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(54) Title: FLAME RETARDANT POLYCARBONATE RESIN COMPOSITION

(57) Abstract: The flame retardant polycarbonate resin composition according to the present invention comprises (A) 45-95 parts by weight of a thermoplastic polycarbonate resin; (B) 1-50 parts by weight of a rubber modified vinyl-grafted copolymer; (C) 0-50 parts by weight of a vinyl copolymer; (D) 1-30 parts by weight of an organophosphorus compound consisting of (d) 1-75 % by weight of a phosphonate compound having a specific structure; and (d) 25-99 % by weight of an oligomeric phosphate ester compound per 100 parts by weight of the sum of (A), (B) and (C); and (E) 0.05-5 parts by weight of a fluorinated polyolefin resin per 100 parts by weight of the sum of (A), (B) and (C).

Description

FLAME RETARDANT POLYCARBONATE RESIN COMPOSITION

Technical Field

[1] The present invention relates to a polycarbonate thermoplastic resin composition with good flame retardancy, heat resistance and mechanical strength. More particularly, the present invention relates to a flame retardant polycarbonate resin composition having good flame retardancy, heat resistance and mechanical strength, by employing an organophosphorus compound consisting of a phosphonate compound having a specific structure and an oligomeric phosphate ester as a flame retardant to a base resin consisting of a polycarbonate resin, a rubber modified vinyl graft copolymer, a vinyl copolymer.

[2]

Background Art

[3] A blend of a polycarbonate and a vinyl copolymer is a well-known resin composition with improved processability maintaining the high notched impact strength. This blend resin composition should further have good flame retardancy as well as high mechanical strength because the resin composition is applied to heat-emitting big-size injection molding products such as computer housings, office supplies, etc. To provide the resin composition with good flame retardancy, a halogen-containing flame retardant and an antimony-containing compound were used.

[4] However, the halogen-containing compound is fatally harmful due to the toxic gases generated during combustion, and therefore nowadays the halogen-free resin compositions are used widely.

[5] As a method for conferring flame-retardancy without using a halogen-based flame retardant, a method using a phosphate ester-based flame retardant is commonly used. U.S. patent Nos. 4,692,488 and 5,061,745 disclose a resin composition comprising aromatic polycarbonate, acrylonitrile-butadiene-styrene graft copolymer, thermoplastic copolymer and monomeric phosphate ester compound.

[6] However, the resin composition using the monomeric phosphate ester compound as a flame retardant has very poor heat resistance and shows, so called, "juicing phenomenon" which occurs during molding process because the flame retardant is volatilized and forms the laminate on the surface of molding product.

[7] As a method for overcoming the juicing problems, the method increasing the molecular weight of phosphoric acid ester is commonly used. And, as a method for increasing the molecular weight of phosphoric acid ester, the introduction of substitute

group to a monomeric phosphate ester compound or the use of an oligomeric phosphate ester compound is proposed.

[8] U.S. patent No. 5,206,404 discloses a composition having stability against acid and hydrolysis by use of alkyl substituted aryl phosphate compound. Further, Japanese Patent Application Laid Open No. 59-202,240 discloses a process of preparing oligomeric phosphate ester compound and describes that such compounds can be used as a flame retardant in polyamide or polycarbonate.

[9] In addition, U.S. patent No. 5,204,394 also discloses a flame retardant resin composition comprising an aromatic polycarbonate resin, a styrene-containing copolymer or a graft copolymer, and oligomeric phosphate as flame retardant.

[10] Although the resin composition improves the juicing phenomenon and heat resistance, but is inferior to the resin composition using the monomeric phosphate ester as flame retardant in flame retardancy. Accordingly, to maintain good flame retardancy, the resin composition should contain more flame retardant than in the resin composition containing the monophosphorous esters as flame retardant.

[11] U.S. patent No. 5,672,645 describes that PC/ABS resin composition containing an aromatic polycarbonate, a vinyl copolymer, a graft copolymer, a combination of a monophosphate ester and an oligomeric phosphate ester as flame retardants, and a fluorinated polyolefin has improved stress cracking resistance.

[12] However, the resin composition still shows juicing phenomenon due to the monomeric phosphate ester compound. And the flame retardation ability of the resin composition is lowered due to the oligomeric phosphate ester.

[13] The present inventors have developed a flame retardant polycarbonate resin composition that comprises a polycarbonate resin, a rubber modified vinyl graft copolymer, a vinyl copolymer, a phosphonate compound having a specific structure, an oligomeric phosphate ester as a flame retardant and a fluorinated polyolefin resin, which has a good balance of physical properties such as flame retardancy, impact strength and heat resistance.

[14]

Disclosure of Invention

Technical Problem

[15] An object of the present invention is to provide a polycarbonate resin composition with good flame retardancy.

[16] Another object of the present invention is to provide a polycarbonate resin composition with excellent heat resistance.

[17] A further object of the present invention is to provide a polycarbonate resin composition with good mechanical properties.

[18] Other objects and advantages of this invention will be apparent from the ensuing disclosure and appended claims.

[19]

Technical Solution

[20] The flame retardant polycarbonate resin composition according to the present invention comprises (A) 45~95 parts by weight of a thermoplastic polycarbonate resin; (B) 1~50 parts by weight of a rubber modified vinyl-grafted copolymer; (C) 0~50 parts by weight of a vinyl copolymer; (D) 1~30 parts by weight of an organophosphorus compound consisting of (d_1) 1~75 % by weight of a phosphonate compound having a specific structure; and (d_2) 25~99 % by weight of an oligomeric phosphate ester compound per 100 parts by weight of the sum of (A), (B) and (C); and (E) 0.05~5 parts by weight of a fluorinated polyolefin resin per 100 parts by weight of the sum of (A), (B) and (C).

[21]

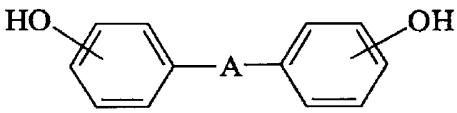
Best Mode for Carrying Out the Invention

[22] (A) Polycarbonate Resin

[23]

[24] The polycarbonate resin is prepared by reacting a diphenol represented by the following formula (I) with a phosgene, a halogen formate or a carboxylic acid diester:

[25]



(I)

[26] wherein A is a single bond, a C_{1-5} alkylene group, a C_{1-5} alkylidene group, a C_{5-6} cycloalkylidene group, S or SO_2.

[27]

[28] The examples of the diphenol include 4,4′-dihydroxydiphenol, 2,2-bis-(4-hydroxyphenyl)-propane, 2,4-bis-(4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane, 2,2-bis-(3-chloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane. More preferable diphenols are 2,2-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane, and 1,1-bis-(4-hydroxyphenyl)-cyclohexane, and most preferable diphenol is 2,2-bis-(4-hydroxyphenyl)-propane called 'bisphenol A'.

[29] Suitable polycarbonates incorporated into the composition of the present invention may be branched in a known manner, in particular preferably by incorporation 0.05 to 2 mol %, based to total quantity of diphenols used, of tri- or higher functional

compounds, for example, those with three or more phenolic groups.

[30] A homopolymer of polycarbonate, a copolymer of polycarbonate or a mixture thereof may be used in this invention.

[31] Some portion of the polycarbonate resin may be replaced with an aromatic polyester-carbonate resin that is obtained by polymerization in the presence of an ester precursor, such as difunctional carboxylic acid.

[32] In the present invention, the polycarbonate resin is used in an amount of about 45 to 95 parts by weight as a base resin.

[33]

[34] (B) Rubber Modified Vinyl Graft Copolymer

[35]

[36] The rubber modified vinyl graft copolymer according to the present invention is prepared by graft copolymerizing (b_1) 5 to 95 parts by weight of a monomer mixture consisting of 50 to 95 % by weight of styrene, α-methylstyrene, halogen- or alkyl-substituted styrene, C_{1-8} methacrylic acid alkyl ester, C_{1-8} acrylic acid alkyl ester, or a mixture thereof and 5 to 50 % by weight of acrylonitrile, methacrylonitrile, C_{1-8} methacrylic acid alkyl ester, C_{1-8} acrylic acid alkyl ester, maleic anhydride, C_{1-4} alkyl- or phenyl N-substituted maleimide or a mixture there of onto (b_2) 5 to 95 parts by weight of a rubber polymer selected from the group consisting of butadiene rubber, acryl rubber, ethylene/propylene rubber, styrene/butadiene rubber, acrylonitrile/ butadiene rubber, isoprene rubber, copolymer of ethylene-propylene-diene (EPDM), polyorganosiloxane/polyalkyl (meth)acrylate rubber complex and a mixture thereof.

[37] The C_{1-8} methacrylic acid alkyl ester or the C_{1-8} acrylic alkyl ester is obtained by reacting methacrylic acid or acrylic acid respectively with monohydric alcohol with 1 to 8 carbon atoms. The examples of the acid alkyl ester include methacrylic acid methyl ester, methacrylic acid ethyl ester, acrylic acid ethyl ester, acrylic acid methyl ester, or methacrylic acid propyl ester.

[38] Preferable examples of the rubber modified vinyl graft copolymer (B) are grafted-copolymers obtained by graft polymerizing a mixture of styrene, acrylonitrile, and optionally (meth)acrylic acid alkyl ester onto butadiene rubber, acryl rubber, or styrene/butadiene rubber.

[39] Another preferable examples of the rubber modified vinyl graft copolymer (B) are grafted-copolymers obtained by graft polymerizing (meth)acrylic acid methyl ester onto butadiene rubber, acryl rubber, or styrene/butadiene rubber.

[40] The most preferable example of the rubber modified vinyl graft copolymer (B) is an acrylonitrile-butadiene-styrene (ABS) graft copolymer.

[41] The rubber polymer(b_2) to prepare the rubber modified vinyl graft copolymer has preferably an average particle size of about 0.05 to 4.0 □ considering the impact

strength and appearance.

[42] The rubber modified graft copolymer according to the present invention can be prepared through a conventional polymerization process such as emulsion, suspension, solution, or bulk process. Among these processes, preferable is the emulsion or bulk polymerization in which said vinyl monomers are added to the rubber polymer using an initiator.

[43] The rubber modified vinyl graft copolymer is used in an amount of about 1 to 50 parts by weight.

[44]

[45] (C) Vinyl Copolymer

[46]

[47] The vinyl copolymer of the present invention is prepared by copolymerizing 40 to 95 % by weight of styrene, α-methylstyrene, halogen- or alkyl-substituted styrene, C_{1-8} methacrylic acid alkyl ester, C_{1-8} acrylic acid alkyl ester, or a mixture thereof and 5 to 60 % by weight of acrylonitrile, methacrylonitrile, C_{1-8} methacrylic acid alkyl ester, C_{1-8} acrylic acid alkyl ester, maleic anhydride, C_{1-4} alkyl- or phenyl N-substituted maleimide or a mixture thereof.

[48] The C_{1-8} methacrylic acid alkyl ester or C_{1-8} acrylic acid alkyl ester is obtained by reacting methacrylic acid or acrylic acid respectively with monohydric alcohol with 1 to 8 carbon atoms. The examples of the acid alkyl ester include methacrylic acid methyl ester, methacrylic acid ethyl ester, acrylic acid ethyl ester, acrylic acid methyl ester, or methacrylic acid propyl ester.

[49] The vinyl copolymer (C) can be produced as by-products when preparing the rubber modified vinyl-grafted copolymer (B). The by-products are mostly produced when a large quantity of monomers are grafted onto a small amount of rubber polymer or when a chain transfer agent is used in excess.

[50] The amount of the vinyl copolymer (C) to be used in this invention does not include the amount of the by-products that might be produced during preparation of the rubber modified vinyl-grafted copolymer (B).

[51] The preferable examples of the vinyl copolymer (C) are those prepared from monomer mixture of styrene, acrylonitrile, and optionally methacrylic acid methyl ester; monomer mixture of α-methyl styrene, acrylonitrile, and optionally methacrylic acid methyl ester; or monomer mixture of styrene, α-methyl styrene acrylonitrile, and optionally methacrylic acid methyl ester. The vinyl copolymer is preferably prepared by emulsion, suspension, solution, or bulk process, and has a preferable weight average molecular weight (M_w) of about 15,000 to 400,000.

[52] Another preferable examples of the vinyl copolymer (C) are those prepared from a mixture of methacrylic acid methyl ester monomers and optionally acrylic acid methyl

ester monomers or acrylic acid ethyl ester monomers. The methacrylic acid methyl ester copolymer (C) of the present invention is preferably prepared by emulsion, suspension, solution or bulk process, and has a weight average molecular weight (M_w) of about 20,000 to 250,000.

[53] Another preferred copolymer (C) is a copolymer of styrene and maleic anhydride, which is prepared by a continuous bulk process and a solution process. The maleic anhydride is preferably used in the amount of about 5 to 60 % by weight. The copolymer of styrene and maleic anhydride has a weight average molecular weight (M_w) of about 20,000 to 200,000 and an intrinsic viscosity of about 0.3 to 0.9 preferably.

[54] The styrene monomer for preparation of the component (C) in this invention can be replaced by p-methylstyrene, vinyltoluene, 2,4-dimethylstyrene, or α-methylstyrene.

[55] The vinyl copolymer (C) is used in single or in combination as a mixture and used in an amount of about 0 to 50 parts by weight.

[56]

[57] (D) Organophosphorus Compound

[58]

[59] The organophosphorus compound of the present invention is a mixture of (d_1) 1~75 % by weight of a phosphonate compound; and (d_2) 25~99 % by weight of an oligomeric phosphate ester compound.

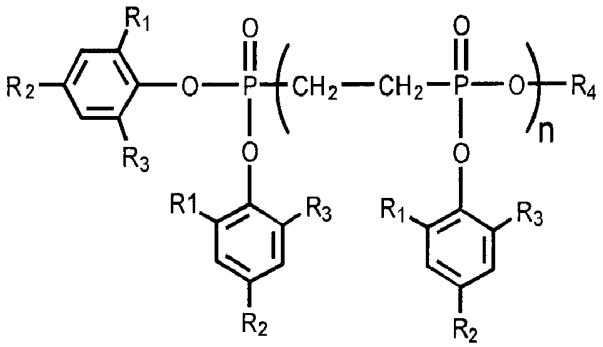
[60]

[61] (d_1) Phosphonate Compound

[62]

[63] The phosphonate compound (d_1) according to the present invention is represented as following Formula (II):

[64]



(II)

[65] wherein R_1,R_2 and R_3 are independently hydrogen or C_{1-4} alkyl group, R_4 is C_{1-4} alkyl group or C_{6-10} aryl group, n is 0 or 1.

[66]

[67] R_1,R_2 and R_3 are preferably hydrogen or methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, t-butyl, isobutyl, more preferably hydrogen or methyl.

[68] R_4 is preferably methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, t-butyl, isobutyl; phenyl, 2,6-dimethylphenyl, 4-t-butylphenyl.

[69] Examples of the phosphonate compound (d_1) are methyl diphenyl phosphonate, ethylene bis(diphenyl) phosphonate etc. In Formula (II), n is preferably 1, considering flame retardancy.

[70] The phosphonate compound (d_1) can be used in single or in combination as a mixture. The phosphonate compound (d_1) comprises of 1~75 % by weight, preferably 1~50 % by weight of organophosphorus compound(D). If the amount of the phosphonate compound is more than 75 % by weight, the flame retardancy and heat resistance of the resin composition are deteriorated. If the amount is less than 1 % by weight, flame retardancy and mechanical strength are degraded.

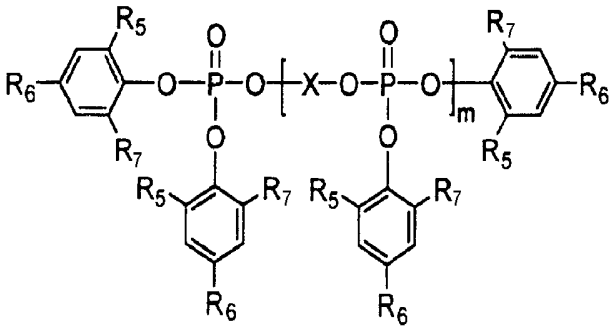
[71]

[72] (d_2) Oligomeric Phosphate Ester Compound

[73]

[74] The oligomeric phosphate ester compound according to the present invention is represented by the following Formula (III):

[75]



(III)

[76] wherein R_5, R_6, and R_7 are independently hydrogen, or C_{1-6} alkyl group; X is a C_{6-20} aryl group or an alkyl-substituted C_{6-20} aryl group, preferably a dialcohol derivative such as resorcinol, hydroquinol and bisphenol-A, m is an integer from 0 to 5. The average value of m of a mixture of the oligomeric phosphate ester compounds is 1 to 3.

[77]

[78] The oligomeric phosphate with a different *m* value can be used alone or a mixture thereof, which is prepared in the course of polymerization, or which is formulated with independent phosphates having the different *n* values.

[79] R_5, R_6, and R_7 are preferably a hydrogen or an alkyl group such as methyl, ethyl,

isopropyl, butyl, sec-butyl, t-butyl, isobutyl group, more preferably a hydrogen, methyl, ethyl, isopropyl, or t-butyl group. X is a derivative from resorcinol or bisphenol-A.

[80] The oligomeric phosphate ester compound(d_2) comprises of 25~99 % by weight, preferably 50~99 % by weight of organophosphorus compound(D).

[81] The organophosphorous compound (D) of the present invention is used in an amount of 1 to 30 parts by weight per 100 parts by weight of (A)+(B)+(C). If the amount is less than 1 part by weight, the resin composition has poor flame retardancy. On the other hand, if the amount is more than 30 parts by weight, the heat resistance and mechanical strength of the resin composition are deteriorated.

[82]

[83] (E) Fluorinated Polyolefin Resin

[84]

[85] The examples of the fluorinated polyolefin resin of the present invention are polytetrafluoroethylene, polyvinylidenefluoride, tetrafluoroethylene/vinylidenefluoride copolymer, tetrafluoroethylene/hexafluoropropylene copolymer, and ethylene/ tetrafluoroethylene copolymer. The fluorinated polyolefin resin may be used in single or in combination as a mixture.

[86] The fluorinated polyolefin resin (E) according to the present invention is prepared by a conventional process, for example, the resin is prepared in an aqueous solvent at 7 to 71 kg/cm^2 and 0 to 200 ℃, preferably 20~100 ℃, in the presence of a free radical forming catalyst such as sodium-, potassium-, or ammonium-peroxydisulphate.

[87] The fluorinated polyolefin resin is used in emulsion state or in powder state. In case using in emulsion state, dispersion of the fluorinated polyolefin resin is good, but the process will be somewhat complicated. Accordingly, if the fluorinated polyolefin resin could be uniformly dispersed in the entire resin composition to form the fibrillar network structure, it is preferable to use the fluorinated polyolefin resin in powder state.

[88]

[89] Preferable example of the fluorinated polyolefin resin is polytetrafluoroethylene having an average particle size of about 0.05 to 1,000 □ and density of about 1.2 to 2.3 g/cm^3.

[90] The fluorinated polyolefin resin is used in an amount of about 0.05 to 5.0 parts by weight as per 100 parts by weight of (A)+(B)+(C) of the thermoplastic resin composition according to the present invention.

[91]

[92] Other additives may be contained in the resin composition of the present invention. The additives include lubricants, releasing agents, nuclear agents, antistatic agents,

stabilizers, impact modifiers, inorganic fillers, pigments or dyes and the likes. The additives are employed in an amount of 0 to 60 parts by weight as per 100 parts by weight of (A)+(B)+(C) of the thermoplastic resin composition, preferably 0.1 to 40 parts by weight.

[93] The polycarbonate resin composition according to the present invention can be prepared by a conventional method. For example, all the components and additives are mixed together and extruded through an extruder and are prepared in the form of pellets.

[94] The polycarbonate thermoplastic resin composition according to the present invention can be applied to housing of electric or electronic goods such as computer housing which require good flame retardancy, heat resistance and impact strength.

[95]

[96] The present invention may be better understood by reference to the following examples that are intended for the purpose of illustration and are not to be construed as in any way limiting the scope of the present invention, which is defined in the claims appended hereto. In the following examples, all parts and percentage are by weight unless otherwise indicated.

[97]

Mode for the Invention

[98] **Examples**

[99]

[100] The components used in Examples and Comparative Examples are as follows:

[101]

[102] (A) Polycarbonate Resin

[103]

[104] Bisphenol-A based polycarbonate with a weight average molecular weight (M_w) of about 25,000 was used.

[105]

[106] (B) Rubber Modified Vinyl-Grafted Copolymer

[107]

[108] (B′) 58 parts of butadiene rubber latex, 31 parts of styrene, 11 parts of acrylonitrile, and 150 parts of deionized water were mixed. To the mixture, 1.0 parts of potassium oleate, 0.4 parts of cumenhydroperoxide, and 0.3 parts of t-dodecyl mercaptane chain transfer agent were added. The mixture was kept at 75 ℃ for 5 hours to obtain ABS latex. To the ABS latex, 1 % sulfuric acid was added, coagulated and dried to obtain graft copolymer resin in powder form.

[109]

[110] (B″) A graft copolymer of EXL-2602 (product name) by Kureha Co. was used, in which methacrylic acid methyl ester monomers are grafted onto butadiene rubber.

[111]

[112] (C) Vinyl Copolymer

[113]

[114] 71 parts of styrene, 29 parts of acrylonitrile, 120 parts of deionized water and 0.17 parts of azobisisobutylonitrile (AIBN) were mixed. To the blend, 0.4 parts of t-dodecyl mercaptan chain transfer agent and 0.5 parts of tricalciumphosphate were added. The mixture was suspension polymerized at 75 ℃ for 5 hours. The resultant was washed, dehydrated and dried to obtain styrene-acrylonitrile copolymer (SAN) in powder state.

[115]

[116] (D) Organic Phosphorous Compound

[117]

[118] (d_1) phosphonate compound

[119] (d_{11}) Methyl diphenyl phosphonate produced by Rhodia Co. was used.

[120] (d_{12}) Ethylene bis(diphenyl) phosphonate was used.

[121]

[122] (d_2) Oligomeric Phosphate Ester Compound

[123] Resorcinol bis(diphenyl) phosphate(product name: PX-200) by Daihachi Chemical IND. was used.

[124]

[125] (E) Fluorinated Polyolefin Resin

[126]

[127] Teflon (registered trademark) 7AJ by Dupont company was used.

[128]

[129] **Examples 1~6**

[130]

[131] The components as shown in Table 1, an antioxidant and a heat stabilizer were added in a conventional mixer and the mixture was extruded through a twin screw extruder with L/D=35 and Φ=45 mm to prepare a product in pellet form. The resin pellets were molded into test specimens for measuring flame retardancy and other properties using a 10 oz injection molding machine at 250 ℃.

[132]

[133] **Comparative Examples 1~7**

[134]

[135] Comparative Example 1 was conducted in the same manner as in Example 1 except that an organic phosphorous compound with the composition out of the claimed range was used.

[136] Comparative Example 2 was conducted in the same manner as in Example 1 except that only methyl diphenyl phosphonate compound(d_{11}) was used as a flame retardant.

[137] Comparative Example 3 was conducted in the same manner as in Example 1 except that only ethylene bis(diphenyl) phosphonate (d_{12}) was used as a flame retardant.

[138] Comparative Example 4 was conducted in the same manner as in Example 1 except that only resorcinol bis(diphenyl) phosphate (d_2) was used as a flame retardant.

[139] Comparative Example 5 was conducted in the same manner as in Example 5 except that only methyl diphenyl phosphonate compound(d_{11}) was used as a flame retardant.

[140] Comparative Example 6 was conducted in the same manner as in Example 5 except that only ethylene bis(diphenyl) phosphonate (d_{12}) was used as a flame retardant.

[141]

[142] Comparative Example 7 was conducted in the same manner as in Example 5 except that only resorcinol bis(diphenyl) phosphate (d_2) was used as a flame retardant.

[143]

[144] The specimens prepared in the Examples 1~6 and the Comparative Examples 1~7 were kept at the relative humidity of 50 % at 23 ℃ for 24 hours. The physical properties of the test specimens were measured in accordance with ASTM regulations.

[145]

[146] (1) Flame Retardancy : The flame retardancy was measured in accordance with UL94. The test specimens have a thickness of 1.6 mm.

[147] (2) Total Flame Out Time : The total flame out time is the sum of the first flame out time and the second flame out time when five specimens were tested twice.

[148] (3) Vicat Softening Temperature (VST): The vicat softening temperature was measured in accordance with ASTM D1525 under 5 kgf.

[149] (4) Flexural Strength : The flexural strength was measured in accordance with ASTM D790.

[150]

[151] The test results of Examples 1~6 and Comparative Examples 1~7 are shown in Table 1 and Table 2 respectively.

[152]

[153] Table 1

		Examples					
		1	2	3	4	5	6
(A) Polycarbonate Resin		75	75	75	75	95	95
(B) Rubber Modified Vinyl-Grafted Copolymer	(B′)	11	11	11	11	-	-
	(B″)	-	-	-	-	5	5

(C) Vinyl Copolymer		14	14	14	14	-	-
(D) Organic Phosphorous Compound	(d_{11})	2	4	-	-	1	-
	(d_{12})	-	-	2	8	-	1
	(d_2)	12	10	12	6	3	3
(E) Fluorinated Polyolefin Resin		0.5	0.5	0.5	0.5	0.5	0.4
UL 94 (1/16")		V-0	V-0	V-0	V-0	V-0	V-0
Total Flame Out Time (sec)		39	35	29	33	26	23
VST (℃)		102	101	103	103	129	130
Flexural Strength		835	845	820	825	950	905

[154]

[155] Table 2

		Comparative Examples						
		1	2	3	4	5	6	7
(A) Polycarbonate Resin		75	75	75	75	95	95	95
(B) Rubber Modified Vinyl-Grafted Copolymer	(B′)	11	11	11	11	-	-	-
	(B″)	-	-	-	-	5	5	5
(C) Vinyl Copolymer		14	14	14	14	-	-	-
(D) Organic Phosphorous Compound	(d_{11})	12	14	-	-	4	-	-
	(d_{12})	-	-	14	-	-	4	-
	(d_2)	2	-	-	14	-	-	4
(E) Fluorinated Polyolefin Resin		0.5	0.5	0.5	0.5	0.4	0.4	0.4
UL 94 (1/16")		V-2	V-2	V-1	V-1	V-1	V-1	V-1
Total Flame Out Time (sec)		-	-	115	58	60	55	70
VST (℃)		96	92	102	103	125	130	130
Flexural Strength		845	850	840	810	955	920	890

[156]

[157] As shown in Table 1 and Table 2, the resin compositions according to the present invention employing a phosphorous mixture of a phosphonate compound and an oligomeric phosphate ester show synergistic effect in flame retardancy and maintaining good heat resistance, compared to those employing a single phosphorous compound or

being deviated from claimed range.

[158]

[159] The present invention can be easily carried out by an ordinary skilled person in the art. Many modifications and changes may be deemed to be with the scope of the present invention as defined in the following claims.

[160]

Claims

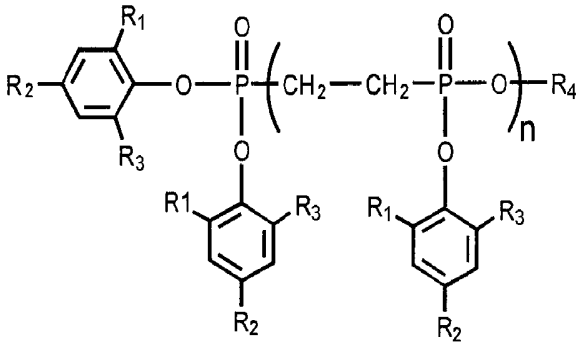
[1] A flame retardant polycarbonate resin composition comprising:

(A) 45 to 95 parts by weight of a polycarbonate resin;

(B) 1 to 50 parts by weight of a rubber modified vinyl-grafted copolymer prepared by graft-polymerizing (b_1) 5 to 95 % by weight of a monomer mixture consisting of 50 to 95 % by weight of at least one selected from the group consisting of styrene, α-methylstyrene, halogen- or alkyl-substituted styrene, C_{1-8} methacrylic acid alkyl ester, C_{1-8} acrylic acid alkyl ester, or a mixture thereof and 5 to 50 % by weight of acrylonitrile, methacylonitrile, C_{1-8} methacrylic acid alkyl ester, C_{1-8} acrylic acid alkyl ester, maleic anhydride, and C_{1-4} alkyl- or phenyl N-substituted maleimide onto (b_2) 5 to 95 % by weight of a rubber polymer selected from the group consisting of butadiene rubber, acryl rubber, ethylene-propylene rubber, styrene-butadiene rubber, acrylonitrile-butadiene rubber, isoprene rubber, copolymer of ethylene-propylene-diene (EPDM), polyorganosiloxane-polyalkyl (meta)acrylate rubber complex and a mixture thereof;

(C) 0 to 50 parts by weight of a vinyl copolymer prepared by copolymerizing (c_1) 40 to 95 % by weight of at least one selected from the group consisting of styrene, α-methyl styrene, halogen or alkyl substituted styrene, C_{1-8} methacrylic acid alkyl ester, and C_{1-8} acrylic acid alkyl ester and (c_2) 5 to 60 % by weight of at least one selected from the group consisting of acrylonitrile, methacrylonitrile, C_{1-8} methacrylic acid alkyl ester, C_{1-8} acrylic acid alkyl ester, maleic anhydride, and C_{1-4} alkyl or phenyl N-substituted maleimide;

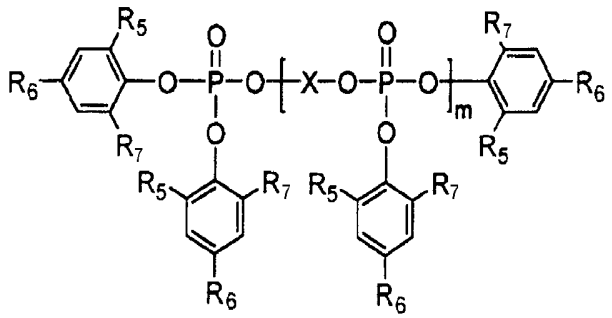
(D) 1~30 parts by weight of a mixture of organophosphorous compounds consisting of (d_1) 1~75 % by weight of a phosphonate compound represented by the following Formula (II) and (d_2) 99~25 % by weight of an oligomeric phosphate ester compound represented by the following Formula (III), per 100 parts by weight of the sum of (A), (B) and (C); and



(II)

(wherein R_1,R_2 and R_3 are independently hydrogen or C_{1-4} alkyl group, R_4 is C_{1-4}

alkyl group or C_{6-10} aryl group, n is 0 or 1)



(III)

(wherein R_5, R_6, and R_7 are independently hydrogen, or C_{1-6} alkyl group; X is a C_{6-20} aryl group or an alkyl-substituted C_{6-20} aryl group, preferably a dialcohol derivative such as resorcinol, hydroquinol and bisphenol-A, m is an integer from 0 to 5. The average value of m of a mixture of the oligomeric phosphate ester compounds is 1 to 3)

(E) 0.05 to 5.0 parts by weight of a fluorinated polyolefin resin per 100 parts by weight of (A)+(B)+(C).

[2] The flame retardant polycarbonate resin composition as defined in claim 1, wherein said phosphonate compound(d_1) is methyl diphenyl phosphonate.

[3] The flame retardant polycarbonate resin composition as defined in claim 1, wherein said phosphonate compound(d_1) is ethylene bis(diphenyl) phosphonate.

[4] The flame retardant polycarbonate resin composition as defined in claim 1, wherein said R_5, R_6, and R_7 are hydrogen, methyl, ethyl, isopropyl or t-butyl group; X is a derivative from resorcinol or bisphenol-A.

[5] The flame retardant polycarbonate resin composition as defined in claim 1, wherein said resin composition further comprises lubricants, releasing agents, nuclear agents, antistatic agents, stabilizers, impact modifiers, inorganic fillers, pigments, dyes and a mixture thereof.

[6] The flame retardant polycarbonate resin composition as defined in claim 1, wherein n in Formula (II) is 1.

[7] A molding article produced from the flame retardant polycarbonate resin composition as defined in any one of claims 1-6.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2005/001830

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C08L 69/00, C08K 5/523

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C08L 69/00, C08K 5/523

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

Korean Patents and applications for inventions since 1975
Korean Utility models and applictions for Utility models since 1975
Japanese Utility models and application for Utility models since 1975

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

KIPASS, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 2003-47384 A (Cheil Industries Inc.) 18 June 2003 See the whole document	1 - 7
Y	JP 9-59287 A (Sanyo Cem Ind. Ltd.) 04 March 1997 See the whole document	1 - 7
A	EP 771852 A (General Electric Co.) 07 May 1997 See the whole document	1 - 7
A	US5672645 A (Bayer AG) 30 September 1997 See the whole document	1 - 7
A	JP16-59898 A (Mitsubishi Eng. Plastics Corp.) 26 February 2004 See the whole document	1 - 7

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR2005/001830

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