(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
4 July 2002 (04.07.2002)

PCT

(10) **International Publication Number**
WO 02/052059 A1

(51) **International Patent Classification**^{7}: **C23C 14/20**

(21) **International Application Number:** PCT/KR00/01523

(22) **International Filing Date:**
22 December 2000 (22.12.2000)

(25) **Filing Language:** Korean

(26) **Publication Language:** English

(71) **Applicant** *(for all designated States except US)*: **SAMSUNG GENERAL CHEMICALS CO., LTD.** [KR/KR]; #San 222-2, Dokgod-ri, Daesan-up, Seosan-shi, Chungcheongnam 356-870 (KR).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **JUNG, In-Sik** [KR/KR]; 107-1001 Sejong apt., Jeonmin-dong, Yuseong-ku, Taejon 305-728 (KR). **HONG, Jong-Soo** [KR/KR]; 108-902 Sejong apt., Jeonmin-dong, Yuseong-ku, Taejon 305-728 (KR). **LEE, Sung-Man** [KR/KR]; 101-802 Hanmaeul apt., Songkang-dong, Yuseong-ku, Taejon 305-503 (KR). **HER, Man-Seang** [KR/KR]; 623-1, Kuam-dong, Yuseong-ku, Taejon 305-801 (KR).

(74) **Agents: YIM, Suk-Jae** et al.; 8th Floor, poonglim Bldg., 823-1 Yeoksam-dong, Kangnam-ku, Seoul 135-784 (KR).

(81) **Designated States** *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) **Designated States** *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/052059 A1

(54) Title: FLAME RETARDANT POLYPROPYLENE RESIN COMPOSITION

(57) **Abstract:** The present invention provides a polypropylene resin composition comprising a polypropylene resin having 4 ~ 18g/min of melt flow rate (MFR), flame retardant additive having low melting point, antimony oxide, UV stabilizer, coupling agent of silanes and titanium dioxide as light blocking agent. The resin composition of this invention provides secondarily processed products which have excellent flame retarding properties, even with its thin thickness and stability against the weather and maintainability of mechanical materials properties by maintaining its excellent original flame retarding properties after the long period of outdoor exposures and hydrothermal dipping treatment.

FLAME RETARDANT POLYPROPYLENE RESIN COMPOSITION

TECHNICAL FIELD

The present invention relates to a flame retardant polypropylene resin composition having polypropylene resin as a main component, and more particularly, to a polypropylene resin composition which comprises a polypropylene resin with melt flow rate of 4~18g/10minutes, a flame retardant additive of halogen with low melting point, an antimony oxide, an ultraviolet stabilizer, a coupling agent of silane, and a titanium dioxide as a light blocking agent, and has good weather proof, maintains the same level of flame retardant property and physical properties after hydrothermal dipping treatment.

BACKGROUND ART

Polypropylene resins are widely used in home electronic appliances, building members, interior decorating materials and automobile parts due to their excellent processing characteristics, chemical resistance and mechanical strength. These resins, however, lack flame retardant property and are difficult to use in automobile parts or electronic components which requires flame retardant property to prepare against the danger of fire. Therefore, much study has been made to impart flame retardant property to polyolefin resin by adding various organic, inorganic or phosphorus flame retardant additives.

Japanese laid open Patent Publication No. 53-92855, 54-29350, 54-77658, 56-26954, 57-87462 and 60-110738 disclose preparation method of flame retardation polypropylene resin composition by adding inorganic flame retardant additives such as magnesium hydroxide, aluminum hydroxide or hydrotalcite to impart the resin flame retardant property. But, in order to obtain flame retardant grade V-0, more than 50% of inorganic filler is needed, resulting in deterioration of processability, generation of gas and decrease in impact strength.

Japanese Patent Publication No. 53-30739 discloses flame retardant polypropylene resin composition produced by adding organic flame retardant additive of halogen compound such as decabromodiphenylether and dodecachloro-dodecahydromethanodibenzocyclooctane. In addition, fpreparation method of flame retardant polypropylene resin composition by adding tetrabromobisphenol A bis-(dibromoprophylether), bis-(tribromophenoxyethyl)tetrabromobisphenol A ether, hexabromo cyclododecan and tetrabomobisphenol A. Though these resin compositions are excellent in flame retardant property and processability, resistance to weather and hot water is inferior and it is difficult to maintain physical properties and initial flame retardant property making it difficult to use the resin in products which are exposed outdoor such as light bulb socket of Christmas tree.

DISCLOSURE OF INVENTION

The object of the invention is to solve the problems mentioned above and to provide a flame retardant polypropylene resin composition which has good flame retardant property at thin width and can produce secondary products which is able to maintain initial good flame retardant property at long outdoor exposure and hydrothermal dipping treatment, as well as maintain good weather proof and physical property.

The flame retardant polypropylene resin composition of the present invention comprises 40~90% by weight of polypropylene resins with melt flow rate 4~18g/10minutes, 9~16% by weight of flame retardant additives of halogen with low melt point, 4~15% by weight of antimony oxides in white granules, 0.2~3.0% by weight of ultraviolet stabilizers, 0.1~5% by weight of coupling agents of silane, and 0.2~5% by weight of titanium dioxide.

In the flame retardant polypropylene resin composition of the present invention, the polypropylene resin used is a crystalline polypropylene homopolymer, or a copolymer of a polypropylene which is the main component, and one or more compounds or a mixture of two or more of compounds, the compounds being selected from the group consisting of ethylene, 1-butene, 1-pentene, 1-hexene, 4-methylpentene, 1-heptene, 1-octene, and 1-decene. The preferable polypropylene resin is a crystalline polypropylene homopolymer. The melt flow rate of the polypropylene resin is 4~18g/10minutes, or more preferably 5~15g/10minutes. The content of polypropylene resin is 40~90% by weight, or more preferably 50~87% by weight in the entire resin composition.

In the flame retardant polypropylene resin composition of the present invention, the flame retardant additive of halogen with low melt point may be tetrabromobisphenol A bis-(dibromopropylether) or tetrabromo dimethysulfone dipropylether, or mixture thereof. Examples of commercially available products are PE-68(manufactured by Great Lake Corporation) or P680G(manufactured by Suzuhiro Chemicals, Co.). Preferable content of tetrabromobisphenol A bis-(dibromoprophylether) or tetrabromodimethylsulfone dipropylether is 9~16% by weight per 100% by weight of composition. When the content of flame retardant additive is below 9 % by weight, flame retardation grade of V-0 cannot be obtained with thickness of 1/32 inch, and when the content of flame retardant additive is above 16% by weight, weather proof is reduced resulting in the undesirable effect of making it difficult to maintain physical properties.

The coupling agent of silane in the flame retardant polypropylene resin composition of the present invention is expressed by the following general formula:

$$RR' SiX_2$$

where R is a hydrocarbon including vinyl, chloro, amino and mercapto, X an organic group that can be hydrolyzed, and R′ may be R or X. When R′ is R, the material of R and R′ can be different, and the materials of X can be different from each other, and the examples are vinyl trimethoxy silane, vinyl triethoxy silane, 3-aminopropyl triethoxy silane, N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, 3-glycydoxypropyl trimethoxy silane, 3-chloropropyl trimethoxy silane, 3-metacryloxypropyl trimethoxy silane and 3-mercaptopropyltrimethoxy silane. In order to improve the dispersive strength and adhesive strength with antimony trioxide and flame retardant additives of halogen, it is preferable to use vinyl trimethoxy silane, vinyl triethoxy silane or 3-mercaptopropyltrimethoxy silane.

The content of coupling agents of silane per 100% by weight of composition is 0.1~5% by weight, preferably 0.15~3% by weight, and more preferably 0.3~1% by weight. When the content is below 0.1% by weight, the dispersive strength and adhesive strength with the antimony trioxide or flame retardant additives of halogen is not improved and cannot prevent blooming of flame retardant additive during dipping in hydrothermal test, making it difficult to maintain V-0 grade of flame retardant property at the width of 1/32inch. When the content is above 5% by weight, the blooming of flame retardant additive is no more improved.

In the flame retardant polypropylene resin composition of the present invention, it is preferable to use UV absorbent and HALS stabilizer simultaneously as ultraviolet stabilizers, and preferable HALS stabilizer has molecular weight of more than 2,000. When molecular weight is below 2, 000, ultraviolet stabilizers easily bloom out of the secondary product, making it difficult to maintain long term ultraviolet stability. The content of each UV absorbent and HALS ultraviolet stabilizer are preferably 0.1~1.5% by weight respectively. When only one of UV absorbent or HALS ultraviolet stabilizer is added, V-0 grade of flame retardant property may be obtained but it is difficult to obtain a environment resistant resin composition which meets F1 standard of for low rate of maintaining tensile impact strength after UV exposure treatment.

In the flame retardant polypropylene resin composition of the present invention, titanium dioxide is used as a light blocking agent to obtain F1 grade of environment resistance, and the preferable content is 0.2~5% by weight. When the content of titanium dioxide used is below 0.2% by weight, there is no synergistic effect with ultraviolet stabilizer, and when the content is above 5% by weight, there is no further effect of blocking the light.

In the flame retardant polypropylene resin composition of the present invention, the antimony oxide used is antimony trioxide or antimony pentaoxide, or mixture thereof, and the content is 4~15% by weight and preferably 5~12% by weight in the entire resin composition.

The flame retardant polypropylene resin composition of the present invention exhibits excellent flame retardancy of V-0 grade at the width of 1/32 inch in the vertical burning test (hereinafter referred to as UL94 vertical burning test) carried out according to the "Flammability Test of Plastic Materials for Parts of Mechanical device" of UL Subject 94. Further, in the test of weather proof and water proof (hereinafter referred to as UL746C weather proof test) carried out according to the "Test for Flammability of Plastic Materials for Parts in Electric Device" of UL subject 746C, the resin composition maintains the same grade of flame retardancy after long times of outdoor exposure and hydrothermal dipping treatment, and exhibits ability of maintaining physical properties. Therefore, the resin composition of the present invention can advantageously used in the production of electric appliances, building members, interior or exterior decorating materials, and automotive parts.

The present invention will be further described in detail with reference to the examples and comparative examples as below. The examples, however, are for the purpose of illustration and are not intended to limit the scope of the invention.

BEST MODE FOR CARRYING OUT THE INVENTION

Example 1

Following components are introduced into the Hensel mixer and mixed by stirring for 3 minutes: 7.9kg of crystalline polypropylene homopolymer with 8g/10minutes of melt flow rate (the melt flow amount of molten resin for 10 minutes at 230°C with 2.16kg of load) as a polypropylene resin, 1.4kg of PE-68(produced by Great Lakes Corporation) as a tetrabromobisphenol A bis-(dibromopropylether), 700g of antimony trioxide (Sb203 produced by Cheil Flame Retardant, Ltd., 1.2μm), and as additives, 10g of calcium stearate, 10g of antioxidant (1010 Produced by CIBA GEIGY), 20g of IRGAFOS 168(produced by CIBA GEIGY), 30g of UV absorbent (Tinuvin 326 produced by CIBA GEIGY), 30g of HALS ultraviolet stabilizer (Chimabsorber 944FD produced by CIBA GEIGY), 200g of light blocking agent TiO_2(R-103 produced by Dupont, Inc.), and 70g of silane coupling agent (A-174 produced by Union carbide). By using a two-axis stirring extruder with diameter of 30mm, the mixture produced is molten and extruded at 190 ° C in the form of pellets. The yielded pellets are dried for three hours at 100 ° C and molded by using an injection-molding machine with maximum temperature of a cylinder fixed at 200 ° C to provide test pieces for test flame retardancy. Then, the flame retardancy and physical properties of the test pieces are tested and the results are shown in Table 1.

Method of treatment

The test pieces are UV exposure treated by the method of ASTM 2565 Type A under the condition of weather proof according to “Tests for Flammability of Plastic Materials for Parts in Electrical device” of UL subject 746C(Underwrites Laboratories Incorporation) (UV irradiation quantity: $0.35W/m^2$(340nm), black board temperature: 63℃, Water spray method). The test pieces are dipped in hydrothermal tank of 70℃ and maintained for 7 days, and then the flame retardancy and physical properties of the test pieces are tested.

Method of evaluation

The evaluation of flame retardancy is carried out based on the vertical (V0) burning tests according to the “Tests for Flammability of Plastic Materials for Parts in Mechanical device” of UL Subject 94(Underwriters Laboratories, Inc.). The thickness of used test piece is 1/32 inch. The tensile impact strength and maintenance rate are evaluated under the impact strength test standard ASTM D-1822, and the measuring instrument is product from TOYOSEIKI with sample of S-type and thickness 1/8 inch.

Examples 2~3 and comparative examples 1~3

The pellets are prepared in the same way as in example 1 except that the amount of R-103 as a light blocking agent in the composition is modified as shown in Table 1. Then, the yielded pellets are molded by using an injection-molding machine to provide test pieces for testing flame retardancy and tensile impact strength. The flame retardancy and physical properties are measured and the results are shown in Table 1.

Comparing the results of examples 1~3 and the results of comparative examples 1~3 as shown in Table 1, it can be shown that when appropriate amounts of TiO_2 are added as a light blocking agent, synergistic effect with UV absorbent and HALS ultraviolet stabilizer arises, making it possible to maintain high tensile impact strength as well as flame retardancy of V-0 grade at UV exposure test. In addition, after hydrothermal dipping treatment, flame retardancy and tensile impact strength are maintained excellently and exhibits high weather proof so that F1 grade of the 764C on outdoor and indoor electrical device.

Example 4

Following components are introduced into the Hensel mixer and mixed by stirring for 3 minutes: 8.2kg of crystalline polypropylene homopolymer with 8g/10minutes of melt flow rate (the melt flow amount of molten resin for 10 minutes at 230°C with 2.16kg of load) as a polypropylene resin, 1.4kg of PE-68(produced by Great Lakes Corporation) as a tetrabromobisphenol A bis-(dibromopropylether), 400g of antimony trioxide (Sb203 produced by Cheil Flame Retardant, Ltd., 1.2μm), and as additives, 10g of calcium stearate, 10g of antioxidant (1010 Produced by CIBA GEIGY), 20g of

IRGAFOS 168(produced by CIBA GEIGY), 30g of UV absorbent (Tinuvin 326 produced by CIBA GEIGY), 30g of HALS ultraviolet stabilizer (Chimabsorber 944FD produced by CIBA GEIGY), 200g of light blocking agent TiO_2(R-103 produced by Dupont, Inc.), and 70g of silane coupling agent (A-174 produced by Union carbide). By using a two-axis stirring extruder with diameter of 30mm, the mixture produced is molten and extruded at 190°C in the form of pellets. The yielded pellets are dried for three hours at 100°C and molded by using an injection-molding machine with maximum temperature of a cylinder fixed at 200°C to provide test pieces for test flame retardancy. Then, the flame retardancy and physical properties of the test pieces are tested. The methods of treatment and evaluation are the same as in example 1 and the results are shown in Table 1.

Examples 5~6 and comparative examples 4~5

The pellets are prepared in the same way as in example 1 except that the amount of antimony trioxide as a flame retardant coagent in the composition is modified as shown in Table 1. Then, the yielded pellets are molded by using an injection-molding machine to provide test pieces for testing flame retardancy and tensile impact strength. The flame retardancy and physical properties are measured and the results are shown in Table 1.

Comparing the results of examples 5~6 and the results of comparative examples 4~5 as shown in Table 1, it can be shown that only when more than certain amounts of flame retardant coagent should be added in order to generate synergistic effect of flame retardancy and to maintain flame retardancy after UV exposure test and hydrothermal dipping treatment. When antimony trioxides are added excessively more than 17%, there is no more synergistic effect in fame retardancy and the rate of maintaining physical property is low, making it impossible to obtain F1 grade.

Example 7

Following components are introduced into the Hensel mixer and mixed by stirring for 3 minutes: 7.9kg of crystalline polypropylene homopolymer with 4g/10minutes of melt flow rate (the melt flow amount of molten resin for 10 minutes at 230°C with 2.16kg of load) as a polypropylene resin, 1.4kg of PE-68(produced by Great Lakes Corporation) as a tetrabromobisphenol A bis-(dibromopropylether), 700g of antimony trioxide (Sb203 produced by Cheil Flame Retardant, Ltd., 1.2μm), and as additives, 10g of calcium stearate, 10g of antioxidant (1010 Produced by CIBA GEIGY), 20g of IRGAFOS 168(produced by CIBA GEIGY), 30g of UV absorbent (Tinuvin 326 produced by CIBA GEIGY), 30g of HALS ultraviolet stabilizer (Chimabsorber 944FD produced by CIBA GEIGY), 200g of light blocking agent TiO_2(R-103 produced by Dupont, Inc.), and 70g of silane coupling agent (A-174 produced by Union carbide). By using a two-axis stirring extruder with diameter of 30mm, the mixture produced is molten and extruded at 190°C in the form of pellets. The yielded pellets are dried for three hours at 100°C and molded by using an injection-molding machine with maximum temperature of a cylinder fixed at 200°C to provide test pieces for test flame retardancy. Then, the flame retardancy and physical properties of the test pieces are tested. The methods of treatment and evaluation are the same as in example 1 and the results are shown in Table 1.

Example 8 and comparative examples 6~7

The pellets are prepared in the same way as in example 1 except that the polypropylene resin is modified to the polypropylene resin of different melt flow rate (the melt flow amount of molten resin for 10 minutes at 230°C with 2.16kg of load) as shown in Table 1. Then, the yielded pellets are molded by using an injection-molding machine to provide test pieces for testing flame retardancy and tensile impact strength. The flame retardancy and physical properties are measured and the results are shown in Table 1.

As shown in Table 1, the melt flow rate of polypropylene resin has much effect on the properties of the composition according to UV exposure test and hydrothermal dipping treatment. When the melt flow rate of polypropylene resin is below 4g/10minitues, initial property is excellent, but after the UV disclosure test, the rate of maintaining physical properties becomes low. And when the melt flow rate is above 20g/10minitues, the initial flame retardancy and the flame retardancy after UV disclosure test and the hydrothermal dipping treatment do not meet the V0 grade of flame retardancy at the thickness of 1/32inch. Therefore, the preferable melt flow rate of polypropylene is 4~18g/10 minutes range to maintain F1 grade of flame retardancy and physical properties.

Example 9

Following components are introduced into the Hensel mixer and mixed by stirring for 3 minutes: 7.9kg of crystalline polypropylene homopolymer with 8g/10minutes of melt flow rate (the melt flow amount of molten resin for 10 minutes at 230°C with 2.16kg of load) as a polypropylene resin, 1.4kg of PE-68(produced by Great Lakes Corporation) as a tetrabromobisphenol A bis-(dibromopropylether), 700g of antimony trioxide (Sb203 produced by Cheil Flame Retardant, Ltd., 1.2μm), and as additives, 10g of calcium stearate, 10g of antioxidant (1010 Produced by CIBA GEIGY), 20g of IRGAFOS 168(produced by CIBA GEIGY), 30g of UV absorbent (Tinuvin 326 produced by CIBA GEIGY), 30g of HALS ultraviolet stabilizer (Chimabsorber 944FD produced by CIBA GEIGY), 200g of light blocking agent TiO_2(R-103 produced by Dupont, Inc.), and 15g of silane coupling agent (A-174 produced by Union carbide). By using a two-axis stirring extruder with diameter of 30mm, the mixture produced is molten and extruded at

190 ° C in the form of pellets. The yielded pellets are dried for three hours at 100 ° C and molded by using an injection-molding machine with maximum temperature of a cylinder fixed at 200 ° C to provide test pieces for test flame retardancy. Then, the flame retardancy and physical properties of the test pieces are tested. The methods of treatment and evaluation are the same as in example 1 and the results are shown in Table 2.

Example 10 and comparative examples 8~10

The pellets are prepared in the same way as in example 1 except that the amount of coupling agents of silane, A-174, in the composition is modified as shown in Table 2.

The pellets yielded in examples 9 and 10 are dried for three hours at 100 ° C and molded by using an injection-molding machine with maximum temperature of a cylinder fixed at 200 ° C to provide test pieces for test flame retardancy. Then, the flame retardancy and physical properties of the test pieces are tested and the results are shown in Table 2.

As shown in Table 2, when appropriate amounts of coupling agent of silane are added, the adhesiveness and dispersibility between retardant agent or retardant coagent and the polypropylene resin, the main composition of the resin, become better, V0 grade of flame retardancy is maintained, and tensile strength is highly maintained, improving resistance to environment to F1 grade. The preferable amount of coupling agent of silane is seen to be 0.3~3% by weight.

Example 11

Following components are introduced into the Hensel mixer and mixed by stirring for 3 minutes: 7.9kg of crystalline polypropylene homopolymer with 8g/10minutes of melt flow rate (the melt flow amount of molten resin for 10 minutes at 230°C with 2.16kg of load) as a polypropylene resin, 1.4kg of PE-68(produced by Great Lakes Corporation) as a tetrabromobisphenol A bis-(dibromopropylether), 700g of antimony trioxide (Sb203 produced by Cheil Flame Retardant, Ltd., 1.2μm), and as additives, 10g of calcium stearate, 10g of antioxidant (1010 Produced by CIBA GEIGY), 20g of IRGAFOS 168(produced by CIBA GEIGY), 70g of UV absorbent (Tinuvin 326 produced by CIBA GEIGY), 70g of HALS ultraviolet stabilizer (Chimabsorber 944FD produced by CIBA GEIGY), 200g of light blocking agent TiO_2(R-103 produced by Dupont, Inc.), and 70g of silane coupling agent (A-174 produced by Union carbide). By using a two-axis stirring extruder with diameter of 30mm, the mixture produced is molten and extruded at 190°C in the form of pellets. The yielded pellets are dried for three hours at 100°C and molded by using an injection-molding machine with maximum temperature of a cylinder fixed at 200°C to provide test pieces for test flame retardancy. Then, the flame retardancy and physical properties of the test pieces are tested. The methods of treatment and evaluation are the same as in example 1 and the results are shown in Table 2.

Examples 12~13 and comparative examples 11~16

The pellets are prepared in the same way as in example 1 except that the mixing content of UV absorbent and HALS ultraviolet stabilizer in the composition is modified as shown in Table 2. Then, the yielded pellets are molded by using an injection-molding machine to provide test pieces for testing flame retardancy and tensile impact strength.

The flame retardancy and physical properties are measured and the results are shown in Table 2.

As shown in Table 2, by using mixture of UV absorbent and HALS ultra violet stabilizer in appropriate amounts, the flame retardancy and resistance to environment are shown to be improved.

Example 14

Following components are introduced into the Hensel mixer and mixed by stirring for 3 minutes: 8.1kg of crystalline polypropylene homopolymer with 8g/10minutes of melt flow rate (the melt flow amount of molten resin for 10 minutes at 230°C with 2.16kg of load) as a polypropylene resin, 1.3kg of PE-68(produced by Great Lakes Corporation) as a tetrabromobisphenol A bis-(dibromopropylether), 650g of antimony trioxide (Sb203 produced by Cheil Flame Retardant, Ltd., 1.2μm), and as additives, 10g of calcium stearate, 10g of antioxidant (1010 Produced by CIBA GEIGY), 20g of IRGAFOS 168(produced by CIBA GEIGY), 30g of UV absorbent (Tinuvin 326 produced by CIBA GEIGY), 30g of HALS ultraviolet stabilizer (Chimabsorber 944FD produced by CIBA GEIGY), 200g of light blocking agent TiO_2(R-103 produced by Dupont, Inc.), and 70g of silane coupling agent (A-174 produced by Union carbide). By using a two-axis stirring extruder with diameter of 30mm, the mixture produced is molten and extruded at 190°C in the form of pellets. The yielded pellets are dried for three hours at 100°C and molded by using an injection-molding machine with maximum temperature of a cylinder fixed at 200°C to provide test pieces for test flame retardancy. Then, the flame retardancy and physical properties of the test pieces are tested. The methods of treatment and evaluation are the same as in example 1 and the results are shown in Table 2.

Examples 15~16 and comparative examples 17~18

The pellets are prepared in the same way as in example 14 except that the amount of PE-68 as a flame retardant agent of tetrabromobisphenol A bis-(dibromopropylether) and antimony trioxide(Sb 203) as a flame retardant coagent in the composition is modified as shown in Table 2. Then, the yielded pellets are molded by using an injection-molding machine to provide test pieces for testing flame retardancy and tensile impact strength. The flame retardancy and physical properties are measured and the results are shown in Table 2.

As shown in Table 2, by using mixture of flame retardant agent and coagent in specific amounts, the flame retardancy and resistance to environment are shown to be improved.

[Table 1]

Composition Component								Before Treatment		1,000 hours after Exposing to UV				168 hours(7 days) after hydrothermal dipping				Final Grade
	A	B	C	D	E	F	G	Flame retardancy (1/32")	Tensile impact strength	Flame retardancy (1/32")	Tensile impact strength	Mainte-nance of FR	Mainte-nance of TIS(%)	Flame retardancy (1/32")	Tensile impact strength	Mainte-nance of FR	Mainte-nance of TIS(%)	
E1	79	14	7	0.30	0.30	2.00	0.70	V0	38.5	V0	35.6	M*	92	V0	42.6	M	111	F1
E2	79	14	7	0.30	0.30	5.00	0.70	V0	39.0	V0	34.1	M	87	V0	39.4	M	101	F1
E3	79	14	7	0.30	0.30	0.20	0.70	V0	37.2	V0	30.1	M	81	V0	37.5	M	101	F1
CE1	79	14	7	0.30	0.30	0.10	0.70	V0	38.9	V0	26.3	M	68	V2	39.4	D	101	NG*
CE2	79	14	7	0.30	0.30	7.00	0.70	V0	39.4	V0	27.5	M	70	V0	36.9	M	94	F1
CE3	79	14	7	0.30	0.30	0.00	0.70	V0	36.0	V2	20.1	D*	56	V2	42.0	D	117	NG
E4	82	14	4	0.30	0.30	2.00	0.70	V0	37.6	V0	34.2	M	91	V0	42.3	M	113	F1
E5	76	14	10	0.30	0.30	2.00	0.70	V0	38.2	V0	35.4	M	93	V0	41.0	M	107	F1
E6	71	14	15	0.30	0.30	2.00	0.70	V0	37.1	V0	34.1	M	92	V0	38.3	M	103	F1
CE4	69	14	17	0.30	0.30	2.00	0.70	V0	39.6	V0	27.5	M	69	V0	37.6	M	95	F2
CE5	83	14	3	0.30	0.30	2.00	0.70	V2	38.3	V2	36.4	B*	95	V2	38.4	B	100	NG
E7	(A1)79	14	7	0.30	0.30	2.00	0.70	V0	39.5	V0	36.3	M	92	V0	42.6	M	108	F1
E8	(A2)79	14	7	0.30	0.30	2.00	0.70	V0	35.4	V0	34.1	M	96	V0	42.6	M	120	F1
CE6	(A3)79	14	7	0.30	0.30	2.00	0.70	V0	44.5	V0	30.4	M	68	V0	42.6	M	96	F2
CE7	(A4)79	14	7	0.30	0.30	2.00	0.70	V2	32.1	V2	30.4	M	95	V2	32.6	M	102	NG

* unit of tensile impact strength : kg.cm/cm square

* NG : No Grade

* FR: Flame Retardancy, TIS: Tensile Impact Strength, NG: No Grade

* M: Maintained, D: Deteriorated, B: Below the standard

[Table 2]

Composition Component								Before Treatment		1,000 hours after Exposing to UV				168 hours(7 days) after hydrothermal dipping				
	A	B	C	D	E	F	G	Flame retardancy (1/32")	Tensile impact strength	Flame retardancy (1/32")	Tensile impact strength	Mainte-nance of FR	Mainte-nance of TIS(%)	Flame retardancy (1/32")	Tensile impact strength	Mainte-nance of FR	Mainte-nance of TIS(%)	Final Grade
E9	79	14	7	0.30	0.30	2.00	0.15	V0	35.1	V0	28.7	M	82	V0	35.2	M	100	F1
E10	79	14	7	0.30	0.30	2.00	3.00	V0	32.6	V0	26.4	M	81	V0	38.6	M	118	F1
CE8	79	14	7	0.30	0.30	2.00	5.00	V0	34.2	V0	25.9	M	76	V2	33.6	D	98	NG
CE9	79	14	7	0.30	0.30	2.00	0.00	V0	40.2	V0	22.4	M	56	V2	38.4	D	96	NG
CE10	79	14	7	0.30	0.30	2.00	0.05	V0	37.1	V0	27.5	M	74	V2	35.6	D	96	NG
E11	79	14	7	0.70	0.70	2.00	0.70	V0	37.0	V0	32.6	M	88	V0	36.3	M	98	F1
E12	79	14	7	1.50	1.50	2.00	0.70	V0	38.4	V0	30.8	M	80	V0	41.4	M	108	F1
E13	79	14	7	0.10	0.10	2.00	0.70	V0	36.8	V0	27.3	M	74	V0	43.5	M	118	F1
CE11	79	14	7	0.05	0.05	2.00	0.70	V0	37.4	V0	21.0	M	56	V0	38.3	M	102	F2
CE12	79	14	7	2.00	2.00	2.00	0.70	V2	32.4	V2	28.2	B	87	V2	33.6	B	104	F2
CE13	79	14	7	0.00	0.70	2.00	0.70	V0	35.4	V0	17.3	M	49	V0	37.9	M	107	F2
CE14	79	14	7	0.00	1.50	2.00	0.70	V0	33.5	V0	18.0	M	54	V0	35.9	M	107	F2
CE15	79	14	7	0.70	0.00	2.00	0.70	V0	36.2	V0	20.3	M	56	V0	37.2	M	103	F2
CE16	79	14	7	1.50	0.00	2.00	0.70	V0	35.7	V0	22.3	M	62	V0	33.6	M	94	F2
E14	81	13	6.5	0.30	0.30	2.00	0.70	V0	38.9	V0	31.2	M	80	V0	39.6	M	102	F1
E15	87	9	4	0.30	0.30	2.00	0.70	V0	43.1	V0	37.8	M	88	V0	39.4	M	91	F1
E16	76	16	8	0.30	0.30	2.00	0.70	V0	32.5	V0	22.6	M	70	V0	33.1	M	102	F1
CE17	73	18	9	0.30	0.30	2.00	0.70	V0	31.4	V2	15.9	B	51	V0	33.0	M	105	F2
CE18	89	7	4	0.30	0.30	2.00	0.70	V2	42.3	V2	37.5	B	89	V2	39.3	B	93	NG

* Unit of Composition Component: 100g , A: Homopolymer of polypropylene with MFR of 8g/10min , A1: Homopolymer of polypropylene with MFR of 4g/10min , A2: Homopolymer of polypropylene with MFR of 18g/10min , A3: Homopolymer of polypropylene with MFR of 2g/10min , A4: Homopolymer of polypropylene with MFR of 20g/10min , B: Flame retardant agent , C: antimony trioxide , D: UV absorbent , E: HALS ultraviolet stabilizer , F: Titanium Dioxide ,
G: silane coupling agent

In Tables 1 and 2, F1 in Final Grade indicates maintaining V-0 grade of flame retardancy and the ratio of more than 70% of maintaining tensile impact strength in UV exposure test and hydrothermal dipping test, and F2 indicates maintaining V-0 grade of flame retardancy and the ratio of more than 70% of maintaining tensile impact strength in UV exposure test or hydrothermal dipping test. NG(No Grade) indicates that the grade is neither F1 nor F2. M(Maintained) in Maintenance of FR indicates that flame retardancy is maintained after treatment, B(Below) indicates that flame retardancy is V-2 both before and after treatment, and D(Deteriorated) indicates that initial flame retardancy of V-0 is reduced to V-2 after treatment.

As can be seen in Tables 1 and 2, the polypropylene resin composition of the present invention, which comprises 40~90 % by weight of polypropylene resins with melt flow rate 4~18g/10minutes, 9~16 % by weight of flame retardant additives of halogen with low melt point, 4~15% by weight of antimony oxides in white granules, 0.2~3.0% by weight of ultraviolet stabilizers, 0.1~5% by weight of coupling agents of silane, and 0.2~5% by weight of titanium dioxide, exhibits excellent weather proof, maintains initial V-0 grade of flame retardancy after hydrothermal dipping test, and also maintains physical properties.

As readily can be seen in the above description, the polypropylene resin composition according to the present invention has excellent flame retardancy, maintains initial high flame retardancy and excellent physical properties after long-term outdoor exposure and long hydrothermal treatment at the width of 1/32inches, making it possible to obtain F1 grade in UL746C environment-resistance test. Secondary products of the resin of the present invention can be used in such products as light bulb socket of Christmas tree which is exposed outdoor for a long time.

WHAT IS CLAIMED IS:

1. A flame retardant polypropylene resin composition comprising 40~90 % by weight of polypropylene resin with melt flow rate of 4~18g/10minutes, 9~16 % by weight of flame retardant additive of halogen with low melting point, 4~15% by weight of antimony oxide in white granules, 0.2~3.0% by weight of ultraviolet stabilizer, 0.1~5% by weight of silane coupling agents, and 0.2~5% by weight of titanium dioxide.

2. The flame retardant polypropylene resin composition according to claim 1, wherein said polypropylene resin is a polypropylene homopolymer or a crystalline polypropylene copolymer.

3. The flame retardant polypropylene resin composition according to claim 1, wherein said flame retardant additive of halogen with low melting point is tetrabromobisphenol A bis-(dibromopropylether) or tetrabromodimethysulfone dipropylether, or mixture thereof.

4. The flame retardant polypropylene resin composition according to claim 1, wherein said antimony oxide is an antimony trioxide or antimony pentaoxide, or mixture thereof.

5. The flame retardant polypropylene resin composition according to claim 1, wherein said ultraviolet stabilizer us a mixture of HALS ultraviolet stabilizer with molecular weight of more than 2,000 and UV absorbent.

6. The flame retardant polypropylene resin composition according to claim 1, wherein said silane coupling agent is a vinyl trimethoxy silane, vinyl triethoxy silane, 3-aminopropyl triethoxy silane, N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, 3-glycydoxypropyl trimethoxy silane, 3-chloropropyl trimethoxy silane, 3-metacryloxypropyl trimethoxy silane or 3-mercaptopropyltrimethoxy silane.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR00/01523

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C23C 14/20

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

B. FIELDS SEARCHED

Minimun documentation searched (classification system followed by classification symbols)
IPC7 C23C

Documentation searched other than minimun documentation to the extent that such documents are included in the fileds searched
KR,JO:IPC as above

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 55-30739 A (TOKYO SIBAHO DENKI.LTD) 4 Match 1980 See the whole document	1
A	JP 57-87462 A (KYOWUKAGAKU KOKYO.LTD) 31 May 1982 See the whole document	1

☐ 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 relevence
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"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 relevence; 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 relevence; 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
21 SEPTEMBER 2001 (21.09.2001)

Date of mailing of the international search report
22 SEPTEMBER 2001 (22.09.2001)

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
Government Complex-Daejeon, Dunsan-dong, Seo-gu, Daejeon
Metropolitan City 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
YOON, Young Han
Telephone No. 82-42-481-5468