Abstract:
The present invention relates to a flame-retardant thermoplastic resin composition and a molded article thereof. More specifically, the present invention provides a flame-retardant thermoplastic resin composition comprising polysiloxane-polycarbonate copolymer having a particular structure and aromatic polycarbonate resin, which has not only better flame retardancy, but also improved physical property balance in optical transparency, flowability, low-temperature impact strength, etc., and a molded article thereof.
Description

Title of Invention: FLAME-RETARDANT THERMOPLASTIC RESIN COMPOSITION AND MOLDED ARTICLE THEREOF

Technical Field

[1] The present invention relates to a flame-retardant thermoplastic resin composition and a molded article thereof. More specifically, the present invention provides a flame-retardant thermoplastic resin composition comprising polysiloxane-polycarbonate copolymer having a particular structure and aromatic polycarbonate resin, which has not only better flame retardancy, but also improved physical property balance in optical transparency, flowability, low-temperature impact strength, etc., and a molded article thereof.

Background Art

[2] Polycarbonate resin has good heat resistance, mechanical properties (in particular, impact strength) and optical transparency, etc. Thus, it has been extensively used in many industries such as electrical components, mechanical components and industrial resin. Heat resistance, mechanical properties and better flame retardancy are particularly required when polycarbonate resin is used as a material for TV housing, computer monitor housing, copier, printer, notebook battery, lithium battery case, etc. in the electric and electronic fields, all of which release considerable heat.

[3] The most conventional way to impart flame retardancy to a polycarbonate resin is to mix polycarbonate resin and halogenated flame retardant including the brominated or chlorinated type compound.

[4] Halogenated flame retardants exhibit sufficient flame retardant properties in case of fire, but hydrogen halide gas is produced during resin processing, which can not only cause cast erosion and environmental issues but also produce dioxin which is toxic and harmful to humans when it burns. Accordingly, there is now a move to regulate use of halogenated flame retardant.

[5] As an alternative to such regulation, flame-retardant polycarbonate resin compositions comprising both alkali metal salt as a non-halogenated flame retardant and fluorinated polyolefin resin as an anti-dripping agent have been developed.

[6] However, use of fluorinated ethylene resin and metal salt flame-retardant to ensure flame retardancy of polycarbonate resin leads to degraded optical transparency — one of the advantages of polycarbonate resin.

[7] In order to overcome such degradation of optical transparency, alloying with silicone-based additives and silicone-based copolymers was proposed.

[8] According to the present inventors' research, however, despite the environmental ad-
vantages of non-halogenated flame retardant, the technique using silicone-based additives has disadvantages such as poor optical transparency, relatively high price and limitation on various coloring when used as an exterior material. In addition, poor flowability to mold a large article makes it difficult to apply to a large article.

Accordingly, requirements still remain for developing polycarbonate resin compositions which not only have sufficient flame retardancy, but also realize balanced physical properties such as excellent optical transparency, flowability, low-temperature impact strength, etc.

Disclosure of Invention
Technical Problem

The object of the present invention is to overcome the above stated problems of prior arts, and to provide a flame-retardant thermoplastic resin composition having good flame retardancy, optical transparency, flowability and mechanical strength (in particular, low-temperature impact strength).

Solution to Problem

The present invention provides a flame-retardant thermoplastic resin composition comprising an aromatic polycarbonate resin; and a polysiloxane-polycarbonate copolymer comprising, as repeating units, a hydroxy-terminated siloxane of the following chemical formula 1 and a polycarbonate block of the following chemical formula 3:

Another aspect of the present invention is to provide a molded article of the above
flame-retardant thermoplastic resin composition.

**Advantageous Effects of Invention**

[24] A flame-retardant thermoplastic resin composition according to the present invention has not only better flame retardancy and optical transparency but also improved physical property balance in processability (in particular, enough flowability to mold a large article), mechanical strength (in particular, low-temperature impact strength), heat resistance, etc. through a suitable combination of polysiloxane-polycarbonate copolymer having a particular structure and thermoplastic aromatic polycarbonate resin. Thus, it can be applied for various uses such as in office machinery, housing for electrical and electronic products, etc., where flame-retardancy and optical transparency, etc. are required.

**Best Mode for Carrying out the Invention**

[25] Hereinafter, the present invention will be described more specifically. The purpose, features and advantages of the present invention will be easily understood through the following embodiments. The present invention is not limited to the embodiments as explained herein and may be reduced to practice in other forms. The embodiments introduced herein are provided in order to make the disclosed matters thorough and complete, and to sufficiently communicate the concept of the present invention to a person skilled in the art. Thus, the present invention is not limited to the following exemplified description and embodiments.

[26] The term "reaction product" as used herein means a substance that is formed by reacting two or more reactants.

[27] In addition, although the terms "first," "second" and the like are used herein for the description of polymerization catalysts, the polymerization catalysts are not limited by these terms. These terms are just used to distinguish the polymerization catalysts from each other. For example, a first polymerization catalyst and a second polymerization catalyst may be of the same kind of catalyst or different kinds of catalyst.

[28] Furthermore, in the chemical formulas described herein, although the English character "R" used for representing hydrogen, halogen atom and/or hydrocarbon group, etc. has a numerical subscript, "R" is not limited by such a subscript. "R" independently represents hydrogen, halogen atom and/or hydrocarbon group, etc. For example, even if two or more "R"s have the same numerical subscript, such "R"s may represent the same hydrocarbon group or different hydrocarbon groups. Also, even if two or more "R"s have different numerical subscripts, such "R"s may represent the same hydrocarbon group or different hydrocarbon groups.

[29]

[30] **[Flame-retardant thermoplastic resin composition]**
A flame-retardant thermoplastic resin composition according to the present invention comprises an aromatic polycarbonate resin, and a polysiloxane-polycarbonate copolymer having a particular structure.

Aromatic polycarbonate (PC) resin

A flame-retardant thermoplastic resin composition of the present invention may comprise any thermoplastic aromatic polycarbonate resin conventionally used in the art.

In one embodiment of the invention, an aromatic polycarbonate resin may be prepared from dihydric phenol, carbonate precursor and molecular weight regulator.

The dihydric phenol as one of the monomers forming the aromatic polycarbonate resin may have the following structure of chemical formula 5:

\[
\text{Chemical formula 5}
\]

in the chemical formula 5,

\[X\] represents alkylene group, unsubstituted, linear, branched or cyclic alkylene group, or linear, branched or cyclic alkylene group substituted with functional groups, such as sulfide, ether, sulfoxide, sulfone, ketone, naphthyl and isobutylphenyl. Preferably, \(X\) may be linear or branched alkylene group having 1 to 10 carbon atoms or cyclic alkylene group having 3 to 6 carbon atoms,

\(\alpha\) and \(R_2\) independently represent hydrogen atom, halogen atom, or alkyl group — for example, linear or branched alkyl group having 1 to 20 carbon atoms or cyclic alkyl group having 3 to 20 (preferably, 3 to 6) carbon atoms, and

\(n\) and \(m\) independently represent an integer of 0 to 4.

Examples of dihydric phenols include, but are not limited to, bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)phenylmethane, bis(4-hydroxyphenyl)naphthylmethane, bis(4-hydroxyphenyl)-(4-isobutylphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 1-ethyl-1,1-bis(4-hydroxyphenyl)propane, 1-phenyl-1,1-bis(4-hydroxyphenyl)ethane, 1-naphthyl-1,1-bis(4-hydroxyphenyl)ethane, 1,2-bis(4-hydroxyphenyl)ethane, 1,10-bis(4-hydroxyphenyl)decane, 2-methyl-1,1-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)propane(bisphenol A), etc., of which preferred one is bisphenol A.

Examples of the carbonate precursor as the other monomer of the aromatic polycarbonate resin include, but are not limited to, carbonyl chloride (phosgene), carbonyl...
bromide, bis halo formate, diphenylcarbonate, dimethylcarbonate, etc., of which preferred one is carbonyl chloride (phosgene).

A molecular weight regulator may be a substance already known in the art—i.e., a monofunctional compound that is similar to a monomer used in making thermoplastic aromatic polycarbonate resin. Examples of the molecular weight regulator include, but are not limited to, phenol-based derivatives (for example, para-isopropylphenol, para-ieri-butylphenol (PTBP), para-cumylphenol, para-isooctylphenol, para-isononylphenol, etc.), aliphatic alcohol, etc., of which preferred one is para-ieri-butylphenol (PTBP).

Examples of the aromatic polycarbonate resin prepared from dihydric phenol, carbonate precursor and molecular weight regulator include, but are not limited to, linear polycarbonate resin, branched polycarbonate resin, copolycarbonate resin and polyestercarbonate resin, etc., which may be used alone or in combination of two or more thereof.

Preferably, the aromatic polycarbonate resin has a viscosity average molecular weight ($M_n$, measured in solution of methylene chloride) of from 15,000 to 40,000, more preferably from 17,000 to 30,000, most preferably from 20,000 to 30,000. If the viscosity average molecular weight of the aromatic polycarbonate resin is less than 15,000, the mechanical properties such as impact strength, tensile strength, etc. may be lowered remarkably. If the viscosity average molecular weight is greater than 40,000, there may be a problem in processing the resin due to the increase of melting viscosity.

Preferably, the amount of aromatic polycarbonate resin is 5 to 90% by weight, more preferably 10 to 70% by weight, based on the total weight of flame-retardant thermoplastic resin composition. If the amount of the aromatic polycarbonate resin is less than 5% by weight based on the total weight of the composition, physical properties such as optical transparency, flowability, heat resistance, room-temperature impact strength, etc. may be lowered. If the amount of the aromatic polycarbonate resin is greater than 70% by weight, the flame retardancy may be not sufficient and low-temperature impact strength may be lowered due to a relative decrease in the amount of polysiloxane-polycarbonate copolymer as described below.

Polysiloxane-polycarbonate copolymer (Si-PC)

A flame-retardant thermoplastic resin composition of the present invention comprises a polysiloxane-polycarbonate copolymer. The polysiloxane-polycarbonate copolymer comprises, as repeating units, the hydroxy-terminated siloxane of the following chemical formula 1 and a polycarbonate block of the following chemical formula 3:

[Chemical formula 1]
in the chemical formula 1,

R_i independently represents hydrogen atom, halogen atom, hydroxy group, or alkyl group, alkoxy group or aryl group having 1 to 20 carbon atoms. For example, the halogen atom may be Cl or Br, and the alkyl group may be an alkyl group having 1 to 13 carbon atoms such as methyl, ethyl or propyl. In addition, for example, the alkoxy group may be an alkoxy group having 1 to 13 carbon atoms such as methoxy, ethoxy or propoxy, and the aryl group may be an aryl group having 6 to 10 carbon atoms such as phenyl, chlorophenyl or tolyl.

R_2 independently represents hydrocarbon group having 1 to 13 carbon atoms or hydroxy group. For example, R_2 may be alkyl or alkoxy group having 1 to 13 carbon atoms, alkenyl or alkenyloxy group having 2 to 13 carbon atoms, cycloalkyl or cycloalkoxy group having 3 to 6 carbon atoms, aryloxy group having 6 to 10 carbon atoms, aralkyl or aralkoxy group having 7 to 13 carbon atoms, or alkaryl or alkaryloxy group having 7 to 13 carbon atoms.

R_3 independently represents alkylene group having 2 to 8 carbon atoms.

A represents X or NH-X-NH, wherein X represents linear or branched aliphatic group having 1 to 20 carbon atoms, cycloalkylene group (for example, having 3 to 6 carbon atoms), or mono- or polycyclic arylene group having 6 to 30 carbon atoms and being unsubstituted or substituted with halogen atom, alkyl group, alkoxy group, aryl group or carboxyl group. For example, X may be aliphatic group that is unsubstituted or substituted with halogen atom, aliphatic group that comprises oxygen, nitrogen or sulfur atom in the main chain, or arylene group that can be derived from bisphenol A, resorcinol, hydroquinone or diphenylphenol, and can be represented, for example, by the following chemical formulas 2a to 2h.
The subscript "m" independently represents an integer of 0 to 10, preferably an integer of 0 to 4. The subscript "n" independently represents an integer of 2 to 1,000, preferably an integer of 2 to 500, and more preferably an integer of 5 to 100.

In one embodiment of the present invention, the hydroxy-terminated siloxane of the above chemical formula 1 may be a reaction product of a hydroxy-terminated siloxane of the following chemical formula 1a with an acyl compound (i.e., the hydroxy-
terminated siloxane having ester linkage).

The hydroxy-terminated siloxane of the above chemical formula la may be prepared, for example, from a compound of the following chemical formula lb having hydroxy group and a double bond, and a compound of the following chemical formula lc containing silicon in a molar ratio of 2:1 in the presence of a platinum catalyst.

Specifically, examples of the hydroxy-terminated siloxane of the above chemical formula la include, but is not limited to, a siloxane monomer from Dow Corning (regarding the preparation of the...
hydroxy-terminated siloxane of the above chemical formula la, US Patent No. 6,072,011 may be referred to.

[96] The acyl compound used for preparing the hydroxy-terminated siloxane of the above chemical formula 1 may have, for example, an aromatic structure, an aliphatic structure, or a mixed type structure comprising both aromatic and aliphatic forms. When the acyl compound is of an aromatic structure or a mixed type structure, it can have 6 to 30 carbon atoms, and when the acyl compound is of an aliphatic structure, it can have 1 to 20 carbon atoms. The acyl compound may further comprise halogen, oxygen, nitrogen or sulfur atom.

[97] In another embodiment of the present invention, the hydroxy-terminated siloxane of the above chemical formula 1 may be a reaction product of a hydroxy-terminated siloxane of chemical formula 1a as defined above with diisocyanate compound (i.e., the hydroxy-terminated siloxane having urethane linkage).

[98] The diisocyanate compound may be, for example, 1,4-phenylenediisocyanate, 1,3-phenylenediisocyanate, or 4,4'-methylenediphenyl diisocyanate.

[99] A polysiloxane-polycarbonate copolymer contained in the flame-retardant thermoplastic resin composition according to the present invention comprises polycarbonate block of the following chemical formula 3 as a repeating unit other than hydroxy-terminated siloxane of the above chemical formula 1.

[100] [Chemical formula 3]

[102] \[
\begin{array}{c}
\text{O} \\
\text{R}_4 \\
\text{O} \\
\text{C}
\end{array}
\]

[103] in the above chemical formula 3,

[105] \( R_4 \) independently represents aromatic hydrocarbon group having 6 to 30 carbon atoms and being unsubstituted or substituted with alkyl group having 1 to 20 carbon atoms (for example, alkyl group having 1 to 13 carbon atoms), cycloalkyl group (for example, cycloalkyl group having 3 to 6 carbon atoms), alkenyl group (for example, alkenyl group having 2 to 13 carbon atoms), alkoxy group (for example, alkoxy group having 1 to 13 carbon atoms), halogen atom or nitro.

[106] The above aromatic hydrocarbon groups may be derived from a compound of the following chemical formula 3a.

[107] [Chemical formula 3a]

[109]
in the above chemical formula 3a,

X represents alkylene group; linear, branched or cyclic alkylene group having no functional group; or linear, branched or cyclic alkylene group comprising a functional group such as sulfide, ether, sulfoxide, sulfone, ketone, naphthyl, isobutylphenyl, etc. Preferably, X may be linear or branched alkylene group having 1 to 10 carbon atoms, or cyclic alkylene group having 3 to 6 carbon atoms.

Each Rₙ independently represents hydrogen atom, halogen atom or alkyl group—for example, linear or branched alkyl group having 1 to 20 carbon atoms, or cyclic alkyl group having 3 to 20 (preferably, 3 to 6) carbon atoms.

The subscripts "n" and "m" independently represent an integer of 0 to 4.

The compound of the above chemical formula 3a may be, for example, bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)phenylmethane, bis(4-hydroxyphenyl)naphthylmethane, bis(4-hydroxyphenyl)(4-isobutylphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 1-ethyl-1,1-bis(4-hydroxyphenyl)propane, 1-phenyl-1,1-bis(4-hydroxyphenyl)ethane, 1-naphthyl-1,1-bis(4-hydroxyphenyl)ethane, 1,2-bis(4-hydroxyphenyl)ethane, 1,10-bis(4-hydroxyphenyl)decane, 2-methyl-1,1-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(4-hydroxyphenyl)pentane, 2,2-bis(4-hydroxyphenyl)hexane, 2,2-bis(4-hydroxyphenyl)nonane, 2,2-bis(3-methyl-4-hydroxyphenyl)propane, 2,2-bis(3-fluoro-4-hydroxyphenyl)propane, 4-methyl-2,2-bis(4-hydroxyphenyl)pentane, 4,4-bis(4-hydroxyphenyl)heptane, diphenylbis(4-hydroxyphenyl)methane, Resorcinol, Hydroquine, 4,4'-dihydroxyphenyl ether, bis(4-hydroxyphenyl)ether, 4,4'-dihydroxy-2,5-dihydroxydiphenyl ether, 4,4'-dihydroxy-3,3'-dichlorodiphenyl ether, bis(3,5-dimethyl-4-hydroxyphenyl)ether, bis(3,5-dichloro-4-hydroxyphenyl)ether, 1,4-dihydroxy-2,5-dichlorobenzene, 1,4-dihydroxy-3-methylbenzene, 4,4'-dihydroxydiphenol[p,p'-dihydroxyphenyl], 3,3'-dichloro-4,4'-dihydroxyphenyl, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane, 1,1-bis(3,5-dichloro-4-hydroxyphenyl)cyclohexane, 1,1-bis(3,5-dimethyl-4-hydroxyphenyl)cyclododecane, 1,1-bis(4-hydroxyphenyl)cyclododecane, 1,1-bis(4-hydroxyphenyl)butane,
1.1- bis(4-hydroxyphenyl)decane, 1,4-bis(4-hydroxyphenyl)propane,
1,4-bis(4-hydroxyphenyl)butane, 1,4-bis(4-hydroxyphenyl)isobutane,
2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(3-chloro-4-hydroxyphenyl)propane,
bis(3,5-dimethyl-4-hydroxyphenyl)methane,
bis(3,5-dichloro-4-hydroxyphenyl)methane,
2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane,
2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane,
2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane,
2,4-bis(4-hydroxyphenyl)-2-methyl-butane,
4,4’-thiodiphenol[bis(4-hydroxyphenyl)sulfone],
bis(3,5-dimethyl-4-hydroxyphenyl)sulfone, bis(3-chloro-4-hydroxyphenyl)sulfone,
bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfoxide,
bis(3,5-dimethyl-4-hydroxyphenyl)sulfide, bis(3,5-dichloro-4-hydroxyphenyl)sulfide,
2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane,
2,4-bis(4-hydroxyphenyl)-2-methyl-butane,
4,4’-thiodiphenol[bis(4-hydroxyphenyl)sulfone],
bis(3,5-dimethyl-4-hydroxyphenyl)sulfone, bis(3-chloro-4-hydroxyphenyl)sulfone,
bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfoxide,
bis(3,5-dimethyl-4-hydroxyphenyl)sulfide, bis(3,5-dichloro-4-hydroxyphenyl)sulfide,
2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane,
2,4-bis(4-hydroxyphenyl)-2-methyl-butane,
4,4’-thiodiphenol[bis(4-hydroxyphenyl)sulfone],
bis(3,5-dimethyl-4-hydroxyphenyl)sulfone, bis(3-chloro-4-hydroxyphenyl)sulfone,
bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfoxide,
bis(3,5-dimethyl-4-hydroxyphenyl)sulfide, bis(3,5-dichloro-4-hydroxyphenyl)sulfide,
2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane,
2,4-bis(4-hydroxyphenyl)-2-methyl-butane,
4,4’-thiodiphenol[bis(4-hydroxyphenyl)sulfone],
bis(3,5-dimethyl-4-hydroxyphenyl)sulfone, bis(3-chloro-4-hydroxyphenyl)sulfone,
bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfoxide,
bis(3,5-dimethyl-4-hydroxyphenyl)sulfide, bis(3,5-dichloro-4-hydroxyphenyl)sulfide,
2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane,
2,4-bis(4-hydroxyphenyl)-2-methyl-butane,
4,4’-thiodiphenol[bis(4-hydroxyphenyl)sulfone],
bis(3,5-dimethyl-4-hydroxyphenyl)sulfone, bis(3-chloro-4-hydroxyphenyl)sulfone,
bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfoxide,
bis(3,5-dimethyl-4-hydroxyphenyl)sulfide, bis(3,5-dichloro-4-hydroxyphenyl)sulfide,
2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane,
2,4-bis(4-hydroxyphenyl)-2-methyl-butane,
4,4’-thiodiphenol[bis(4-hydroxyphenyl)sulfone],
bis(3,5-dimethyl-4-hydroxyphenyl)sulfone, bis(3-chloro-4-hydroxyphenyl)sulfone,
bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfoxide,
bis(3,5-dimethyl-4-hydroxyphenyl)sulfide, bis(3,5-dichloro-4-hydroxyphenyl)sulfide,
2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane,
2,4-bis(4-hydroxyphenyl)-2-methyl-butane,
4,4’-thiodiphenol[bis(4-hydroxyphenyl)sulfone],
bis(3,5-dimethyl-4-hydroxyphenyl)sulfone, bis(3-chloro-4-hydroxyphenyl)sulfone,
bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfoxide,
bis(3,5-dimethyl-4-hydroxyphenyl)sulfide, bis(3,5-dichloro-4-hydroxyphenyl)sulfide,
2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane,
2,4-bis(4-hydroxyphenyl)-2-methyl-butane,
4,4’-thiodiphenol[bis(4-hydroxyphenyl)sulfone],
bis(3,5-dimethyl-4-hydroxyphenyl)sulfone, bis(3-chloro-4-hydroxyphenyl)sulfone,
bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfoxide,
bis(3,5-dimethyl-4-hydroxyphenyl)sulfide, bis(3,5-dichloro-4-hydroxyphenyl)sulfide,
preferred amount of the siloxane in the polysiloxane-polycarbonate copolymer is 0.5 to 20% by weight, more preferably 0.5 to 10% by weight. If the amount of the siloxane is less than 0.5% by weight based on total weight of the copolymer, the flame retardancy and low-temperature impact strength may be lowered. If the amount of the siloxane is greater than 20% by weight, physical properties such as optical transparency, flowability, heat resistance, room-temperature impact strength, etc. may be lowered and manufacturing costs may be increased due to a relative decrease in the amount of polycarbonate in the copolymer.

Preferably, the polysiloxane-polycarbonate copolymer has a viscosity average molecular weight (Mₐ) of from 15,000 to 200,000, more preferably from 15,000 to 70,000. If the viscosity average molecular weight of the copolymer is less than 15,000, the mechanical properties may be lowered remarkably. If the viscosity average molecular weight is greater than 200,000, there may be a problem in the processing of resin due to the increase of melt viscosity.

The preferred amount of the above polysiloxane-polycarbonate copolymer is 10 to 95% by weight, more preferably 30 to 90% by weight, based on total weight of the flame-retardant thermoplastic resin composition. If the amount of the copolymer is less than 10% by weight based on total weight of the composition, the flame retardancy may not be sufficient and low-temperature impact strength may be lowered. If the amount of the copolymer is greater than 95% by weight, physical properties such as optical transparency, flowability, heat resistance, room-temperature impact strength, etc. may be lowered, due to a relative decrease in the amount of aromatic poly-carbonate resin.

The composition according to the present invention may further include a conventional flame retardant (or an auxiliary flame retardant) known in the art other than the above polysiloxane-polycarbonate copolymer to improve its flame retardancy. Examples of the flame retardant that can be used may include, but are not limited to, one or more selected from the group consisting of organic phosphate ester compound, phosphazene compound, metal salt compound and halogen-containing compound.

The metal salt compounds are generally known and may be used in polycarbonate-containing compounds in a large amount. Any metal salt compound suitable for use in polycarbonate-containing resin composition may be used in the composition according to the present invention. Examples of the metal salt compounds include, but are not necessarily limited to, organic and inorganic sulfonate (for example, sodium trichlorobenzene sulfonate), salt of sulfone sulfonate (for example, potassium salt of diphenylsulfone sulfonate), salt of perfluoroalkane sulfonic acid and sodium aluminum hexafluoride.

Examples of halogen-containing compounds include, but are not necessarily limited
to, decabromodiphenyl ether, octabromodiphenyl ether and other oligomeric or polymeric bromine compounds derived from tetrabromobisphenol A or polyphenylene ether whose scaffold is brominated.

When a separate flame retardant is contained in the composition of the present invention, its preferred amount may be 0.001 to 10 parts by weight, more preferably 0.1 to 7 parts by weight, based on 100 parts by weight of the total amount of the aromatic polycarbonate resin and the polysiloxane-polycarbonate copolymer. If the amount of flame retardant used is less than 0.001 part by weight based on 100 parts by weight of the total amount of the aromatic polycarbonate resin and the polysiloxane-polycarbonate copolymer, the synergistic effects in flame retardancy may be small. If the amount of flame-retardant used is greater than 10 parts by weight, physical properties such as mechanical strength, heat resistance, etc. may be lowered due to the relative decrease in the amount of other components.

The composition according to the present invention may further include metal compounds (for example, antimony oxide) acting as a synergist. Such synergists are commonly used in combination with halogen-containing compounds. In addition, the composition according to the present invention may include inorganic fillers such as silica, silicate, alumina, glass fiber, glass bead, glass flake, clay, talc, mica, calcium carbonate, etc. in order to increase hardness, heat resistance and dimensional stability, which may be included in an amount of 0.1 to 50% by weight based on the total weight of the composition. The composition according to the present invention may also include organic fillers such as carbon fiber, carbon black, etc. in order to realize black coloration and increase conductivity, which may be included in an amount of 0.1 to 30% by weight based on the total weight of the composition. In addition, the composition according to the present invention may further include antioxidant, heat stabilizer, releasing agent, lubricant, ultraviolet light stabilizer, etc. as processing aids, which may be included in an amount of 0.01 to 0.5% by weight based on the total weight of the composition.

Method for preparation of flame-retardant thermoplastic resin composition

The flame-retardant thermoplastic resin composition of the present invention may be prepared through a step of reacting a hydroxy-terminated siloxane and an oligomeric polycarbonate under interfacial reaction conditions, composed of aqueous alkaline solution and an organic phase to form a polysiloxane-polycarbonate intermediate; a step of polymerizing said intermediate by using a first polymerization catalyst to prepare a polysiloxane-polycarbonate copolymer; and a step of mixing the prepared polysiloxane-polycarbonate copolymer and an aromatic polycarbonate resin.

In a preferred embodiment, the step to form said intermediate may comprise a step of
mixing the hydroxy-terminated siloxane and the oligomeric polycarbonate in a weight ratio of 0.5:99.5 to 20:80 (more preferably, 0.5:99.5 to 10:90).

The polycarbonate used in the preparation of the polysiloxane-polycarbonate copolymer may be an oligomeric polycarbonate having a viscosity average molecular weight of from 800 to 20,000 (more preferably, from 1,000 to 15,000). If the viscosity average molecular weight of the oligomeric polycarbonate is less than 800, molecular weight distribution may be broad and physical properties may be lowered. If the viscosity average molecular weight of the oligomeric polycarbonate is greater than 20,000, reactivity may be lowered.

In one embodiment, the oligomeric polycarbonate may be prepared by adding the above dihydric phenol compound to an aqueous alkali solution to make a phenol salt state, and then adding the phenol compound of the phenol salt state to dichloromethane in which phosgene gas is injected. To prepare the oligomer, it is preferable to maintain the molar ratio of phosgene to bisphenol within a range of about 1:1 to 1.5:1, more preferably about 1:1 to 1.2:1. If the molar ratio of phosgene to bisphenol is less than 1, reactivity may be lowered. If the molar ratio of phosgene to bisphenol is greater than 1.5, processability may be lowered due to excessive increase in molecular weight.

The above oligomer-forming reaction may generally be conducted at a temperature range of about 15 to 60°C. In order to adjust the pH of the reaction mixture, alkali metal hydroxide may be utilized. The alkali metal hydroxide may be, for example, sodium hydroxide.

In an embodiment, the step to form said intermediate comprises a step of forming a mixture comprising said hydroxy-terminated siloxane and said oligomeric polycarbonate, and the mixture may further comprise a phase transfer catalyst, a molecular weight regulator and a second polymerization catalyst. In addition, the step to form said intermediate comprises a step of forming a mixture comprising said hydroxy-terminated siloxane and said oligomeric polycarbonate; and a step of extracting an organic phase from the mixture which is obtained from the reaction of said hydroxy-terminated siloxane and said oligomeric polycarbonate. Here, the step of polymerizing said intermediate may comprise a step of providing said first polymerization catalyst to the extracted organic phase.

Concretely, the polysiloxane-polycarbonate copolymer according to the present invention may be prepared by adding the hydroxy-terminated siloxane of the above chemical formula 1 to an organic phase-aqueous phase mixture containing the polycarbonate, and subsequently feeding a molecular weight regulator and a catalyst step by step.

As for the molecular weight regulator, a monofunctional compound which is similar to a monomer used in preparation of polycarbonate may be used as described earlier.
Preferably, para-ieri-butylphenol (PTBP) is used.

As for the catalyst, a polymerization catalyst and/or a phase transfer catalyst may be used. The polymerization catalyst be, for example, triethylamine (TEA), and the phase transfer catalyst may be a compound having the following chemical formula 6.

In the above chemical formula 6, $R_7$ represents alkyl group having 1 to 10 carbon atoms, $Q$ represents nitrogen or phosphorus, and $X$ represents halogen atom or $-OR_8$ wherein $R_8$ represents hydrogen atom, alkyl group having 1 to 18 carbon atoms or aryl group having 6 to 18 carbon atoms.

The amount of the phase transfer catalyst is preferably about 0.01 to 10% by weight, more preferably 0.1 to 10% by weight based on total weight of the mixture consisting of hydroxy-terminated siloxane and oligomeric polycarbonate. If the amount of the phase transfer catalyst is less than 0.01% by weight, the reactivity may be lowered. If the amount of the phase transfer catalyst is greater than 10% by weight, precipitate may be generated or optical transparency may be lowered.

In one embodiment, after the polysiloxane-polycarbonate copolymer is prepared, the organic phase dispersed in methylene chloride is washed with alkali and then separated. Subsequently, the organic phase is washed with 0.1 N solution of hydrochloric acid and then rinsed with distilled water 2 or 3 times. After rinsing is completed, the concentration of the organic phase dispersed in methylene chloride is adjusted constantly and then granulated by using a certain amount of demineralized water in a range of 30 to 100°C, preferably 60 to 80°C. If the temperature of the demineralized water is lower than 30°C, the granulation rate is slow and thus the granulation time may be too long. If the temperature of the demineralized water is higher than 100°C, it may be difficult to obtain uniformly sized polycarbonate morphology. After the granulation is completed, it is preferable to dry the product at 100 to 120°C for 5 to 10 hours, more preferably at 100 to 110°C for 5 to 10 hours at first, and then at 110 to 120°C for 5 to 10 hours.

The method of mixing the prepared polysiloxane-polycarbonate copolymer and aromatic polycarbonate resin has no particular limit. Preferably, the flame-retardant thermoplastic resin composition of the present invention may finally be prepared by kneading the polysiloxane-polycarbonate copolymer and the aromatic polycarbonate
resin in a weight ratio of 10:90 to 95:5.

[152] [Molded article of the flame-retardant thermoplastic resin composition]
[153] In another aspect of the present invention, a molded article of the flame-retardant thermoplastic resin composition according to the present invention is provided. The method for molding the composition of the present invention has no particular limit, and it can be any conventional method used in the art of plastic molding.

[155] The molded article manufactured from the flame-retardant thermoplastic resin composition of the present invention can be usefully applied to interior and exterior materials requiring flame retardancy and optical transparency — for example, computer terminal, office machinery, electrical and electronic product housing, etc.

[156] The following examples and comparative examples are meant to illustrate the invention, but they do not limit its scope.

[157] Examples and Comparative Examples

[159] Raw materials compounded according to the formulation shown in Table 1 were uniformly dispersed by using a Henschel mixer. A pellet-type of product was formed by extrusion using a biaxial melt-kneading extruder with L/D=40 and Φ=25mm at a temperature of 240 to 270°C. The product was dried in a hot air dryer of 80 to 120°C for 4 hours or more followed by injection molding at 260 to 280°C to form a specimen.

[160] The raw materials used were as follows.

[162] (A) Aromatic polycarbonate resin

[164] Linear polycarbonate derived from bisphenol A: TRIREX 3022IR, an intrinsic viscosity (as measured in methylene chloride, 25°C) of 0.50 dl/g, a viscosity average molecular weight (Mv) of 21,200.

[165] (B) Polysiloxane-polycarbonate copolymer

[166] <Preparation of hydroxy-terminated siloxane>

[169] In a 500mL three-necked flask equipped with a condenser, under nitrogen atmosphere, 0.4 mol of monomer (BY 16-799, Dow Corning) was dissolved in 300mL of chloroform, and then 67mL of triethylamine (TEA) catalyst was added thereeto. With refluxing the resulting solution, 0.2 mol of terephthaloylchloride (TCL) dissolved in 1,000mL of chloroform was slowly added thereto for 1 hour, and the resulting solution was refluxed for 12 hours. After the reaction was completed, the solvent was removed from the solution, and the product was dissolved in acetone and washed with hot
distilled water. By drying for 24 hours in a vacuum oven, the hydroxy-terminated siloxane having ester linkage of the following chemical formula 7 was prepared. The synthesis was confirmed by H-NMR analysis wherein the peak of methylene group of the polysiloxane was observed at 2.6ppm, the peak of hydrogen of benzene ring of TCL was observed at 8.35ppm, and the peak of hydrogen of benzene ring of the polysiloxane was observed at 6.75-7.35ppm.

[170] [Chemical formula 7]

[172] <Preparation of polysiloxane-polycarbonate copolymer>

Interfacial reaction of bisphenol A in an aqueous solution and phosgene gas was conducted in the presence of methylene chloride to prepare 400mL of an oligomeric polycarbonate mixture having a viscosity average molecular weight of about 1,000. To the obtained oligomeric polycarbonate mixture, 4.5% by weight of the hydroxy-terminated siloxane having ester linkage of chemical formula 7 which was dissolved in methylene chloride, 1.8mL of tetrabutylammonium chloride (TBAC1), 1.5g of p-tert-butylphenol (PTBP) and 275µl of triethylamine (TEA, 15 wt% aqueous solution) were admixed and reacted for 30 minutes. The reacted oligomeric polycarbonate mixture was kept for phase separation. After the phases were separated, only the organic phase was collected and thereto 170g of an aqueous solution of sodium hydroxide, 360g of methylene chloride and 300µl of triethylamine (15 wt% aqueous solution) were admixed and reacted for 2 hours. After phase separation, the viscosity-increased organic phase was washed with alkali and separated. Next, the resulting organic phase was washed with 0.1N hydrochloric acid solution and then rinsed with distilled water 2 to 3 times repeatedly. After the rinse was completed, the concentration of the organic phase was adjusted constantly and then granulated by using a certain amount of demineralized water at 76°C. After the granulation was completed, the product was dried first at 110°C for 8 hours and then at 120°C for 10 hours. The synthesis of the copolymer (Mr:2,000) was confirmed by H-NMR analysis wherein the peaks of methylene group of the polysiloxane were observed at 2.6ppm and 2.65ppm, the peak of hydrogen of benzene ring of TCL was observed at 8.35ppm, and the peak of hydrogen of benzene ring of the polysiloxane was observed at 6.95-7.5ppm.

[176] H-NMR data and viscosity average molecular weight (Mr) were measured as follows.

[177] (a) H-NMR (nuclear magnetic resonance spectroscopy): This analysis was conducted
by using Avance DRX 300 (Bruker).

(b) Viscosity average molecular weight \( (\text{M}_{\text{v}}) \): The viscosity of methylene chloride solution was measured by using an Ubbelohde Viscometer at 20°C, and the limiting viscosity \([\eta]\) therefrom was calculated according to the following equation.

\[
[\eta] = 1.23 \times 10^{-5} \text{M}^{0.85}
\]

(c) Flame-retardant compounds

(C.1) Aromatic sulfonic acid flame retardant

[Chemical formula 8]

\[
(SO_3M)_x - R_1 - S - R_2 - (SO_3M)_y
\]

in the chemical formula 8.

R₁ and R₂ are independently selected from the group consisting of aliphatic group having 1 to 6 carbon atoms, phenyl group, biphenyl group, alkyl-substituted phenyl group and combinations thereof,

M represents a metal cation group,

x represents an integer of 0 to 6, and

y represents an integer of 1 to 6.

(C.2) Metal salt of perfluoroalkanesulfonic acid

[Chemical formula 9]

\[
\begin{array}{c}
\text{F} \\
\cdot \\
\text{C} \\
\text{S} \\
\text{O} - \text{M}^+ \\
\text{F} \\
\cdot \\
\text{F}
\end{array}
\]

in the chemical formula 9.

M represents a metal cation group, and j represents an integer of 1 to 8.

Table 1
Measurement of physical properties

The physical properties of the injection-molded specimens according to Examples 1 to 7 and Comparative Example 1 to 5 were measured by the following methods, and the results are shown in the following Table 3.

(1) Flowability: The flowability was measured at 300°C under a load of 1.2 kgf in accordance with ASTM D1238.

(2) Impact strength: The impact strength was measured in accordance with ASTM D256 using a notched test specimen. The final test results were presented as an average value of test results on ten different specimens.

(3) Low-temperature impact strength: The low-temperature impact strength was measured in accordance with ASTM D256 using a notched test specimen after keeping the same at -50°C for 30 minutes. The final test results were presented as an average value of test results on ten different specimens.

(4) Total transmittance: The total transmittance was measured in accordance with ASTM D1003 using a 3mm-thick test specimen.

(5) Color stability: yellowness index (YI) values were measured according to ASTM D1925 using a transmission method. In order to determine base color and color stability under high-temperature processing condition, injection molding was conducted at 270°C and 300°C, respectively. Base color was determined from the yellowness index of test specimen molded at 270°C and color stability was determined from the difference between the yellowness indexes of test specimens molded at 270°C and 300°C (ΔYI_{270°C-300°C}).

(6) Flame retardancy: Flame retardancy was measured according to UL-94 flammability test method defined by Underwriters Laboratories Inc. in the USA. This method was to evaluate the flame retardancy from burning time and drip property after a vertically fixed specimen having a certain size is contacted with flame of burner for
10 seconds. Burning time was the time length that test specimen continued to naked ignition after removal from the flame far away. Ignition of the cotton layer placed about 300 mm below the specimen by any drips of flaming particles from the specimen was also observed. Flame-retardancy ratings are shown in Table 2.

[Table 2]

<table>
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<tr>
<th>1/2^nd burning time of each specimen</th>
<th>V-2</th>
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<tr>
<td>30s or less</td>
<td>30s or less</td>
<td>10s or less</td>
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<tr>
<td>Total burning time of 5 specimens</td>
<td>250s or less</td>
<td>250s or less</td>
<td>50s or less</td>
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<tr>
<td>Ignition of cotton layer by drips</td>
<td>Yes</td>
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[Table 3]

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<tr>
<td>1</td>
<td>2</td>
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<tr>
<td>Flowability (g/10min)</td>
<td>12</td>
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<td>Impact strength (1/8&quot;, kg/cm/cm)</td>
<td>82</td>
<td>81</td>
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<tr>
<td>Low temp. impact strength (&lt;50°C, 1/8&quot;, kg/cm/cm)</td>
<td>65</td>
<td>62</td>
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<tr>
<td>Total transmittance (%)</td>
<td>89</td>
<td>88</td>
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<tr>
<td>Yellowness index (Y15°C)</td>
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<td>1.25</td>
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<tr>
<td>Yellowness index (Y300°C)</td>
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<td>1.35</td>
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<tr>
<td>UL 94 flame retardancy (2.0 mm)</td>
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<td>V-0</td>
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<tr>
<td>Total burning time (sec)</td>
<td>15</td>
<td>12</td>
</tr>
</tbody>
</table>

As shown in Table 3, the Examples were superior to the Comparative examples in flame-retardancy, low-temperature impact strength and various physical properties such as optical transparency, flowability, base color, color stability, etc.
Claims

[Claim 1] A flame-retardant thermoplastic resin composition comprising an aromatic polycarbonate resin; and a polysiloxane-polycarbonate copolymer comprising, as repeating units, a hydroxy-terminated siloxane of the following chemical formula 1 and a polycarbonate block of the following chemical formula 3:

[Chemical formula 1]

in the chemical formula 1,

- $R_i$ independently represents hydrogen atom, halogen atom, hydroxy group, or alkyl group, alkoxy group or aryl group having 1 to 20 carbon atoms;
- $R_2$ independently represents hydrocarbon group having 1 to 13 carbon atoms or hydroxy group;
- $R_3$ independently represents alkyne group having 2 to 8 carbon atoms;
- $A$ is $X$ or $\text{NH-X-NH}$, wherein $X$ represents linear or branched aliphatic group having 1 to 20 carbon atoms, cycloalkylene group, or mono- or polycyclic arylene group having 6 to 30 carbon atoms and being unsubstituted or substituted with halogen atom, alkyl group, alkoxy group, aryl group or carboxyl group;
- $m$ independently represents an integer of 0 to 10; and
- $n$ independently represents an integer of 2 to 1,000;

[Chemical formula 3]

in the chemical formula 3,

- $R_4$ represents aromatic hydrocarbon group having 6 to 30 carbon atoms and being unsubstituted or substituted with alkyl group, cycloalkyl group, alkenyl group, alkoxy group, halogen atom, or nitro.

[Claim 2] The flame-retardant thermoplastic resin composition according to claim 1, wherein the aromatic polycarbonate resin has a viscosity average molecular weight of 15,000 to 40,000.

[Claim 3] The flame-retardant thermoplastic resin composition according to claim 1, wherein the polysiloxane-polycarbonate copolymer has the following
chemical formula 4a or 4b:

[Chemical formula 4a]

[Chemical formula 4b]

in the chemical formulas 4a and 4b,

Rᵢ independently represents hydrogen atom, halogen atom, hydroxy group, or alkyl group, alkoxy group or aryl group having 1 to 20 carbon atoms;

R₂ independently represents hydrocarbon group having 1 to 13 carbon atoms or hydroxy group;

R₃ independently represents alkylene group having 2 to 8 carbon atoms;

R₄ represents aromatic hydrocarbon group having 6 to 30 carbon atoms and being unsubstituted or substituted with alkyl group, cycloalkyl group, alkenyl group, alkoxy group, halogen atom or nitro;

m independently represents an integer of 0 to 10;

n independently represents an integer of 2 to 1,000; and

₁ represents an integer of 1 to 20.

[Claim 4] The flame-retardant thermoplastic resin composition according to claim 1, wherein the polysiloxane-polycarbonate copolymer has a viscosity average molecular weight of 15,000 to 200,000.

[Claim 5] The flame-retardant thermoplastic resin composition according to claim 1, wherein the amount of siloxane in the polysiloxane-polycarbonate copolymer is from 0.5 to 20% by weight.

[Claim 6] The flame-retardant thermoplastic resin composition according to claim 1, wherein the composition comprises from 5 to 90% by weight of the aromatic polycarbonate resin; and from 10 to 95% by weight of the polysiloxane-polycarbonate copolymer.

[Claim 7] The flame-retardant thermoplastic resin composition according to claim 1, wherein the composition further comprises a flame retardant selected from the group consisting of organic phosphate ester compound, phosphazene compound, metal salt compound and halogen-containing compound, in an amount of from 0.001 to 10 parts by weight based on 100 parts by weight of the total of the aromatic polycarbonate resin and the polysiloxane-polycarbonate copolymer.
[Claim 8] A molded article of the flame-retardant thermoplastic resin composition according to any of claims 1 to 7.
INTERNATIONAL SEARCH REPORT

International application No. PCT/KR2012/0011527

A. CLASSIFICATION OF SUBJECT MATTER

C08L 69/00(2006.01)i, C08L 83/10(2006.01)i, C08G 77/448(2006.01)i, C08J 5/00(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)
C08L 69/00; C08G 77/448; C08G 77/42; C07F 7/08; C08G 63/64; C08K 5/42; C08G 77/445; C08G 18/42; C08G 64/08; C08G 64/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: flame retardant, aromatic polycarbonate resin, polysiloxane-polycarbonate copolymer, optical transparency

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US 2007-0299174 (CHEN, J. et al.) 27 December 2007 See abstract; claims 1, 15, 16, 26, 27; paragraphs [0015], [0057]-[0071], [0077], [0088].</td>
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<td>KR 10-2011-0108610 (SAMYANG CORP.) 06 October 2011 See abstract; claims 1, 3, 4, 5; paragraphs [0026], [0027], [0111]-[0119].</td>
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<td>JP 05-222173 (GENERAL ELECTRIC COMPANY) 31 August 1993 See abstract; claims 1-7.</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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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 22 April 2013 (22.04.2013)

Date of mailing of the international search report 23 April 2013 (23.04.2013)

Name and mailing address of the ISA/KR
Korean Intellectual Property Office 189 Cheongna-ro, Seo-gu, Daejeon Metropolitan City 302-70; 1 Republic of Korea
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Authorized officer
KIM, Seung Beom
Telephone No. 82-42-481-3371

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