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(54) Title: FLAME RETARDANT POLYCARBONATE RESIN COMPOSITION

(57) Abstract: The flame retardant polycarbonate resin composition of the present invention includes (A) a polycarbonate resin, (B) a rubber-modified vinyl-based graft copolymer, (C) a metal salt of sulfonic acid, and (D) an anti-drip agent including a fluorinated terpolymer. The polycarbonate resin composition of the present invention has excellent flame retardancy, heat resistance, and mechanical strength, well-balanced mechanical properties such as impact resistance, heat resistance, and fine workability, and an excellent appearance characteristic. Therefore, it is useful for fabrication of molded products such as electric household appliances, office appliances, electrical and electronic devices, and internal parts thereof.



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【SPECIFICATION】**【Invention Title】**

FLAME RETARDANT POLYCARBONATE RESIN COMPOSITION

【Technical Field】

5 The present invention relates to a flame retardant polycarbonate resin composition. More particularly, the present invention relates to a flame retardant polycarbonate resin composition of which mechanical and appearance characteristics are not deteriorated.

【Background Art】

10 A polycarbonate resin has a variety of applications, such as for office automative devices, communication devices, and electrical and electronic products, due to its transparency, excellent electrical characteristics, and fine mechanical properties, e.g., high resistance against impact.

 A resin composition used for office automation devices and electrical and
15 electronic products requires strict safety specifications, and particularly, it should satisfy a flame retardant specification. To give a resin composition flame retardancy, a flame retardant agent such as a halogen-containing compound, a phosphor-containing compound, a metal salt of a sulfonic acid compound, or a silicon-based compound is used.

20 U.S. Patent Nos. 4,983,658 and 4,883,835 disclose examples of a halogen-containing compound used as a flame retardant, U.S. Patent Nos. 5,061,745 and 4,883,835 disclose examples of a phosphor-containing compound used as a flame retardant, U.S. Patent Nos. 3,535,300 and 3,775,367

disclose examples of a metal salt of sulfonic acid used as a flame retardant, and U.S. Patent Nos. 3,971,756 and 6,001,921 disclose examples of a silicon-based compound used as a flame retardant.

To acquire flame retardancy with a thinner thickness, a flame retardant polycarbonate resin composition with a flame retardant agent and an anti-drip agent, such as a fluorinated polyolefin, is generally used. A polyolefin-based resin has a fibrillar network forming capability. Therefore, when the polyolefin-based resin is used as an anti-drip agent for a polycarbonate resin composition, fine pitting and/or silver streaking occur in the surface of molded products, which is problematic.

To overcome the problem, U.S. Patent No. 4,649,168 discloses an example of using a mixed co-coagulation of fluorinated polyethylene and a styrene-containing copolymer as an anti-drip agent for a polycarbonate resin composition using a metal salt of sulfonic acid as a flame retardant. However, since the mixed co-coagulation has a complex preparation process, production cost is increased. Also, the content of the fluorinated polyethylene is relatively small. Therefore, when the mixed co-coagulation is used as an anti-drip agent, it should be used at a content of more than that of existing fluorinated polyethylene, which is problematic as well.

U.S. Patent No. 6,180,702 discloses an example of using a mixed co-coagulation of fluorinated polyethylene and poly(meth)acrylic acid alkyl ester resin as an anti-drip agent for a polycarbonate resin composition using a metal salt of sulfonic acid as a flame retardant.

When the mixed co-coagulation is used as an anti-drip agent, the

dispersion property of a resin composition is improved, which results in an improvement in the appearance problems such as fine pitting and/or silver streaking to some extent. However, its flame retardancy is deteriorated compared to that of a composition using a typical fluorinated polyethylene-based resin as an anti-drip agent.

【DETAILED DESCRIPTION】

【Technical Problem】

An embodiment of the present invention provides a polycarbonate resin composition having excellent flame retardancy without decreasing mechanical and appearance characteristics.

Another embodiment of the present invention provides a polycarbonate resin composition with balanced mechanical properties such as heat resistance, impact strength, and workability.

Yet another embodiment of the present invention provides a molded product fabricated using the polycarbonate resin composition.

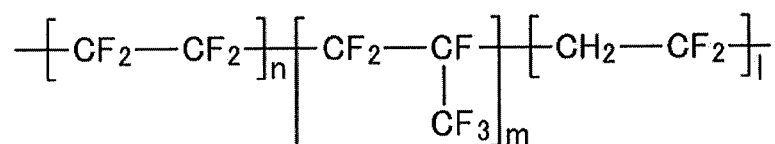
The embodiments of the present invention are not limited to the above technical purposes, and a person of ordinary skill in the art can understand other technical purposes.

【Technical Solution】

According to one embodiment of the present invention, a flame retardant polycarbonate resin composition is provided that includes: (A) a polycarbonate resin; (B) a rubber-modified vinyl-based graft copolymer; (C) a metal salt of sulfonic acid; and (D) an anti-drip agent including a fluorinated terpolymer

including a repeating unit represented by the following Chemical Formula 1.

[Chemical Formula 1]



In the above Chemical Formula 1, each of n, m, and l refers to a mole
 5 ratio of the repeating units, where n ranges from 15 to 50, m ranges from 20 to 40, and l ranges from 30 to 60.

According to another embodiment of the present invention, a molded product fabricated using the polycarbonate resin composition is provided.

Hereinafter, further embodiments of the present invention will be
 10 described in detail.

【Advantageous Effects】

The polycarbonate resin composition of the present invention has excellent flame retardancy, heat resistance, and mechanical strength, well-balanced mechanical properties such as impact resistance, heat resistance,
 15 and fine workability, and an excellent appearance characteristic. Therefore, it is useful for fabrication of molded products such as electric household appliances, office appliances, electrical and electronic devices, and internal parts thereof.

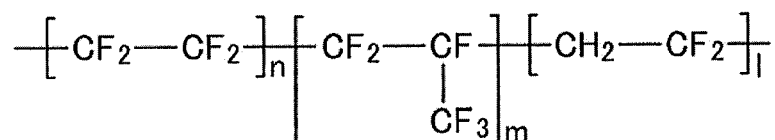
【Best Mode】

20 Exemplary embodiments of the present invention will hereinafter be described in detail. However, these embodiments are only exemplary, and the present invention is not limited thereto.

As used herein, the terms substituted alkyl, substituted alkylene, substituted alkylidene, substituted cycloalkylene, substituted cycloalkylidene, substituted aryl, and substituted arylene respectively refer to an alkyl, an alkylene, an alkylidene, a cycloalkylene, a cycloalkylidene, an aryl, and an
 5 arylene that are independently substituted with a halogen, a C1 to C30 alkyl, a C6 to C30 aryl, a C2 to C30 heteroaryl, or a C1 to C20 alkoxy.

The flame retardant polycarbonate resin composition according to one embodiment of the present invention includes (A) a polycarbonate resin, (B) a rubber-modified vinyl-based graft copolymer, (C) a metal salt of sulfonic acid,
 10 and (D) an anti-drip agent including a fluorinated terpolymer including the repeating unit represented by the following Chemical Formula 1.

[Chemical Formula 1]



In the above Chemical Formula 1, each of n, m, and l refers to a mole
 15 ratio of the repeating unit, where n ranges from 15 to 50, m ranges from 20 to 40, and l ranges from 30 to 60.

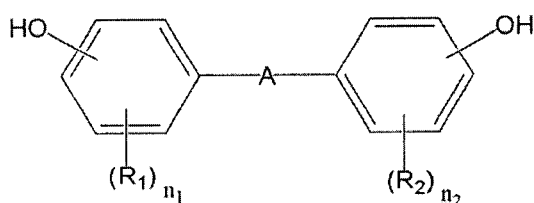
It is preferable that the polycarbonate resin composition includes 1 to 10 parts by weight of the rubber-modified vinyl-based graft copolymer (B), 0.01 to 3 parts by weight of the metal salt of sulfonic acid (C), and 0.01 to 3 parts by
 20 weight of the anti-drip agent including a fluorinated terpolymer including the repeating unit represented by the above Chemical Formula 1 based on 100 parts by weight of the polycarbonate resin (A).

Exemplary components included in the polycarbonate resin composition according to embodiments of the present invention will hereinafter be described in detail.

(A) Polycarbonate resin

The polycarbonate resin as a base constituting component may be prepared by reacting diphenols of the following Chemical Formula 2 with a compound selected from the group consisting of a phosgene, a halogen formate, a carbonate diester, and a combination thereof.

[Chemical Formula 2]



In the above Chemical Formula 2, A is a single bond, a substituted or unsubstituted C1 to C5 alkylene, a substituted or unsubstituted C1 to C5 alkylidene, a substituted or unsubstituted C3 to C6 cycloalkylene, a substituted or unsubstituted C5 to C6 cycloalkylidene, CO, S, or SO₂, R₁ and R₂ are a substituted or unsubstituted C1 to C30 alkyl, or a substituted or unsubstituted C6 to C30 aryl, and n₁ and n₂ are independently integers ranging from 0 to 4.

As used herein, the term "substituted" refers to one substituted with at least a substituent selected from the group consisting of a halogen, a C1 to C30 alkyl, a C1 to C30 haloalkyl, a C6 to C30 aryl, a C1 to C20 alkoxy, and combinations thereof.

Specific examples of the diphenols include hydroquinone, resorcinol,

4,4'-dihydroxy diphenyl, 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, or
5 2,2-bis(3,5-dichloro-4-hydroxyphenyl)-propane. Of the diphenols,
2,2-bis(4-hydroxyphenyl)-propane,
2,2-bis(3,5-dichloro-4-hydroxyphenyl)-propane, or
1,1-bis(4-hydroxyphenyl)-cyclohexane may be preferable.
2,2-bis(4-hydroxyphenyl)-propane (also referred to as bisphenol-A) may be
10 more preferable.

The polycarbonate resin has a weight average molecular weight ranging from 10,000 to 200,000, and in another embodiment, it has a weight average molecular weight ranging from 15,000 to 80,000, but is not limited thereto.

The polycarbonate resin may be a branched polycarbonate resin, and
15 may preferably be prepared by further adding a multi-functional compound including three or more phenol groups in an amount of 0.05 to 2 mol% based on the total weight of the phenols during polymerization.

The polycarbonate resin may be a homo-polycarbonate resin or a co-polycarbonate resin, and the co-polycarbonate resin and
20 homo-polycarbonate resin may be used as a blend thereof.

The polycarbonate resin may be partially or totally replaced by an aromatic polyester-carbonate resin that is obtained by polymerizing an ester precursor, for example difunctional carboxylic acid.

The amounts of the components (B) to (E) in the resin composition of the

present invention are based on 100 parts by weight of the polycarbonate resin (A).

(B) Rubber-modified vinyl-based graft copolymer

The rubber-modified vinyl-based graft copolymer functions as an impact
5 modifier in a resin composition. The rubber-modified vinyl-based graft copolymer is obtained by graft-copolymerizing (b₁) 5 to 95 parts by weight of a vinyl-based monomer into (b₂) 5 to 95 parts by weight of a rubbery polymer.

The vinyl-based monomer (b₁) includes (b₁₁) 50 to 95 parts by weight of a first vinyl-based monomer selected from the group consisting of styrene, a
10 halogen-substituted styrene, an alkyl-substituted styrene such as alpha-methylstyrene, methacrylic acid alkyl esters, acrylic acid alkyl esters, and mixtures thereof, (b₁₂) 5 to 50 parts by weight of a second vinyl-based monomer selected from the group consisting of acrylonitrile, methacrylonitrile, methacrylic acid alkyl esters, acrylic acid alkyl esters, anhydrous maleic acid, C₁-C₄ alkyl
15 N-substituted maleimide, phenyl N-substituted maleimide, and mixtures thereof. The first and second vinyl-based monomers may be different from each other.

The alkyl substituted styrene includes a C₁ to C₈ alkyl.

The methacrylic acid alkyl esters or acrylic acid alkyl esters include a C₁ to C₈ alkyl. The methacrylic acid alkyl esters or acrylic acid alkyl esters are
20 alkyl esters of methacrylic acid or acrylic acid, respectively. For example, C₁ to C₈ alkyl esters may be obtained from monohydryl alcohols including a C₁ to C₈ carbon atom. Specific examples of the monohydryl alcohols include methacrylic acid methyl ester, methacrylic acid ethyl ester, acrylic acid ethyl ester, acrylic acid methyl ester, and methacrylic acid propyl ester. For example,

methacrylic acid methyl ester is most preferable.

The rubbery polymer (b₂) may be selected from the group consisting of a butadiene rubber, an acryl rubber, an ethylene/propylene rubber, a styrene/butadiene rubber, an acrylonitrile/butadiene rubber, an isoprene rubber, an ethylene-propylene-diene terpolymer (EPDM), a polyorganosiloxane/polyalkylmethacrylate rubber composite, and mixtures thereof.

When the graft copolymer is prepared, the rubbery polymer may have a particle diameter of 0.05 to 4 μm to improve the impact strength and the surface characteristic of a molded product.

The rubber-modified vinyl-based graft copolymer may be obtained by graft-copolymerizing a styrene/acrylonitrile vinyl-based monomer or a methacrylic acid alkyl ester monomer, or mixtures thereof, to a butylacrylate rubber.

The rubber-modified vinyl-based graft copolymer may also be obtained by graft-copolymerizing a methacrylic acid methyl ester monomer, or optionally an acrylic acid methyl ester or acrylic acid ethyl ester monomer, to an acryl rubber or polyorganosiloxane/polyalkyl(meth)acrylate rubber polymer.

A method of preparing the rubber-modified vinyl-based graft copolymer is widely known to those skilled in the art to which the present invention pertains, and any one among emulsion polymerization, suspension polymerization, solution polymerization, and bulk polymerization can be used to prepare the rubber-modified vinyl-based graft copolymer. One of the preferred preparation methods is to perform emulsion polymerization or bulk polymerization by

inputting the vinyl-based monomer in the presence of a rubbery polymer and using a polymerization initiator.

The rubber-modified vinyl-based graft copolymer may be used in an amount of 1 to 10 parts by weight based on 100 parts by weight of the (A) polycarbonate resin. When the content of the rubber-modified vinyl-based graft copolymer is less than 1 part by weight, the impact resistance may be deteriorated. When it exceeds 10 parts by weight, flame retardancy and heat resistance may be deteriorated. Therefore, it is preferable to use the rubber-modified vinyl-based graft copolymer in the above content range to balance the impact resistance, flame retardancy, and heat resistance.

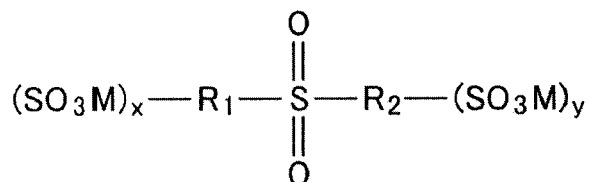
(C) Metal salt of sulfonic acid

The metal salt of sulfonic acid may be selected from the group consisting of (C₁) a metal salt of aromatic sulfonic acid, (C₂) a metal salt of perfluoroalkane sulfonic acid, and a mixture thereof. Exemplary components will hereinafter be described in detail.

(C₁) Metal salt of aromatic sulfonic acid

The metal salt of aromatic sulfonic acid may be represented by the following Chemical Formula 3.

[Chemical Formula 3]



In the above Chemical Formula 3, R₁ and R₂ are independently selected from the group consisting of a C₁ to C₆ aliphatic group, a phenyl, a biphenyl, an

alkyl-substituted phenyl, and combinations thereof, x is an integer ranging from 0 to 6, y is an integer ranging from 1 to 6, and M is a metal cationic group.

Further, M is selected from the group consisting of a group I metal (an alkaline metal) such as sodium, potassium, and the like, a group II metal (an alkaline-earth metal), copper, aluminum, and combinations thereof. An alkaline metal is preferable.

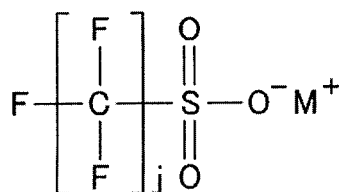
The metal salt of aromatic sulfonic acid represented by the above Chemical Formula 3 is selected from the group consisting of a metal salt of diphenylsulfone-3-sulfonic acid, a metal salt of diphenylsulfone-3,3'-disulfonic acid, a metal salt of diphenylsulfone-3,4'-disulfonic acid, and mixtures thereof. The metal is selected from the group consisting of a group I metal (an alkaline metal) such as sodium, potassium, and the like, a group II metal (an alkaline-earth metal), copper, aluminum, and combinations thereof. An alkaline metal is preferable.

For example, the metal salt of aromatic sulfonic acid represented by the above Chemical Formula 3 may be potassium diphenylsulfone-3-sulfonate.

(C₂) Metal salt of perfluoroalkane sulfonic acid

The metal salt of perfluoroalkane sulfonic acid may be represented by the following Chemical Formula 4.

[Chemical Formula 4]



In the above Chemical Formula 4, M is a metal cationic group, and j is an integer ranging from 1 to 8.

M is selected from the group consisting of a group I metal (an alkaline metal) such as sodium, potassium, and the like, a group II metal (an alkaline-earth metal), copper, aluminum, and combinations thereof. An alkaline metal is preferable.

The metal salt of perfluoroalkane sulfonic acid of the above Chemical Formula 4 includes one selected from the group consisting of a metal salt of perfluoromethane sulfonic acid, a metal salt of perfluoroethane sulfonic acid, a metal salt of perfluoropropane sulfonic acid, a metal salt of perfluorobutanesulfonic acid, a metal salt of perfluoropentane sulfonic acid, a metal salt of perfluorohexane sulfonic acid, a metal salt of perfluoroheptane sulfonic acid, a metal salt of perfluorooctane sulfonic acid, and mixtures thereof. The metal is selected from the group consisting of a group I metal (an alkaline metal) such as sodium, potassium, and the like, a group II metal (an alkaline-earth metal), copper, aluminum, and combinations thereof. An alkaline metal is preferable. A specific example of the metal salt of perfluoroalkane sulfonic acid may be potassium fluorobutane sulfonate.

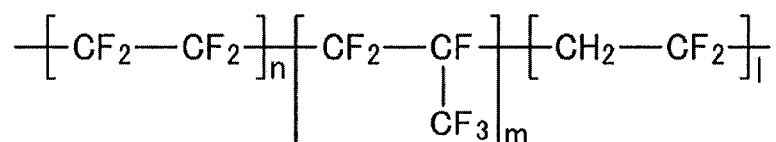
The metal salt of sulfonic acid may be included in a content of 0.01 to 3 parts by weight based on 100 parts by weight of the (A) polycarbonate resin. When the content of the metal salt of sulfonic acid is less than the range, the flame retardancy is not sufficiently improved. When the content exceeds the range, thermal stability may be deteriorated at a high temperature. Therefore, it

is preferable to use the metal salt of sulfonic acid in the above content range to balance the improvement effects of flame retardancy and thermal stability.

(D) Anti-drip agent

The anti-drip agent contributes to increasing flame retardancy with a thinner thickness. In the resin composition prepared according to an embodiment of the present invention, the anti-drip agent may be a fluorinated terpolymer including a repeating unit of the following Chemical Formula 1.

[Chemical Formula 1]



In the above Chemical Formula 1, each of n, m, and l refers to a mole ratio (mol%) of a repeating unit. Specifically, n ranges from 15 to 50, m ranges from 20 to 40, and l ranges from 30 to 60.

The fluorinated terpolymer may be prepared using a known polymerization method. For example, it may be prepared in an aqueous medium including a free radical forming catalyst such as sodium, potassium, or ammonium peroxydisulfate at a temperature of 0 to 200° C, and specifically from 20 to 100° C, under a pressure of 7 to 71 kg/cm².

The anti-drip agent may further include a fluorinated polyolefin-based resin along with the fluorinated terpolymer.

The fluorinated polyolefin-based resin includes polytetrafluoroethylene, polyvinylidene fluoride, a tetrafluoroethylene/vinylidene fluoride copolymer, a tetrafluoroethylene/hexafluoropropylene copolymer, or an

ethylene/tetrafluoroethylene copolymer, and the like.

The fluorinated polyolefin-based resin forms a fibrillar network in the resin to thereby decrease flow viscosity of the resin and increase shrinkage during combustion, when it is mixed with another resin containing different
5 components from the fluorinated polyolefin-based resin and extruded. Essentially, it prevents the resin from dripping.

When used together with the fluorinated polyolefin-based resin, the fluorinated polyolefin-based resin and the fluorinated terpolymer may be mixed and used in a weight ratio of 50:50 to 90:10, and specifically in a weight ratio of
10 70:30 to 90:10.

When the fluorinated polyolefin-based resin and the fluorinated terpolymer are mixed in the above weight ratio range, it is possible to improve the dispersion property of the resin composition and the appearance characteristic without pitting and/or silver streaking, as well as to increase the
15 flame retardancy of the resin composition. Therefore, it is preferable to mix the fluorinated polyolefin-based resin and the fluorinated terpolymer in the above weight ratio range to balance the appearance characteristic and the flame retardancy.

The above-mentioned anti-drip agent may have a particle size of 0.05 to
20 1000 μ m. When the particle size of the anti-drip agent is out of the particle size range, pitting and/or silver streaking may occur. Therefore, it is preferable to have the particle size in the above range in consideration of the appearance characteristic.

Also, the anti-drip agent may have a specific gravity of 1.2 to 2.3 g/cm³.

The anti-drip agent may be of an emulsion type or a powder type. An emulsion-type anti-drip agent has a fine dispersion property in the resin composition, but its preparation process may be somewhat complicated. Thus, it is preferred to use a powder-type anti-drip agent for simplification of the process. Also, even if the anti-drip agent is of a powder type, if it is sufficiently dispersed in the resin composition to form a fibrillar network, it is better to use the anti-drip agent of the powder type than the emulsion type.

The anti-drip agent may be included in a content of 0.01 to 3 parts by weight based on 100 parts by weight of the polycarbonate resin (A). Within the content range of the anti-drip agent, the resin composition shows well-balanced mechanical properties of increased flame retardancy and excellent impact strength.

(E) Other additive

The polycarbonate resin composition may further include an additive including an ultraviolet (UV) stabilizer, a fluorescent whitening agent, a lubricant, a release agent, a nucleating agent, an antistatic agent, a stabilizer, a reinforcing material, an inorganic material additive, and a colorant such as a pigment or a dye along with the above (A) to (D) components, according to its use.

The ultraviolet (UV) stabilizer suppresses a color change and a decrease in photo-reflectivity of the resin composition that may be caused by UV irradiation. Examples of the UV stabilizer include a benzotriazole-based compound, a benzophenone-based compound, and a triazine-based compound.

The fluorescent whitening agent improves photo-reflectivity of a polycarbonate resin composition. Examples of the fluorescent whitening agent

include stilbene-bisbenzoxazole derivatives such as 4-(benzoxazol-2-yl)-4'-(5-methylbenzoxazol-2-yl)stilbene and 4,4'-bis(benzoxazol-2-yl)stilbene.

As for the release agent, a fluorine-containing polymer, silicone oil, a metal salt of stearate, a metal salt of montanic acid, or an ester wax or
5 polyethylene wax of montanic acid may be used. The nucleating agent may be talc or clay.

The inorganic material additive includes glass fiber, silica, clay, calcium carbonate, calcium sulfate, or glass beads.

The additive may be used in a content range of not more than 60 parts
10 by weight, and specifically 1 to 40 parts by weight, based on 100 parts by weight of the (A) polycarbonate resin. When the additive is used in the above content range, balanced mechanical properties can be acquired.

A polycarbonate resin composition having the above-mentioned composition may be prepared in a known method for preparing a resin
15 composition. For example, a polycarbonate resin composition can be prepared in a pellet type by simultaneously mixing the above-mentioned components and other additives, and melting and extruding the mixture in an extruder.

The polycarbonate resin composition may be used for molding diverse products. Particularly, it can be used for fabricating external parts of electrical
20 and electronic produces such as TVs, computers, mobile phones, and office automation devices, and precise parts for automobiles, which require superb mechanical and appearance characteristics with excellent flame retardancy.

Hereinafter, the present invention is illustrated in more detail with reference to examples. However, the embodiments of the present invention

are exemplary, and the present invention is not limited thereto.

Examples

Components of polycarbonate resin compositions used in the examples of the present invention and comparative examples were as follows.

5 (A) Polycarbonate resin

A bisphenol-A type polycarbonate having a weight average molecular weight of 25,000g/mol, PANLITE L-1250WP of Teijin Company, Japan, was used.

(B) Rubber-modified vinyl-based graft copolymer

10 Metablen C223A of Mitsubishi Rayon Chemical Company, Japan, was used.

(C) Metal salt of sulfonic acid

(C-1) KSS (potassium diphenylsulfone-3-sulfonate) of Seal Sand Chemical Company, England, was used.

15 (C-2) FR-2025 (potassium perfluorobutane-sulfonate) of 3M, U.S., was used.

(D) Anti-drip agent

(D-1) A mixture of a powder-type polytetrafluoroethylene and fluorinated terpolymer (in a mixing weight ratio range of 7:3 to 8:2), MM5935EF of 3M
20 Company, U.S., was used.

(D-2) A powder-type polytetrafluoroethylene, 850-A of DuPont Company, U.S., was used.

(D-3) An emulsion-type polytetrafluoroethylene, FR-301B of 3F Company, China, was used.

(D-4) A mixed co-coagulation of a powder-type polyethylene and a styrene-containing copolymer, AD-541 of 3F Company, China, was used.

Examples 1 and 2 and Comparative Examples 1 to 6

The components were mixed in a typical mixer according to the compositions shown in the following Table 1. The mixtures were extruded using a twin screw extruder with L/D=35 and $\Phi=45\text{mm}$, and the extrusions were prepared in a pellet shape.

Specimens for measuring mechanical properties and evaluating flame retardancy at an injection temperature of 280 to 300° C were fabricated using a 10 oz injection molding device and the prepared pellets.

(Table 1)

(unit: parts by weight)

		Examples		Comparative Examples					
		1	2	1	2	3	4	5	6
(A)		100	100	100	100	100	100	100	100
(B)		4	4	4	4	4	4	4	4
(C)	C-1	0.3	-	0.3	0.3	0.3	-	-	-
	C-2	-	0.1	-	-	-	0.1	0.1	0.1
(D)	D-1	0.4	0.4	-	-	-	-	-	-
	D-2	-	-	0.4	-	-	0.4	-	-
	D-3	-	-	-	0.6	-	-	0.6	-
	D-4	-	-	-	-	0.6	-	-	0.6

The specimens fabricated as above were kept alone at 23° C, at a relative humidity of 50% for 48 hours, and their mechanical properties were evaluated. The results are represented in the following Table 2.

(1) Flame retardancy: Evaluated using 1.5mm-thick specimens in accordance with UL-94 regulation.

(2) Notched Izod impact strength: Measured using 1/8" specimens in accordance with ASTM D256 specification.

3 Heat resistance: Evaluated by measuring Vicat softening temperature in accordance with ASTM D1525 specification.

(4) Appearance evaluation of injection moldings: Plate-type specimens having dimensions of vertical and horizontal lengths of 10×10 inches with a thickness 1/8" were fabricated. Then, the number of silver streaks and pitting formed in the surface of the acquired specimens were observed with bare eyes and evaluated based on the following references.

◎: 0, ○: less than 10, △: less than 11 to 50, ×: more than 50

(Table 2)

	Examples		Comparative Examples					
	1	2	1	2	3	4	5	6
UL 94 flame retardancy (1.5mm)	V-0	V-0	V-2	V-2	Fail	V-1	V-1	V-2
Combustion time	34	23	69	78	-	54	57	65

(second)								
1/8" IZOD impact strength (kgf · cm/cm)	64	68	52	65	49	53	63	51
Vicat softening temperature (° C)	141	142	141	141	138	141	142	138
appearance	◎	◎	×	◎	△	×	○	△

As shown in Table 2, Comparative Examples 1, 2, and 3 used the anti-drip agents D-2, D-3, and D-4, respectively, instead of D-1 in the resin composition of Example 1. Compared to Example 1, Comparative Example 1
5 had superior heat resistance but showed remarkable deterioration in flame retardancy, impact strength, and appearance characteristics. Comparative Example 2 showed superior appearance, heat resistance, and impact strength, but had remarkably deteriorated flame retardancy. Comparative Example 3 showed remarkable deterioration in flame retardancy, impact strength, heat
10 resistance, and appearance characteristics.

Comparative Examples 4, 5, and 6 use the anti-drip agents D-2, D-3, and D-4, respectively, instead of D-1 as in the resin composition of Example 2. Compared to Example 2, Comparative Example 4 had fine heat resistance but it showed remarkable deterioration in flame retardancy, impact strength, and
15 appearance characteristics. Comparative Example 5 had superior appearance,

heat resistance, and impact strength characteristics, but showed remarkable deterioration in flame retardancy. Comparative Example 6 showed remarkable deterioration in flame retardancy, impact strength, heat resistance, and appearance characteristics.

5 The results show that it is possible to acquire flame a retardant polycarbonate resin composition without deterioration in heat resistance, IZOD impact strength, and appearance characteristics of injection moldings by adding a polycarbonate resin, a rubber-modified vinyl-based graft copolymer, a metal salt of sulfonic acid, and a fluorinated terpolymer mixture in optimal content
10 ranges, compared to a conventional resin composition using an anti-drip agent.

 While this invention has been described in connection with what is presently considered to be practical exemplary embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but, on the contrary, is intended to cover various modifications and equivalent
15 arrangements included within the spirit and scope of the appended claims. Therefore, the aforementioned embodiments are exemplary in every way, and the present invention is not limited thereto.

【CLAIMS】**【Claim 1】**

A polycarbonate resin composition, comprising:

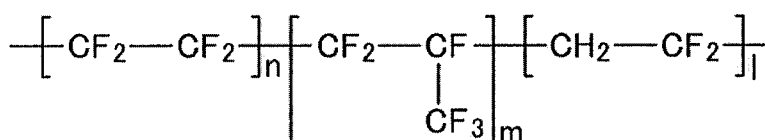
(A) a polycarbonate resin;

5 (B) a rubber-modified vinyl-based graft copolymer;

(C) a metal salt of sulfonic acid; and

(D) an anti-drip agent including a fluorinated terpolymer including the repeating unit represented by the following Chemical Formula 1:

[Chemical Formula 1]



10

wherein, in the above Chemical Formula 1, each of n, m, and l refers to a mole ratio of the repeating units, n ranges from 15 to 50, m ranges from 20 to 40, and l ranges from 30 to 60.

15 **【Claim 2】**

The polycarbonate resin composition of claim 1, wherein the polycarbonate resin composition comprises: 1 to 10 parts by weight of the rubber-modified vinyl-based graft copolymer (B); 0.01 to 3 parts by weight of the metal salt of sulfonic acid (C); and 0.01 to 3 parts by weight of the anti-drip agent including a fluorinated terpolymer including a repeating unit represented by the above Chemical Formula 1 based on 100 parts by weight of the polycarbonate resin (A).

20

【Claim 3】

The polycarbonate resin composition of claim 1, wherein the vinyl-based graft copolymer is prepared by graft-copolymerizing (b₁) 5 to 95 parts by weight
5 of a vinyl-based monomer into (b₂) 5 to 95 parts by weight of a rubbery polymer,

wherein the vinyl-based monomer (b₁) includes: (b₁₁) 50 to 95 parts by weight of a first vinyl-based monomer selected from the group consisting of styrene, a halogen substituted styrene, an alkyl substituted styrene such as alpha-methylstyrene, methacrylic acid alkyl esters, and acrylic acid alkyl esters,
10 and mixtures thereof; (b₁₂) 5 to 50 parts by weight of a second vinyl-based monomer selected from the group consisting of acrylonitrile, methacrylonitrile, methacrylic acid alkyl esters, acrylic acid alkyl esters, anhydrous maleic acid, a C₁-C₄ alkyl N-substituted maleimide, a phenyl N-substituted maleimide, and mixtures thereof, and the first and second vinyl-based monomers are different
15 from each other, and

the rubbery polymer (b₂) is selected from the group consisting of a butadiene rubber, an acryl rubber, an ethylene/propylene rubber, a styrene/butadiene rubber, an acrylonitrile/butadiene rubber, an isoprene rubber, an ethylene-propylene-diene terpolymer (EPDM), a polyorganosiloxane/poly
20 alkylmethacrylate rubber composite, and mixtures thereof.

【Claim 4】

The polycarbonate resin composition of claim 1, wherein the vinyl-based

graft copolymer is obtained by graft-copolymerizing a styrene/acrylonitrile vinyl-based monomer, or a methacrylic acid alkyl ester monomer, or mixtures thereof, into a butylacrylate rubber, or

by graft-copolymerizing a methacrylic acid methyl ester monomer, or
 5 optionally an acrylic acid methyl ester or acrylic acid ethyl ester monomer, into an acryl rubber or polyorganosiloxane/polyalkyl(meth)acrylate rubber polymer.

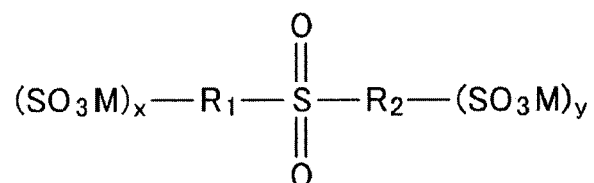
【Claim 5】

The polycarbonate resin composition of claim 1, wherein the metal salt of
 10 sulfonic acid is selected from the group consisting of a metal salt of an aromatic sulfonic acid, a metal salt of perfluoroalkanesulfonic acid, and a mixture thereof.

【Claim 6】

The polycarbonate resin composition of claim 5, wherein the metal salt of
 15 an aromatic sulfonic acid is represented by the following Chemical Formula 3:

[Chemical Formula 3]



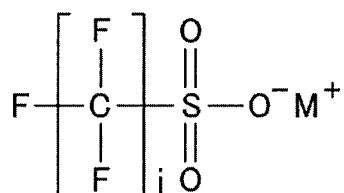
wherein, in the above Chemical Formula 3, R₁ and R₂ are independently selected from the group consisting of a C₁ to C₆ aliphatic group, a phenyl, a
 20 biphenyl, an alkyl-substituted phenyl, and combinations thereof, x is an integer ranging from 0 to 6, y is an integer ranging from 1 to 6, and M is a metal cationic

group.

【Claim 7】

The polycarbonate resin composition of claim 5, wherein the metal salt of
 5 perfluoroalkanesulfonic acid may be represented by the following Chemical
 Formula 4:

[Chemical Formula 4]



wherein, in the above Chemical Formula 4, M is a metal cationic group,
 10 and j is an integer ranging from 1 to 8.

【Claim 8】

The polycarbonate resin composition of claim 1, wherein the metal salt of
 sulfonic acid is selected from the group consisting of potassium
 15 diphenylsulfone-3-sulfonate, potassium perfluorobutane-sulfonate, and mixtures
 thereof.

【Claim 9】

The polycarbonate resin composition of claim 1, wherein the anti-drip
 20 agent further comprises a fluorinated polyolefin-based resin along with the
 fluorinated terpolymer.

【Claim 10】

The polycarbonate resin composition of claim 9, wherein the anti-drip agent comprises the fluorinated polyolefin-based resin and fluorinated
5 terpolymer at a weight ratio of 50:50 to 90:10.

【Claim 11】

The polycarbonate resin composition of claim 1, wherein the anti-drip agent has a particle size of 0.05 to 1000 μ m.
10

【Claim 12】

The polycarbonate resin composition of claim 1, wherein the polycarbonate resin composition further comprises an additive selected from the group consisting of an ultraviolet (UV) stabilizer, a fluorescent whitening agent, a
15 lubricant, a release agent, a nucleating agent, an antistatic agent, a stabilizer, a reinforcing material, an inorganic material additive, a pigment, a dye, and mixtures thereof.

【Claim 13】

20 A molded product fabricated using the polycarbonate resin composition according to one of claims 1 to 12.

A. CLASSIFICATION OF SUBJECT MATTER*C08L 69/00(2006.01)i*

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)

IPC 8: C08L 69/00

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

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

eKOMPASS(KIPO internal), PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP08-157732 A (JAPAN SYNTHETIC RUBBER CO LTD) 18 Jun. 1996 Abstract; Claim 1; Par. [3]-[4], [14]-[16]	1-5, 9-13
A	KR10-0511756 B1 (CHEIL INDUSTRIES INC.) 25 Aug. 2005 Whole document	1-13
A	KR10-0744730 B1 (LG CHEM. LTD. et al.) 25 Jul. 2007 Whole document	1-13



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

11 AUGUST 2009 (11.08.2009)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2008/007904

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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