disclosure provides another composition. In an embodiment, a substituted phenylene aromatic diester of the structure (II) is provided:

(II)



wherein R_1 - R_{14} are the same or different. Each of R_1 , R_3 , R_4 is hydrogen, R_2 is a hydrocarbyl group having 1 to 20 carbon atoms. At least one of R_7 and R_{12} is a halogen or a primary or secondary hydrocarbyl group having 1 to 20 carbon atoms which may optionally be substituted with halogen, silicon, or an alkoxy group. Each of R_5 - R_6 , R_8 - R_{11} and R_{13} - R_{14} is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

[00110] In an embodiment, R_2 is an alkyl group having 1 to 20 carbon atoms.

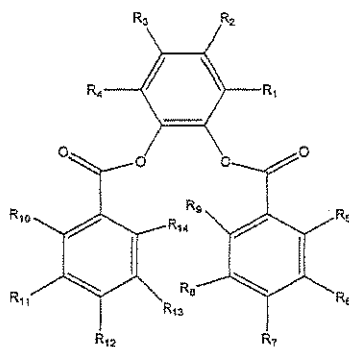
[00111] In an embodiment, each of R_7 and R_{12} is a halogen or an alkyl group having 1 to 6 carbon atoms.

[00112] In an embodiment, R_2 is a methyl group. Each of R_7 and R_{12} is a halogen or methyl group. The remaining R groups are hydrogen.

[00113] In an embodiment, each of R_2 and R_4 is a methyl group. Each of R_7 and R_{12} is a halogen or a methyl group. The remaining R groups are hydrogen.

[00114] The present disclosure provides another composition. In an embodiment, a substituted phenylene aromatic diester of the structure (II) is provided:

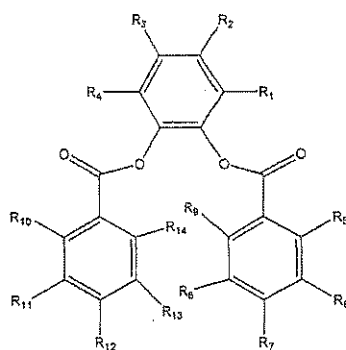
(II)



wherein R_1 - R_{14} are the same or different. R_1 is an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms. R_2 - R_4 are selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. Each of R_5 - R_{14} is selected from an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

[00115] The present disclosure provides another composition. In an embodiment, a substituted phenylene aromatic diester of the structure (II) is provided:

(II)



wherein R_1 - R_{14} are the same or different. R_2 is an alkyl group having 2 to 20 carbon atoms. Each other R group of R_1 - R_4 is hydrogen. Each of R_5 - R_{14} is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. R_2 , R_7 , and R_{12} are not simultaneously a *t*-butyl group. In other words, when R_2 is a *t*-butyl group R_7 and R_{12} are not a *t*-butyl group (or when R_7 is a *t*-butyl group, R_2 and R_{12} are not a *t*-butyl group; or when R_{12} is a *t*-butyl group, R_2 and R_7 are not a *t*-butyl group).

[00116] In an embodiment, structure (II) includes R_2 that is ethyl and each of R_5 - R_{14} is hydrogen.

[00117] In an embodiment, structure (II) includes R_2 that is *t*-butyl and each of R_5 - R_{14} is hydrogen.

[00118] In an embodiment, structure (II) includes R_2 that is 2,4,4-trimethylpentan-2-yl and each of R_5 - R_{14} is hydrogen.

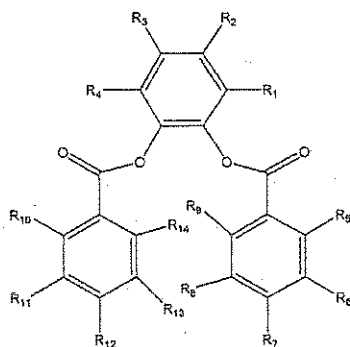
[00119] Nonlimiting examples of suitable substituted 1,2-phenylene dibenzoate include 4-ethyl-1,2-phenylene dibenzoate; 4-propyl-1,2-phenylene dibenzoate; 4-isopropyl-

1,2-phenylene dibenzoate; 4-butyl-1,2-phenylene dibenzoate; 4-isobutyl-1,2-phenylene dibenzoate; 4-cyclopentyl-1,2-phenylene dibenzoate; 4-cyclohexyl-1,2-phenylene dibenzoate; 4-(2,4,4-trimethylpentan-2-yl)-1,2-phenylene dibenzoate; and/or biphenyl-3,4-diyl dibenzoate.

[00120] In an embodiment, two or more of R_1 - R_4 are substituted. Each of the substituted R groups of R_1 - R_4 is selected from an unsubstituted hydrocarbyl group having 2 to 20 carbon atoms. R_1 is not a tertiary alkyl group.

[00121] The present disclosure provides another composition. In an embodiment, a substituted phenylene aromatic diester is provided. The substituted 1,2-phenylene aromatic diester has the structure (II) below.

(II)



[00122] R_1 - R_{14} are the same or different. Each of R_1 , R_3 , R_4 is hydrogen. R_2 is a hydrocarbyl group having 1 to 20 carbon atoms. At least one of R_7 and R_{12} is a halogen. Each of R_5 - R_6 , R_8 - R_{11} and R_{13} - R_{14} is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

[00123] In an embodiment, only atoms selected from C, H, Si, and/or a halogen are bonded to the phenyl groups at substituent points R_1 - R_{14} of structure (II).

[00124] In an embodiment, R_2 is an alkyl group having 1 to 20 carbon atoms.

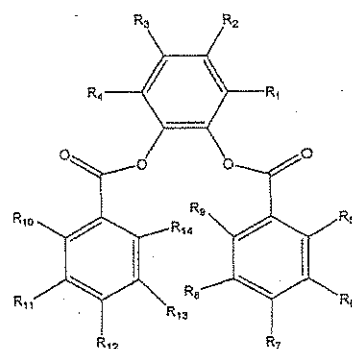
[00125] In an embodiment, each of R_7 and R_{12} is a halogen. In a further embodiment, each of R_5 , R_7 , R_{10} , and R_{12} is a halogen.

[00126] In an embodiment, structure (II) includes R_2 that is methyl and R_7 and R_{12} that are chlorine. Each other R-group of R_1 - R_{14} groups is hydrogen.

[00127] In an embodiment, structure (II) includes R₂ that is t-butyl and R₇ and R₁₂ that are chlorine. Each other R-group of R₁-R₁₄ groups is hydrogen.

[00128] The disclosure provides another composition. In an embodiment, a substituted phenylene aromatic diester is provided having the structure (II):

(II)



wherein R₁-R₁₄ are the same or different. Each of R₁, R₃, R₄ is hydrogen. R₂ is a hydrocarbyl group having 1 to 20 carbon atoms. Each of R₅-R₁₄ is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. At least one of R₅-R₆, R₈-R₁₁ and R₁₃-R₁₄ is selected from a C₁-C₆ alkyl group, a halogen, and combinations thereof.

[00129] In an embodiment, only atoms selected from C, H, Si, and/or a halogen are bonded to the phenyl groups at substituent points R₁-R₁₄ of structure (II).

[00130] In an embodiment, R₂ is an alkyl group having 1 to 20 carbon atoms.

[00131] In an embodiment, each of R₇ and R₁₂ is a methyl group. In a further embodiment, each of R₅, R₇, R₁₀, and R₁₂ is a methyl group.

[00132] In an embodiment, structure (II) includes each of R₂, R₇ and R₁₂ as a methyl group. Each other R group of R₁-R₁₄ is hydrogen.

[00133] In an embodiment, structure (II) includes R₂ that is t-butyl group and each of R₇ and R₁₂ is a methyl group. Each other R group of R₁-R₁₄ is hydrogen.

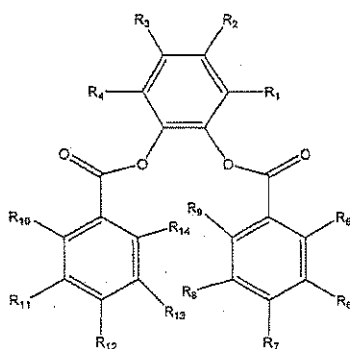
[00134] In an embodiment, structure (II) includes R₂ that is a methyl group and each of R₇ and R₁₂ is a dimethylamino group. Each other R group of R₁-R₁₄ is hydrogen.

[00135] In an embodiment, structure (II) includes R₂ that is a t-butyl group and each of R₇ and R₁₂ is a dimethylamino group. Each other R group of R₁-R₁₄ is hydrogen.

[00136] Nonlimiting examples of suitable substituted 1,2-phenylene dibenzoate include 3-ethyl-1,2-phenylene dibenzoate; 3-propyl-1,2-phenylene dibenzoate; 3-isopropyl-1,2-phenylene dibenzoate; 3-butyl-1,2-phenylene dibenzoate; 3-isobutyl-1,2-phenylene dibenzoate; 3-cyclopentyl-1,2-phenylene dibenzoate; 3-cyclohexyl-1,2-phenylene dibenzoate; 3-(2,4,4-trimethylpentan-2-yl)-1,2-phenylene dibenzoate, and/or biphenyl-2,3-diyl dibenzoate.

[00137] The disclosure provides another composition. In an embodiment, a substituted 1,2-phenylene aromatic diester of the structure (II) is provided:

(II)



wherein R₁-R₁₄ are the same or different. R₁ is not a secondary alkyl group or a tertiary alkyl group. Each of R₁ and R₄ is selected from an unsubstituted alkyl group having 2 to 20 carbon atoms, an unsubstituted alkenyl group having 2 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. Each of R₂-R₃ and each of R₅-R₁₄ is selected from hydrogen, unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

[00138] In an embodiment, structure (II) includes R₂ and R₃ that are each a hydrogen.

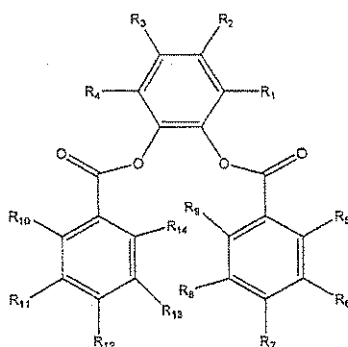
[00139] In an embodiment, structure (II) includes R₁, R₃, and R₄, each of which is an isopropyl group. Each of R₂, R₅-R₉ and R₁₀-R₁₄ is hydrogen.

[00140] Nonlimiting examples of suitable substituted 1,2-phenylene dibenzoate include the following compounds as well as their derivatives with R₅-R₁₄ substitution(s) as defined above: 3-ethyl-6-methyl-1,2-phenylene dibenzoate; 3-methyl-6-propyl-1,2-phenylene dibenzoate; 3-butyl-6-methyl-1,2-phenylene dibenzoate; 3-isobutyl-6-methyl-1,2-phenylene dibenzoate; 3-cyclopentyl-6-methyl-1,2-phenylene dibenzoate; 3-cyclohexyl-6-

methyl-1,2-phenylene dibenzoate; 4-methylbiphenyl-2,3-diyl dibenzoate; 3,6-diethyl-1,2-phenylene dibenzoate; 3-ethyl-6-propyl-1,2-phenylene dibenzoate; 3-ethyl-6-isopropyl-1,2-phenylene dibenzoate; 3-butyl-6-ethyl-1,2-phenylene dibenzoate; 3-ethyl-6-isobutyl-1,2-phenylene dibenzoate; 3-cyclopentyl-6-ethyl-1,2-phenylene dibenzoate; 3-cyclohexyl-6-ethyl-1,2-phenylene dibenzoate; 4-ethylbiphenyl-2,3-diyl dibenzoate; 3,6-dipropyl-1,2-phenylene dibenzoate; 3-isopropyl-6-propyl-1,2-phenylene dibenzoate; 3-butyl-6-propyl-1,2-phenylene dibenzoate; 3-isobutyl-6-propyl-1,2-phenylene dibenzoate; 3-cyclopentyl-6-propyl-1,2-phenylene dibenzoate; 3-cyclohexyl-6-propyl-1,2-phenylene dibenzoate; 4-propylbiphenyl-2,3-diyl dibenzoate; 3,6-diisopropyl-1,2-phenylene dibenzoate; 3-butyl-6-isopropyl-1,2-phenylene dibenzoate; 3-isobutyl-6-isopropyl-1,2-phenylene dibenzoate; 3-cyclopentyl-6-isopropyl-1,2-phenylene dibenzoate; 3-cyclohexyl-6-isopropyl-1,2-phenylene dibenzoate; 4-isopropylbiphenyl-2,3-diyl dibenzoate; 3,6-dibutyl-1,2-phenylene dibenzoate; 3-butyl-6-isobutyl-1,2-phenylene dibenzoate; 3-butyl-6-cyclopentyl-1,2-phenylene dibenzoate; 3-butyl-6-cyclohexyl-1,2-phenylene dibenzoate; 4-butylbiphenyl-2,3-diyl dibenzoate; 3,6-diisobutyl-1,2-phenylene dibenzoate; 3-cyclopentyl-6-isobutyl-1,2-phenylene dibenzoate; 3-cyclohexyl-6-isobutyl-1,2-phenylene dibenzoate; 4-isobutylbiphenyl-2,3-diyl dibenzoate; 3,6-dicyclopentyl-1,2-phenylene dibenzoate; 3-cyclohexyl-6-cyclopentyl-1,2-phenylene dibenzoate; 4-cyclopentylbiphenyl-2,3-diyl dibenzoate; 3,6-dicyclohexyl-1,2-phenylene dibenzoate; 4-cyclohexylbiphenyl-2,3-diyl dibenzoate; and/or 3,6-phenyl-1,2-phenylene dibenzoate.

[00141] The disclosure provides another composition. In an embodiment, a substituted 1,2-phenylene aromatic diester of the structure (II) is provided:

(II)



wherein R₁-R₁₄ are the same or different. Each of R₁, R₂, and R₄ is selected from an alkyl group having 2 to 20 carbon atoms, an alkenyl group having 2 to 20 carbon atoms, a halohydrocarbyl group, a silicon-containing hydrocarbyl group, and combinations thereof. Each of R₅-R₁₄ is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

[00142] In an embodiment, each of R₁, R₂, and R₄ is selected from an alkyl group having 2 to 20 carbon atoms, an alkenyl group having 2 to 20 carbon atoms, a halohydrocarbyl group, a silicon-containing hydrocarbyl group, and combinations thereof.

[00143] In an embodiment, R₃ is hydrogen. Each of R₁, R₂, and R₄ is selected from a hydrocarbon group having 2 to 20 carbon atoms. Each of R₁ and R₄ is not a tertiary alkyl group. Each of R₅-R₁₄ is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

[00144] Nonlimiting examples of suitable substituted 1,2-phenylene dibenzoate include the following compounds as well as their derivatives with R₅-R₁₄ substitution(s) as defined above: 3,4,6-trimethyl-1,2-phenylene dibenzoate; 3-ethyl-4,6-dimethyl-1,2-phenylene dibenzoate; 4,6-dimethyl-3-propyl-1,2-phenylene dibenzoate; 3-isopropyl-4,6-dimethyl-1,2-phenylene dibenzoate; 3-butyl-4,6-dimethyl-1,2-phenylene dibenzoate; 3-isobutyl-4,6-dimethyl-1,2-phenylene dibenzoate; 3-cyclopentyl-4,6-dimethyl-1,2-phenylene dibenzoate; 3-cyclohexyl-4,6-dimethyl-1,2-phenylene dibenzoate; 4,6-dimethylbiphenyl-2,3-diyl dibenzoate; 4-ethyl-3,6-dimethyl-1,2-phenylene dibenzoate; 3,4-diethyl-6-methyl-1,2-phenylene dibenzoate; 4-ethyl-6-methyl-3-propyl-1,2-phenylene dibenzoate; 4-ethyl-3-isopropyl-6-methyl-1,2-phenylene dibenzoate; 3-butyl-4-ethyl-6-methyl-1,2-phenylene dibenzoate; 4-ethyl-3-isobutyl-6-methyl-1,2-phenylene dibenzoate; 3-cyclopentyl-4-ethyl-6-methyl-1,2-phenylene dibenzoate; 3-cyclohexyl-4-ethyl-6-methyl-1,2-phenylene dibenzoate; 6-ethyl-4-methylbiphenyl-2,3-diyl dibenzoate; 3,6-dimethyl-4-propyl-1,2-phenylene dibenzoate; 3-ethyl-6-methyl-4-propyl-1,2-phenylene dibenzoate; 6-methyl-3,4-dipropyl-1,2-phenylene dibenzoate; 3-isopropyl-6-methyl-4-propyl-1,2-phenylene dibenzoate; 3-butyl-6-methyl-4-propyl-1,2-phenylene dibenzoate; 3-isobutyl-6-methyl-4-propyl-1,2-phenylene dibenzoate; 3-cyclopentyl-6-methyl-4-propyl-1,2-phenylene dibenzoate; 3-cyclohexyl-6-

methyl-4-propyl-1,2-phenylene dibenzoate; 4-methyl-6-propylbiphenyl-2,3-diyl dibenzoate; 4-isopropyl-3,6-dimethyl-1,2-phenylene dibenzoate; 3-ethyl-4-isopropyl-6-methyl-1,2-phenylene dibenzoate; 4-isopropyl-6-methyl-3-propyl-1,2-phenylene dibenzoate; 3,4-diisopropyl-6-methyl-1,2-phenylene dibenzoate; 3-butyl-4-isopropyl-6-methyl-1,2-phenylene dibenzoate; 3-isobutyl-4-isopropyl-6-methyl-1,2-phenylene dibenzoate; 3-cyclopentyl-4-isopropyl-6-methyl-1,2-phenylene dibenzoate; 3-cyclohexyl-4-isopropyl-6-methyl-1,2-phenylene dibenzoate; 6-isopropyl-4-methylbiphenyl-2,3-diyl dibenzoate; 4-butyl-3,6-dimethyl-1,2-phenylene dibenzoate; 4-butyl-3-ethyl-6-methyl-1,2-phenylene dibenzoate; 4-butyl-6-methyl-3-propyl-1,2-phenylene dibenzoate; 4-butyl-3-isopropyl-6-methyl-1,2-phenylene dibenzoate; 3,4-dibutyl-6-methyl-1,2-phenylene dibenzoate; 4-butyl-3-isobutyl-6-methyl-1,2-phenylene dibenzoate; 4-butyl-3-cyclopentyl-6-methyl-1,2-phenylene dibenzoate; 4-butyl-3-cyclohexyl-6-methyl-1,2-phenylene dibenzoate; 4-butyl-6-methyl-3-(2,4,4-trimethylpentan-2-yl)-1,2-phenylene dibenzoate; 6-butyl-4-methylbiphenyl-2,3-diyl dibenzoate; 4-isobutyl-3,6-dimethyl-1,2-phenylene dibenzoate; 3-ethyl-4-isobutyl-6-methyl-1,2-phenylene dibenzoate; 4-isobutyl-6-methyl-3-propyl-1,2-phenylene dibenzoate; 4-isobutyl-3-isopropyl-6-methyl-1,2-phenylene dibenzoate; 3-butyl-4-isobutyl-6-methyl-1,2-phenylene dibenzoate; 3,4-diisobutyl-6-methyl-1,2-phenylene dibenzoate; 3-cyclopentyl-4-isobutyl-6-methyl-1,2-phenylene dibenzoate; 3-cyclohexyl-4-isobutyl-6-methyl-1,2-phenylene dibenzoate; 6-isobutyl-4-methylbiphenyl-2,3-diyl dibenzoate; 4-tert-butyl-3,6-dimethyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-ethyl-6-methyl-1,2-phenylene dibenzoate; 4-tert-butyl-6-methyl-3-propyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-isopropyl-6-methyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-butyl-6-methyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-isobutyl-6-methyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-cyclopentyl-6-methyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-cyclohexyl-6-methyl-1,2-phenylene dibenzoate; 4-cyclopentyl-3,6-dimethyl-1,2-phenylene dibenzoate; 4-cyclopentyl-3-ethyl-6-methyl-1,2-phenylene dibenzoate; 4-cyclopentyl-6-methyl-3-propyl-1,2-phenylene dibenzoate; 4-cyclopentyl-3-isopropyl-6-methyl-1,2-phenylene dibenzoate; 3-butyl-4-cyclopentyl-6-methyl-1,2-phenylene dibenzoate; 4-cyclopentyl-3-isobutyl-6-methyl-1,2-phenylene dibenzoate; 3,4-dicyclopentyl-6-methyl-1,2-phenylene dibenzoate; 3-cyclohexyl-4-cyclopentyl-6-methyl-1,2-phenylene dibenzoate; 6-cyclopentyl-4-methylbiphenyl-2,3-diyl dibenzoate; 4-cyclohexyl-3,6-dimethyl-1,2-phenylene dibenzoate; 4-cyclohexyl-3-ethyl-6-

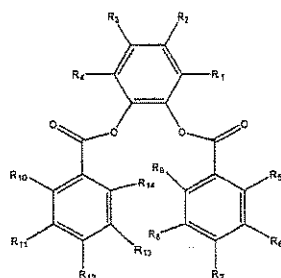
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 cyclohexyl-6-methyl-1,2-phenylene dibenzoate; 4-cyclohexyl-3-isobutyl-6-methyl-1,2-
 phenylene dibenzoate; 4-cyclohexyl-3-cyclopentyl-6-methyl-1,2-phenylene dibenzoate; 3,4-
 dicyclohexyl-6-methyl-1,2-phenylene dibenzoate; 6-cyclohexyl-4-methylbiphenyl-2,3-diyl
 dibenzoate; 2,5-dimethylbiphenyl-3,4-diyl dibenzoate; 2-ethyl-5-methylbiphenyl-3,4-diyl
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 dibenzoate; 4,6-diethyl-3-isopropyl-1,2-phenylene dibenzoate; 3-butyl-4,6-diethyl-1,2-
 phenylene dibenzoate; 4,6-diethyl-3-isobutyl-1,2-phenylene dibenzoate; 3-cyclopentyl-4,6-
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 dibenzoate; 3-cyclohexyl-6-ethyl-4-isopropyl-1,2-phenylene dibenzoate; 4-ethyl-6-

isopropylbiphenyl-2,3-diyl dibenzoate; 4-butyl-6-ethyl-3-methyl-1,2-phenylene dibenzoate; 4-butyl-3,6-diethyl-1,2-phenylene dibenzoate; 4-butyl-6-ethyl-3-propyl-1,2-phenylene dibenzoate; 4-butyl-6-ethyl-3-isopropyl-1,2-phenylene dibenzoate; 3,4-dibutyl-6-ethyl-1,2-phenylene dibenzoate; 4-butyl-6-ethyl-3-isobutyl-1,2-phenylene dibenzoate; 4-butyl-3-cyclopentyl-6-ethyl-1,2-phenylene dibenzoate; 4-butyl-3-cyclohexyl-6-ethyl-1,2-phenylene dibenzoate; 6-butyl-4-ethylbiphenyl-2,3-diyl dibenzoate; 6-ethyl-4-isobutyl-3-methyl-1,2-phenylene dibenzoate; 3,6-diethyl-4-isobutyl-1,2-phenylene dibenzoate; 6-ethyl-4-isobutyl-3-propyl-1,2-phenylene dibenzoate; 6-ethyl-4-isobutyl-3-isopropyl-1,2-phenylene dibenzoate; 3-butyl-6-ethyl-4-isobutyl-1,2-phenylene dibenzoate; 6-ethyl-3,4-diisobutyl-1,2-phenylene dibenzoate; 3-cyclopentyl-6-ethyl-4-isobutyl-1,2-phenylene dibenzoate; 3-cyclohexyl-6-ethyl-4-isobutyl-1,2-phenylene dibenzoate; 4-ethyl-6-isobutylbiphenyl-2,3-diyl dibenzoate; 4-tert-butyl-6-ethyl-3-methyl-1,2-phenylene dibenzoate; 4-tert-butyl-3,6-diethyl-1,2-phenylene dibenzoate; 4-tert-butyl-6-ethyl-3-propyl-1,2-phenylene dibenzoate; 4-tert-butyl-6-ethyl-3-isopropyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-butyl-6-ethyl-1,2-phenylene dibenzoate; 4-tert-butyl-6-ethyl-3-isobutyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-cyclopentyl-6-ethyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-cyclohexyl-6-ethyl-1,2-phenylene dibenzoate; 4-cyclopentyl-6-ethyl-3-methyl-1,2-phenylene dibenzoate; 4-cyclopentyl-3,6-diethyl-1,2-phenylene dibenzoate; 4-cyclopentyl-6-ethyl-3-propyl-1,2-phenylene dibenzoate; 4-cyclopentyl-6-ethyl-3-isopropyl-1,2-phenylene dibenzoate; 3-butyl-4-cyclopentyl-6-ethyl-1,2-phenylene dibenzoate; 4-cyclopentyl-6-ethyl-3-isobutyl-1,2-phenylene dibenzoate; 3,4-dicyclopentyl-6-ethyl-1,2-phenylene dibenzoate; 3-cyclohexyl-4-cyclopentyl-6-ethyl-1,2-phenylene dibenzoate; 6-cyclopentyl-4-ethylbiphenyl-2,3-diyl dibenzoate; 4-cyclohexyl-6-ethyl-3-methyl-1,2-phenylene dibenzoate; 4-cyclohexyl-3,6-diethyl-1,2-phenylene dibenzoate; 4-cyclohexyl-6-ethyl-3-propyl-1,2-phenylene dibenzoate; 4-cyclohexyl-6-ethyl-3-isopropyl-1,2-phenylene dibenzoate; 3-butyl-4-cyclohexyl-6-ethyl-1,2-phenylene dibenzoate; 4-cyclohexyl-6-ethyl-3-isobutyl-1,2-phenylene dibenzoate; 4-cyclohexyl-3-cyclopentyl-6-ethyl-1,2-phenylene dibenzoate; 3,4-dicyclohexyl-6-ethyl-1,2-phenylene dibenzoate; 6-cyclohexyl-4-ethylbiphenyl-2,3-diyl dibenzoate; 5-ethyl-2-methylbiphenyl-3,4-diyl dibenzoate; 2,5-diethylbiphenyl-3,4-diyl dibenzoate; 5-ethyl-2-propylbiphenyl-3,4-diyl dibenzoate; 5-ethyl-2-isopropylbiphenyl-3,4-diyl dibenzoate; 2-butyl-5-ethylbiphenyl-3,4-diyl dibenzoate; 5-ethyl-2-isobutylbiphenyl-3,4-diyl dibenzoate; 2-

cyclopentyl-5-ethylbiphenyl-3,4-diyl dibenzoate; 2-cyclohexyl-5-ethylbiphenyl-3,4-diyl dibenzoate, 5-ethyl-2-(2,4,4-trimethylpentan-2-yl)biphenyl-3,4-diyl dibenzoate; 3,4-diphenyl-6-ethyl-1,2-phenylene dibenzoate; 3,4-dimethyl-6-propyl-1,2-phenylene dibenzoate; 3-ethyl-4-methyl-6-propyl-1,2-phenylene dibenzoate; 4-methyl-3,6-dipropyl-1,2-phenylene dibenzoate; 3-isopropyl-4-methyl-6-propyl-1,2-phenylene dibenzoate; 3-butyl-4-methyl-6-propyl-1,2-phenylene dibenzoate; 3-isobutyl-4-methyl-6-propyl-1,2-phenylene dibenzoate; 3-cyclopentyl-4-methyl-6-propyl-1,2-phenylene dibenzoate; 3-cyclohexyl-4-methyl-6-propyl-1,2-phenylene dibenzoate; 6-methyl-4-propylbiphenyl-2,3-diyl dibenzoate; 4-ethyl-3-methyl-6-propyl-1,2-phenylene dibenzoate; 3,4-diethyl-6-propyl-1,2-phenylene dibenzoate; 4-ethyl-3,6-dipropyl-1,2-phenylene dibenzoate; 4-ethyl-3-isopropyl-6-propyl-1,2-phenylene dibenzoate; 3-butyl-4-ethyl-6-propyl-1,2-phenylene dibenzoate; 4-ethyl-3-isobutyl-6-propyl-1,2-phenylene dibenzoate; 3-cyclopentyl-4-ethyl-6-propyl-1,2-phenylene dibenzoate; 3-cyclohexyl-4-ethyl-6-propyl-1,2-phenylene dibenzoate; 6-ethyl-4-propylbiphenyl-2,3-diyl dibenzoate; 3-methyl-4,6-dipropyl-1,2-phenylene dibenzoate; 3-ethyl-4,6-dipropyl-1,2-phenylene dibenzoate; 3,4,6-tripropyl-1,2-phenylene dibenzoate; 3-isopropyl-4,6-dipropyl-1,2-phenylene dibenzoate; 3-butyl-4,6-dipropyl-1,2-phenylene dibenzoate; 3-isobutyl-4,6-dipropyl-1,2-phenylene dibenzoate; 3-cyclopentyl-4,6-dipropyl-1,2-phenylene dibenzoate; 3-cyclohexyl-4,6-dipropyl-1,2-phenylene dibenzoate; 4,6-dipropylbiphenyl-2,3-diyl dibenzoate; 4-isopropyl-3-methyl-6-propyl-1,2-phenylene dibenzoate; 3-ethyl-4-isopropyl-6-propyl-1,2-phenylene dibenzoate; 4-isopropyl-3,6-dipropyl-1,2-phenylene dibenzoate; 3,4-diisopropyl-6-propyl-1,2-phenylene dibenzoate; 3-butyl-4-isopropyl-6-propyl-1,2-phenylene dibenzoate; 3-isobutyl-4-isopropyl-6-propyl-1,2-phenylene dibenzoate; 3-cyclopentyl-4-isopropyl-6-propyl-1,2-phenylene dibenzoate; 3-cyclohexyl-4-isopropyl-6-propyl-1,2-phenylene dibenzoate; 6-isopropyl-4-propylbiphenyl-2,3-diyl dibenzoate; 4-butyl-3-methyl-6-propyl-1,2-phenylene dibenzoate; 4-butyl-3-ethyl-6-propyl-1,2-phenylene dibenzoate; 4-butyl-3,6-dipropyl-1,2-phenylene dibenzoate; 4-butyl-3-isopropyl-6-propyl-1,2-phenylene dibenzoate; 3,4-dibutyl-6-propyl-1,2-phenylene dibenzoate; 4-butyl-3-isobutyl-6-propyl-1,2-phenylene dibenzoate; 4-butyl-3-cyclopentyl-6-propyl-1,2-phenylene dibenzoate; 4-butyl-3-cyclohexyl-6-propyl-1,2-phenylene dibenzoate; 6-butyl-4-propylbiphenyl-2,3-diyl dibenzoate; 4-isobutyl-3-methyl-6-propyl-1,2-phenylene dibenzoate; 3-ethyl-4-isobutyl-6-propyl-1,2-phenylene dibenzoate; 4-isobutyl-3,6-dipropyl-

1,2-phenylene dibenzoate; 4-isobutyl-3-isopropyl-6-propyl-1,2-phenylene dibenzoate; 3-butyl-4-isobutyl-6-propyl-1,2-phenylene dibenzoate; 3,4-diisobutyl-6-propyl-1,2-phenylene dibenzoate; 3-cyclopentyl-4-isobutyl-6-propyl-1,2-phenylene dibenzoate; 3-cyclohexyl-4-isobutyl-6-propyl-1,2-phenylene dibenzoate; 6-isobutyl-4-propylbiphenyl-2,3-diyl dibenzoate; 4-tert-butyl-3-methyl-6-propyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-ethyl-6-propyl-1,2-phenylene dibenzoate; 4-tert-butyl-3,6-dipropyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-isopropyl-6-propyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-butyl-6-propyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-isobutyl-6-propyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-cyclopentyl-6-propyl-1,2-phenylene dibenzoate; 4-tert-butyl-3-cyclohexyl-6-propyl-1,2-phenylene dibenzoate; 4-cyclopentyl-3-methyl-6-propyl-1,2-phenylene dibenzoate; 4-cyclopentyl-3-ethyl-6-propyl-1,2-phenylene dibenzoate; 4-cyclopentyl-3,6-dipropyl-1,2-phenylene dibenzoate; 4-cyclopentyl-3-isopropyl-6-propyl-1,2-phenylene dibenzoate; 3-butyl-4-cyclopentyl-6-propyl-1,2-phenylene dibenzoate; 4-cyclopentyl-3-isobutyl-6-propyl-1,2-phenylene dibenzoate; 3,4-dicyclopentyl-6-propyl-1,2-phenylene dibenzoate; 3-cyclohexyl-4-cyclopentyl-6-propyl-1,2-phenylene dibenzoate; 6-cyclopentyl-4-propylbiphenyl-2,3-diyl dibenzoate; 4-cyclohexyl-3-methyl-6-propyl-1,2-phenylene dibenzoate; 4-cyclohexyl-3-ethyl-6-propyl-1,2-phenylene dibenzoate; 4-cyclohexyl-3,6-dipropyl-1,2-phenylene dibenzoate; 4-cyclohexyl-3-isopropyl-6-propyl-1,2-phenylene dibenzoate; 3-butyl-4-cyclohexyl-6-propyl-1,2-phenylene dibenzoate; 4-cyclohexyl-3-isobutyl-6-propyl-1,2-phenylene dibenzoate; 4-cyclohexyl-3-cyclopentyl-6-propyl-1,2-phenylene dibenzoate; 3,4-dicyclohexyl-6-propyl-1,2-phenylene dibenzoate; 6-cyclohexyl-4-propylbiphenyl-2,3-diyl dibenzoate; 2-methyl-5-propylbiphenyl-3,4-diyl dibenzoate; 2-ethyl-5-propylbiphenyl-3,4-diyl dibenzoate; 2,5-dipropylbiphenyl-3,4-diyl dibenzoate; 2-isopropyl-5-propylbiphenyl-3,4-diyl dibenzoate; 2-butyl-5-propylbiphenyl-3,4-diyl dibenzoate; 2-isobutyl-5-propylbiphenyl-3,4-diyl dibenzoate; 2-cyclopentyl-5-propylbiphenyl-3,4-diyl dibenzoate; 2-cyclohexyl-5-propylbiphenyl-3,4-diyl dibenzoate; and/or 3,4-diphenyl-6-propyl-1,2-phenylene dibenzoate.

[00145] Another composition is provided. In an embodiment, a substituted phenylene aromatic diester of the structure (II) is provided:

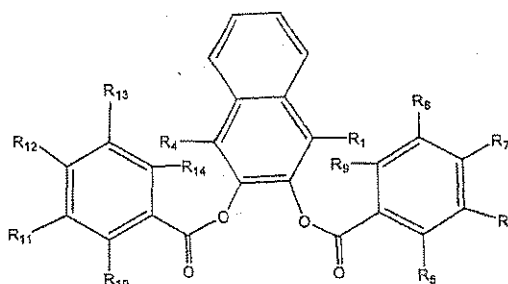


wherein R_1 - R_{14} are the same or different. Each of R_1 - R_{14} is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof. At least one of R_5 - R_9 is different than its respective R_{10} - R_{14} mate.

[00146] In an embodiment, at least one of R_1 - R_4 is substituted and is selected from an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a substituted hydrocarbyl group having 1 to 20 atoms, and a halogen.

[00147] Another composition is provided. In an embodiment, a substituted phenylene aromatic diester is provided with the structure (IV) below.

(IV)



[00148] R_{5-14} are the same or different. Each of R_1 , R_4 and R_{5-14} is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a substituted hydrocarbyl having 1 to 20 atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

[00149] In an embodiment, any R group of R_1 , R_4 and R_{5-14} that is not hydrogen is an unsubstituted hydrocarbyl group. In a further embodiment, the hydrocarbyl group is an alkyl group.

[00150] In an embodiment, each of R_1 and R_4 is hydrogen. R_{5-14} are the same or different. At least one of R_{5-14} is selected from an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl

group, and combinations thereof. R_7 and R_{12} are not simultaneously a methyl group. In other words, R_7 is not a methyl group when R_{12} is a methyl group (and vice versa).

[00151] The 2,3-naphthalene moiety may or may not be substituted. In one embodiment, the 2,3-naphthalene moiety may be substituted with one or more $C_2 - C_{20}$ alkyl groups or more than 2 methyl groups. In another embodiment, the 2,3-naphthalene moiety is unsubstituted (*i.e.*, R_1 and R_4 are hydrogen).

[00152] In an embodiment, each R group of $R_5 - R_{14}$ is a non-cyclic structure.

[00153] Any of the compositions disclosed herein may include two or more embodiments disclosed herein.

[00154] Any of the compositions disclosed herein may be made by one or more processes disclosed herein.

[00155] In an embodiment, one, some, or all of the foregoing compositions include no substituent that contains an active hydrogen. Nonlimiting examples of substituents with an active hydrogen include a hydroxyl group and a carboxylic acid group. Not wishing to be bound by any particular theory, it is believed that the active hydrogen(s) may react with $TiCl_4$ and/or other catalyst components during catalyst synthesis and impair the performance of the resultant catalyst. It is also preferred to minimize the number of electron donating groups in the $R_1 - R_{14}$ substituents. It is believed that extra electron donating group(s) may poison catalyst active sites.

[00156] The present compositions may comprise two or more embodiments disclosed herein.

[00157] The present substituted phenylene aromatic diester(s) may be used in procatalyst compositions and/or catalyst compositions for the polymerization of olefin-based polymers. For example, the present substituted phenylene aromatic diester(s) may be used as an internal electron donor and/or an external electron donor in a Ziegler-Natta catalyst system. Provision of the present substituted phenylene aromatic diester(s) in catalyst systems advantageously enhances catalyst stereoselectivity and catalyst activity. Catalyst systems which include the present substituted phenylene aromatic diester(s) advantageously produce olefin-based polymers (and propylene-based polymers in particular) with broad molecular weight distribution and high catalyst activity.

[00158] Any of the substituted phenylene aromatic diesters disclosed herein may be a component of a procatalyst composition and/or a catalyst composition as disclosed in U.S. Patent Application No. 61/141,902 filed on December 31, 2008, (Attorney Docket No. 67797), the entire content of which is incorporated by reference herein.

[00159] DEFINITIONS

[00160] All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Groups or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight. For purposes of United States patent practice, the contents of any patent, patent application, or publication referenced herein are hereby incorporated by reference in their entirety (or the equivalent US version thereof is so incorporated by reference), especially with respect to the disclosure of synthetic techniques, definitions (to the extent not inconsistent with any definitions provided herein) and general knowledge in the art.

[00161] The term "comprising," and derivatives thereof, is not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term "comprising" may include any additional additive, adjuvant, or compound whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, "consisting essentially of" excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term "consisting of" excludes any component, step or procedure not specifically delineated or listed. The term "or", unless stated otherwise, refers to the listed members individually as well as in any combination.

[00162] Any numerical range recited herein, includes all values from the lower value to the upper value, in increments of one unit, provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component, or a value of a compositional or a physical property, such as, for example, amount of a blend component, softening temperature, melt index, etc., is between 1

and 100, it is intended that all individual values, such as, 1, 2, 3, etc., and all subranges, such as, 1 to 20, 55 to 70, 197 to 100, etc., are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1, as appropriate. These are only examples of what is specifically intended, and all possible combinations of numerical values between the lowest value and the highest value enumerated, are to be considered to be expressly stated in this application. In other words, any numerical range recited herein includes any value or subrange within the stated range. Numerical ranges have been recited, as discussed herein, reference melt index, melt flow rate, and other properties.

[00163] The terms "blend" or "polymer blend," as used herein, is a blend of two or more polymers. Such a blend may or may not be miscible (not phase separated at molecular level). Such a blend may or may not be phase separated. Such a blend may or may not contain one or more domain configurations, as determined from transmission electron spectroscopy, light scattering, x-ray scattering, and other methods known in the art.

[00164] The term "composition," as used herein, includes a mixture of materials which comprise the composition, as well as reaction products and decomposition products formed from the materials of the composition.

[00165] The term "polymer" is a macromolecular compound prepared by polymerizing monomers of the same or different type. "Polymer" includes homopolymers, copolymers, terpolymers, interpolymers, and so on. The term "interpolymer" means a polymer prepared by the polymerization of at least two types of monomers or comonomers. It includes, but is not limited to, copolymers (which usually refers to polymers prepared from two different types of monomers or comonomers, terpolymers (which usually refers to polymers prepared from three different types of monomers or comonomers), tetrapolymers (which usually refers to polymers prepared from four different types of monomers or comonomers), and the like.

[00166] The term "olefin-based polymer" is a polymer containing, in polymerized form, a majority weight percent of an olefin, for example ethylene or propylene, based on the total weight of the polymer. Nonlimiting examples of olefin-based polymers include ethylene-based polymers and propylene-based polymers.

[00167] The term, "propylene-based polymer," as used herein, refers to a polymer that comprises a majority weight percent polymerized propylene monomer (based on the total

amount of polymerizable monomers), and optionally may comprise at least one polymerized comonomer.

[00168] The term "alkyl," as used herein, refers to a branched or unbranched, saturated or unsaturated acyclic hydrocarbon radical. Nonlimiting examples of suitable alkyl radicals include, for example, methyl, ethyl, n-propyl, i-propyl, 2-propenyl (or allyl), vinyl, n-butyl, t-butyl, i-butyl (or 2-methylpropyl), etc. The alkyls have 1 and 20 carbon atoms.

[00169] The term "substituted alkyl," as used herein, refers to an alkyl as just described in which one or more hydrogen atom bound to any carbon of the alkyl is replaced by another group such as a halogen, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, halogen, haloalkyl, hydroxy, amino, phosphido, alkoxy, amino, thio, nitro, and combinations thereof. Suitable substituted alkyls include, for example, benzyl, trifluoromethyl and the like.

[00170] The term "aryl," as used herein, refers to an aromatic substituent which may be a single aromatic ring or multiple aromatic rings which are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The aromatic ring(s) may include phenyl, naphthyl, anthracenyl, and biphenyl, among others. The aryls have 1 and 20 carbon atoms.

[00171] By way of example and not by limitation, examples of the present disclosure will now be provided.

[00172] 1. Synthesis of 1,2-phenylene aromatic diester.

[00173] Method A: A 250-ml round-bottom flask is charged with catechol (0.025 mol), pyridine (0.05 mol, 1.0 equiv.), and dichloromethane (50 ml). The flask is cooled in an ice-water bath, and acyl chloride (0.05 mol, 1.0 equiv.) is added dropwise. Upon completion of addition, the reaction mixture is warmed up to room temperature and stirred overnight. The mixture is diluted with additional dichloromethane, and washed with saturated $\text{NH}_4\text{Cl}/1\text{N HCl}$, water, saturated sodium bicarbonate, and brine consequently. The organic layer is collected and dried over magnesium sulfate. After filtration, the filtrate is concentrated, and the residue is dried in *vacuo*. Most of the crude products are pure enough, which can also be further purified by recrystallization from ethanol (for solid) or by distillation in *vacuo* to yield the product as white to yellow solid/liquid.

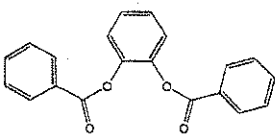
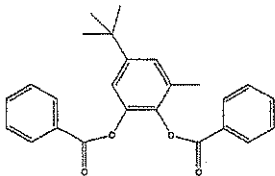
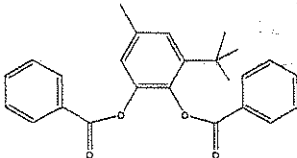
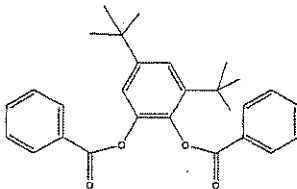
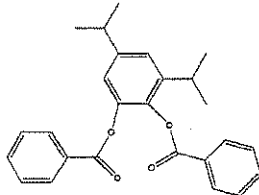
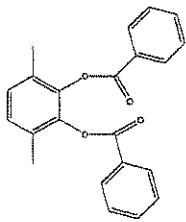
[00174] Method B: To 250-ml round-bottom flask was charged with catechol (68.0 mmol, 1.0 equiv.), pyridine (0.14 mol, 2.0 equiv.) and 50 ml of methylene chloride. The flask is cooled to 0°C in ice-water bath, and acyl chloride (0.14 mol, 2.0 equiv.) is added dropwise. The reaction mixture is stirred overnight at room temperature. The solvent is removed under vacuum residue is dissolved in 200 ml of ether, and filtered to remove solid. The filtrate is washed successively with 100 ml of 0.1 N HCl, water and brine, dried over Na₂SO₄. After filtration, the filtrate is concentrated to give the crude product, which is purified by recrystallization in ethanol to yield final product.

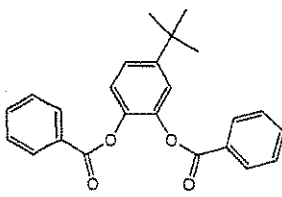
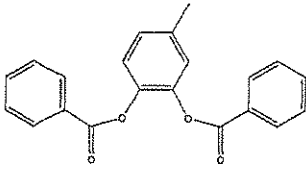
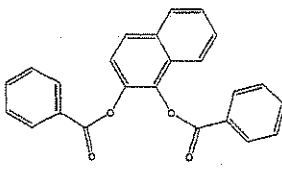
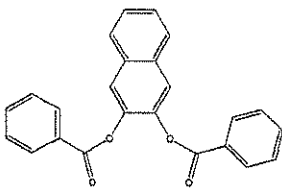
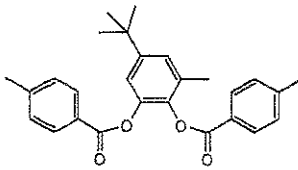
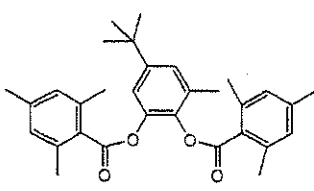
[00175] Method C: A 250-ml round-bottom flask is charged with 4-*tert*-butylbenzene-1,2-diol (0.03 mol), benzyl chloride (0.066 mol, 2.2 equiv.), bismuth triflate (1.05 mmol, 0.035 equiv.) and dichloromethane (100 ml). The reaction mixture is stirred overnight at room temperature. The solvent is removed via evaporation under vacuum. The residue is dissolved with ethyl acetate, and washed with aqueous K₂CO₃, water, and brine consequently. The organic layer is collected and dried over sodium sulfate. After filtration, the filtrate is concentrated. The crude product is purified by recrystallization from ethyl ether and hexanes.

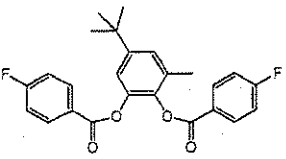
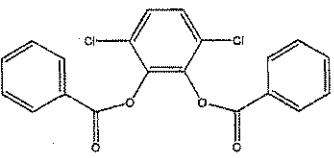
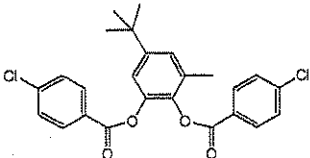
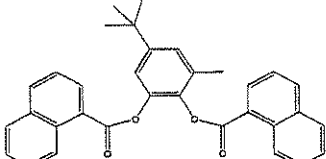
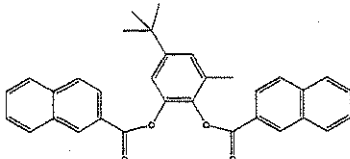
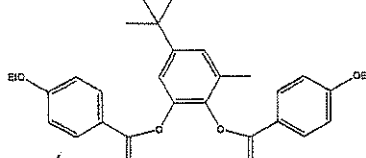
[00176] Method D: A 250-ml round-bottom flask is charged with 5-*tert*-butyl-3-methylbenzene-1,2-diol (0.02 mol), acyl chloride (0.044 mol, 2.2 equiv.), bismuth triflate (0.7 mmol, 0.035 equiv.) and dichloromethane (100 ml). The reaction mixture is stirred overnight at room temperature. The solvent is removed via evaporation under vacuum. The residue is dissolved with ethyl acetate, and washed with aqueous K₂CO₃, water, and brine consequently. The organic layer is collected and dried over sodium sulfate. After filtration, the filtrate is concentrated. The crude product is purified by recrystallization from ethyl ether and hexanes.

[00177] Nonlimiting examples of compounds produced by way of the foregoing synthesis are provided in Table 1 below.

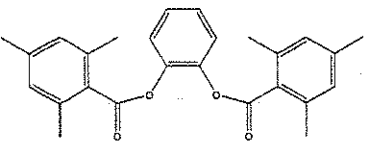
Table 1

Compound	Synthesis Method	Structure	¹ H NMR (500 MHz, CDCl ₃ , ppm)
1,2-phenylene dibenzoate	A		8.08 (dd, 4H), 7.54 (tt, 2H), 7.34-7.43 (m, 8H).
3-methyl-5-tert-butyl-1,2-phenylene dibenzoate	A		8.08 (dd, 2H), 8.03 (dd, 2H), 7.53 (tt, 1H), 7.50 (tt, 1H), 7.38 (t, 2H), 7.34 (t, 2H), 7.21 (d, 1H), 7.19 (d, 1H), 2.28 (s, 3H), 1.34 (s, 9H).
3-tert-butyl-5-methyl-1,2-phenylene dibenzoate	A		8.08 (dd, 2H), 7.93 (dd, 2H), 7.53 (tt, 1H), 7.43 (tt, 1H), 7.38 (t, 2H), 7.25 (t, 2H), 7.16 (d, 1H), 7.11 (d, 1H), 2.41 (s, 3H), 1.38 (s, 9H).
3,5-di-tert-butyl-1,2-phenylene dibenzoate	A		8.08 (dd, 2H), 7.94 (dd, 2H), 7.52 (tt, 1H), 7.44 (tt, 1H), 7.36-7.40 (m, 3H), 7.23-7.27 (m, 3H), 1.40 (s, 9H), 1.38 (s, 9H).
3,5-diisopropyl-1,2-phenylene dibenzoate	A		8.08 (dd, 2H), 7.00 (dd, 2H), 7.53 (tt, 1H), 7.48 (tt, 1H), 7.39 (t, 2H), 7.31 (t, 2H), 7.11 (d, 1H), 7.09 (d, 1H), 3.11 (heptat, 1H), 2.96 (heptat, 1H), 1.30 (d, 6H), 1.26 (d, 6H).
3,6-dimethyl-1,2-phenylene dibenzoate	A		8.08 (d, 2H), 7.51 (t, 1H), 7.34 (d, 2H), 7.11 (s, 2H), 2.23 (s, 6H).

Compound	Synthesis Method	Structure	¹ H NMR (500 MHz, CDCl ₃ , ppm)
4- <i>t</i> -butyl-1,2-phenylene dibenzoate	C		8.07 (dd, 4H), 7.54 (m, 2H), 7.30-7.40 (m, 7H), 1.37 (s, 9H).
4-methyl 1,2-phenylene dibenzoate	B		8.07 (d, 4H), 7.54 (t, 2H), 7.37 (t, 4H), 7.27 (d, 1H), 7.21 (s, 1H), 7.15 (d, 1H), 2.42 (s, 3H).
1,2-naphthalene dibenzoate	A		8.21-8.24 (m, 2H), 8.08-8.12 (m, 2H), 7.90-7.96 (m, 2H), 7.86 (d, 1H), 7.60 (m, 1H), 7.50-7.55 (m, 4H), 7.46 (t, 2H), 7.37 (t, 2H).
2,3-naphthalene dibenzoate	A		8.08-8.12 (m, 4H), 7.86-7.90 (m, 4H), 7.51-7.58 (m, 4H), 7.38 (t, 4H).
3-methyl-5- <i>tert</i> -butyl-1,2-phenylene di(4-methylbenzoate)	B		7.98 (d, 2H), 7.93 (d, 2H), 7.18 (d, 4H), 7.15 (d, 2H), 2.38 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H), 1.35 (s, 9H).
3-methyl-5- <i>tert</i> -butyl-1,2-phenylene di(2,4,6-trimethylbenzoate)	B		7.25 (s, 1H), 7.21 (s, 1H), 6.81 (d, 4H), 2.36 (s, 3H), 2.30 (d, 6H), 2.25 (s, 6H), 2.23 (s, 6H), 1.36 (s, 9H).

Compound	Synthesis Method	Structure	¹ H NMR (500 MHz, CDCl ₃ , ppm)
3-methyl-5-tert-butyl-1,2-phenylene di(4-fluorobenzoate)	D		δ 8.07 (m, 4H), 7.21 (s, 1H), 7.17 (s, 1H), 7.04 (m, 4H), 2.27 (s, 3H), 1.34 (s, 9H)
3,6-dichloro-1,2-phenylene dibenzoate			8.10 (d, 2H), 7.57 (t, 1H), 7.41 (d, 2H), 7.49 (s, 2H).
3-methyl-5-tert-butyl-1,2-phenylene di(4-chlorobenzoate) (IED12)	D		7.98 (dd, 4H), 7.36 (dd, 4H), 7.21 (s, 1H), 7.17 (s, 1H), 2.26 (s, 3H), 1.34 (s, 9H).
3-methyl-5-tert-butyl-1,2-phenylene di(1-naphthoate)	B		
3-methyl-5-tert-butyl-1,2-phenylene di(2-naphthoate)	B		
3-methyl-5-tert-butyl-1,2-phenylene di(4-ethoxybenzoate)	B		δ 8.02 (d, 2H), 7.97(d, 2H), 7.17 (m, 2H), 6.83(d, 2H), 6.79(d, 2H), 4.04 (m, 4H), 2.25 (s, 3H), 1.41 (m, 6H), 1.33 (s, 9H)

Compound	Synthesis Method	Structure	¹ H NMR (500 MHz, CDCl ₃ , ppm)
3-methyl-5-(2,4,4-trimethylpentan-2-yl)-1,2-phenylene dibenzoate	B		δ 8.09 (d, 2H), 8.03 (d, 2H), 7.50 (m, 2H), 7.38 (t, 2H), 7.33 (t, 2H), 7.19 (s, 2H), 2.27 (s, 3H), 1.75 (s, 2H), 1.40 (s, 6H), 0.81 (s, 9H)
3-fluoro-1,2-phenylene dibenzoate	D		δ 8.10 (d, 2H), 8.07 (d, 2H), 7.56 (m, 2H), 7.40 (m, 4H), 7.31 (m, 1H), 7.18 (m, 2H)
4-tert-butyl-1,2-phenylene di(2-methylbenzoate)	D		δ 8.04 (d, 1H), 8.00 (d, 1H), 7.39 (m, 3H), 7.34 (m, 1H), 7.28 (d, 1H), 7.22 (m, 2H), 7.17 (m, 2H), 2.57 (s, 6H), 1.36 (s, 9H)
4-methyl-1,2-phenylene di(2-methylbenzoate)	D		δ 8.01 (d, 2H), 7.39 (m, 2H), 7.22 (m, 3H), 7.15 (m, 4H), 2.57 (s, 3H), 2.56 (s, 3H), 2.42 (s, 3H)
4-tert-butyl-1,2-phenylene di(2,4,6-trimethylbenzoate)	D		δ 7.36 (s, 3H), 6.83 (s, 4H), 2.29 (s, 6H), 2.26 (s, 12H), 1.34 (s, 9H)
4-methyl-1,2-phenylene di(2,4,6-trimethylbenzoate)	D		δ 7.29 (d, 1H), 7.22 (m, 1H), 7.14 (m, 1H), 6.83 (m, 3H), 2.42 (s, 3H), 2.29 (s, 6H), 2.25 (s, 6H), 2.24 (s, 6H)

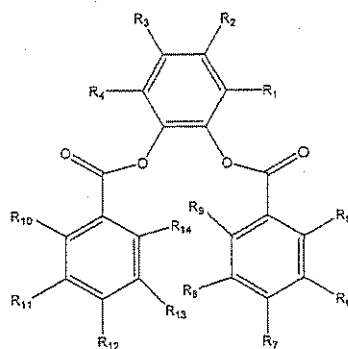
Compound	Synthesis Method	Structure	¹ H NMR (500 MHz, CDCl ₃ , ppm)
1,2-phenylene di(2,4,6-trimethylbenzoate)	D		δ 7.43 (m, 2H), 7.35 (m, 2H), 6.84 (s, 4H), 2.29 (s, 6H), 2.25 (s, 12H).

[00178] It is specifically intended that the present disclosure not be limited to the embodiments and illustrations contained herein, but include modified forms of those embodiments including portions of the embodiments and combinations of elements of different embodiments as come within the scope of the following claims.

CLAIMS

1. A substituted phenylene aromatic diester of the structure (II):

(II)

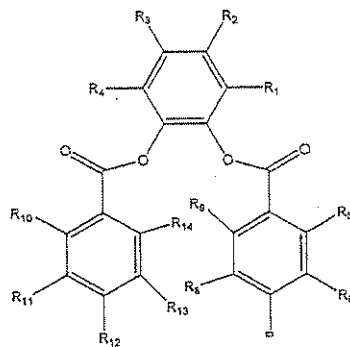


wherein R₁-R₁₄ are the same or different, R₁ is not an isopropyl group or a tertiary alkyl group, and each of R₁ and R₃ is selected from the group consisting of an unsubstituted alkyl group having 1 to 20 carbon atoms, an unsubstituted alkenyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof; and

each of R₂, R₄, and R₅-R₁₄ is selected from the group consisting of hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, and combinations thereof.

2. The substituted phenylene aromatic diester of claim 1 wherein each of R₂ and R₄ is hydrogen.
3. The substituted phenylene aromatic diester of any of claims 1-2 wherein R₁ is a methyl group and R₃ is a branched alkyl group.
4. A substituted phenylene aromatic diester of the structure (II):

(II)



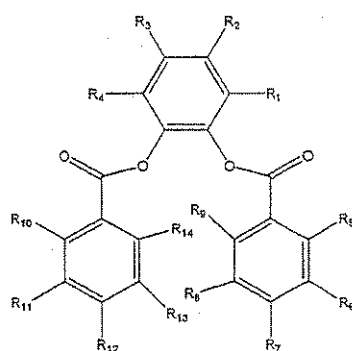
wherein R_1 - R_{14} are the same or different, R_2 is an alkyl group having 2 to 20 carbon atoms and each of the other R groups of R_1 - R_4 is hydrogen;

each of R_5 - R_{14} is selected from the group consisting of hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof; and

each of R_2 , R_7 , and R_{12} is simultaneously not a t-butyl group.

5. A substituted phenylene aromatic diester of the structure (II):

(II)



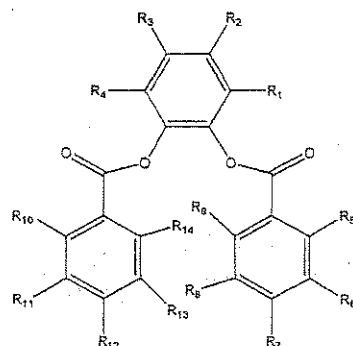
wherein R_1 - R_{14} are the same or different, each of R_1 , R_3 , R_4 is hydrogen, R_2 is a hydrocarbyl group having 1 to 20 carbon atoms;

at least one of R_7 and R_{12} is selected from the group consisting of a halogen, a primary hydrocarbyl group having 1 to 20 carbon atoms which may optionally be substituted with halogen, silicon, or an alkoxy group, and a secondary hydrocarbyl group having 1 to 20 carbon atoms which may optionally be substituted with halogen, silicon, or an alkoxy group; and

each of R_5 - R_6 , R_8 - R_{11} and R_{13} - R_{14} is selected from the group consisting of hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

6. A substituted phenylene aromatic diester of the structure (II):

(II)



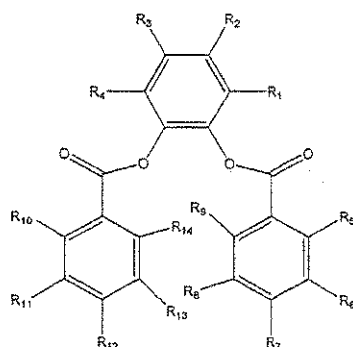
wherein R_1 - R_{14} are the same or different, each of R_1 , R_3 , R_4 is hydrogen, R_2 is a hydrocarbyl group having 1 to 20 carbon atoms;

each of R_5 - R_{14} is selected from the group consisting of hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof; and

at least one of R_5 - R_6 , R_8 - R_{11} and R_{13} - R_{14} is selected from the group consisting of a C_1 - C_6 alkyl group, a halogen, and combinations thereof.

7. A substituted phenylene aromatic diester of the structure (II):

(II)

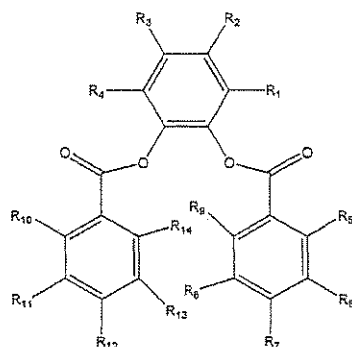


wherein R_1 - R_{14} are the same or different, each of R_1 , R_2 , and R_4 is selected from the group consisting of an alkyl group having 2 to 20 carbon atoms, an alkenyl group having 2 to 20 carbon atoms, a halohydrocarbyl group, a silicon-containing hydrocarbyl group, and combinations thereof; and

each of R_3 and R_5 - R_{14} is selected from the group consisting of hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

8. A substituted phenylene aromatic diester of the structure (II):

(II)

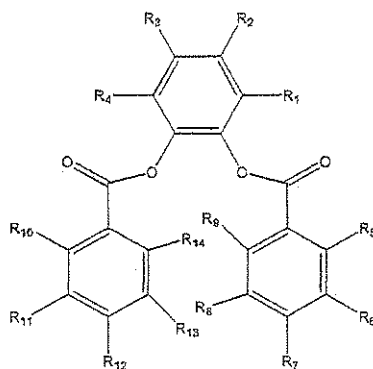


wherein R_1 - R_{14} are the same or different, each of R_1 - R_4 is selected from the group consisting of an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof; and

each of R_5 - R_{14} is selected from the group consisting of hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof.

9. A substituted phenylene aromatic diester of the structure (II):

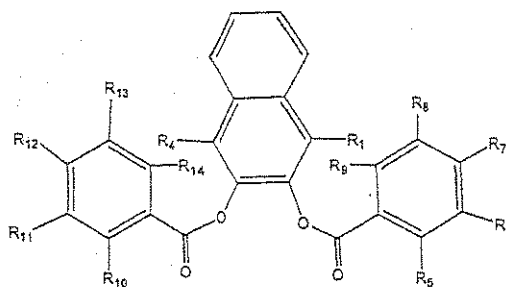
(II)



wherein R_1 - R_{14} are the same or different, each of R_1 - R_{14} is selected from hydrogen, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof; and at least one of R_5 - R_9 is different than its respective R_{10} - R_{14} mate.

10. A substituted phenylene aromatic diester of the structure (IV):

(IV)



wherein R_5 - R_{14} are the same or different, each of R_1 and R_4 is hydrogen; and at least one of R_5 - R_{14} is selected from the group consisting of an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, a halohydrocarbyl group, a halogen, a silicon-containing hydrocarbyl group, and combinations thereof, and each of R_7 and R_{12} is simultaneously not a methyl group.