

DESCRIPTION

TITLE OF THE INVENTION: FLAME-RETARDANT POLYAMIDE RESIN
COMPOSITION AND MOLDED ARTICLE COMPRISING SAME

TECHNICAL FIELD

[0001]

The present invention relates to a non-halogen-based flame-retardant polyamide resin composition. Specifically, the present invention relates to a non-halogen-based flame-retardant polyamide resin composition having high flame retardancy, good toughness, especially suitable for moldings having hinges.

BACKGROUND ART

[0002]

Polyamide resins are used in various fields of electric and electronic parts, automobile parts and the like by utilizing their excellent mechanical properties, electrical properties, chemical resistance and the like. In these fields, when flame retardancy is required to be imparted by a non-reinforced and non-halogenated flame retardant, a melamine cyanurate is used as the flame retardant (for example, Patent Documents 1 and 2).

However, the melamine cyanurate has disadvantages such as deterioration in the mechanical properties of the polyamide resin because of poor dispersibility in the

polyamide resin, bleeding, decomposition into melamine and cyanuric acid by thermal decomposition, which easy sublimation, and occurrence of silver color on the surface of a molded article and easy contamination of the surface of a mold during molding processing due to the influence of the sublimated melamine and cyanuric acid as the blending amount increases.

[0003]

In recent years, various required levels for electric and electronic components and automobile components and the like have increased. In a component having a thin portion such as a hinge part, flame retardancy is required to be at a level of V-0 with a thickness of UL94 of 0.4 mm, and in a molded article having a hinge part, excellent bending durability of the hinge part is desired.

PRIOR ART DOCUMENTS

PATENT DOCUMENT

[0004]

Patent Document 1: JP-B-58-25379

Patent Document 2: JP-B-58-35541

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005]

An object of the present invention is to provide a flame-retardant polyamide resin composition which is suitable for a molded component having a thin portion such as a hinge part, and which not only has flame retardancy at a level of V-0 with a thickness of UL94 of 0.4 mm, but also makes it possible to mold a hinge part holding molded article excellent in bending durability of the hinge part, particularly bending durability of the hinge part even under a low temperature environment or after an annealing treatment.

MEANS FOR SOLVING THE PROBLEMS

[0006]

As a result of diligent studies to solve the above problems, the present inventors have completed the present invention.

[0007]

That is, the present invention has the following configuration.

[1] A flame-retardant polyamide resin composition including:

97.5 to 93 parts by mass of a polyamide resin (A);

2.5 to 7 parts by mass of a melamine cyanurate (B);

and 0.01 to 2 parts by mass of a metal hypophosphite (C)

based on 100 parts by mass of a total of the components (A)

and (B);

a lubricant (D), a phosphorus-based antioxidant (E),
and a hindered phenol-based antioxidant (F),

wherein

the flame-retardant polyamide resin composition
satisfies requirements described in the following (a) to
(c):

(a) $10 \leq$ terminal amino group concentration
(eq/ton) of polyamide resin (A) ≤ 39

(b) melt flow rate (275°C, 1 kgf) ≥ 40

(c) $236^{\circ}\text{C} \leq$ temperature lowering
crystallization temperature (Tc2) $\leq 242^{\circ}\text{C}$.

[2] A method for producing a flame-retardant
polyamide resin composition according to [1], the method
including the step of melt-kneading a polyamide resin (A),
melamine cyanurate (B) and a metal hypophosphite (C),
wherein the polyamide resin (A) includes 45 to 75% by mass
of a polyamide 66 resin (A1), 10 to 40% by mass of a
polyamide 6 resin (A2), and 0 to 8% by mass of an amorphous
polyamide resin (A3) based on a total amount of the
polyamide resin (A).

[3] The flame-retardant polyamide resin composition
according to [1] or [2], further including 0.01 to 1 parts

by mass of the lubricant (D), 0.01 to 1 parts by mass of the phosphorus-based antioxidant (E), and 0.01 to 1 parts by mass of the hindered phenol-based antioxidant (F) based on 100 parts by mass of the flame-retardant polyamide resin composition.

[4] The flame-retardant polyamide resin composition according to any one of [1] to [3], wherein the phosphorus-based antioxidant (E) is a compound having a pentaerythritol diphosphite skeleton.

[5] The flame-retardant polyamide resin composition according to any one of [1] to [4], wherein the flame-retardant polyamide resin composition is used for a hinge member.

[6] A molded article having a hinge part, the molded article including the flame-retardant polyamide resin composition according to any one of [1] to [4].

[7] The molded article according to [5], wherein the molded article having a hinge part is any one of a ferrite core cover, a binding band, and an electric wiring protection member.

EFFECT OF THE INVENTION

[0008]

The flame-retardant polyamide resin composition of the present invention not only has flame retardancy at a level of V-0 with a thickness of UL94 of 0.4 mm, but also makes it possible to mold a hinge part holding molded article excellent in bending durability of the hinge part.

MODE FOR CARRYING OUT THE INVENTION

[0009]

Hereinafter, the present invention will be specifically described.

A flame-retardant polyamide resin composition of the present invention includes 97.5 to 93 parts by mass of a polyamide resin (A) 2.5 to 7 parts by mass of a melamine cyanurate (B), and 0.01 to 2 parts by mass of a metal hypophosphite (C) based on 100 parts by mass of a total of the components (A) and (B), wherein the flame-retardant polyamide resin composition satisfies requirements described in the following (a) to (c):

(a) $10 \leq$ terminal amino group concentration (eq/ton) of polyamide resin (A) ≤ 39

(b) melt flow rate (275°C, 1 kgf) ≥ 40

(c) $236^{\circ}\text{C} \leq$ temperature lowering crystallization temperature (Tc2) $\leq 242^{\circ}\text{C}$.

[0010]

In the case of a mixture of a plurality of polyamide resins, an average terminal amino group concentration (eq/ton) in the requirement (a) of the present invention is a value (average AEG) calculated from the terminal amino group concentration (eq/ton) of each of the resins and the mixing ratio thereof. $10 \leq (\text{average AEG}) \leq 38$ is preferably set, and $10 \leq (\text{average AEG}) \leq 37$ is more preferably set. When the (average AEG) is more than 39, the effect of delaying a crystallization rate by an amide exchange reaction is less likely to be promoted, and the relaxation of resin orientation is less likely to occur in the vicinity of a mold, and therefore cracks are apt to occur in a hinge part.

[0011]

The melt flow rate in the requirement (b) of the present invention has melt fluidity (MFR) of the flame-retardant polyamide resin composition of the present invention according to the ISO 1133 method, and is preferably 50 or more, and more preferably 60 or more. When the (MFR) has melt fluidity lower than the requirement (b) of the present invention, the resin orientation is formed in the vicinity of the mold, and therefore cracks are apt to occur in the hinge part.

[0012]

A temperature lowering crystallization temperature (Tc2) in the requirement (c) of the present invention is a temperature measured by heat flux differential scanning calorimetry (heat flux DSC), and is preferably $238^{\circ}\text{C} \leq (\text{Tc2}) \leq 241^{\circ}\text{C}$. When the (Tc2) is higher than 242°C , the relaxation of the resin orientation is less likely to occur in the vicinity of the mold, and cracks are apt to occur in the hinge part. When the (Tc2) is lower than 236°C , the moldability of the flame-retardant polyamide resin composition tends to be poor.

[0013]

Hereinafter, various raw materials used in the present invention will be described in detail.

A polyamide resin (A) in the present invention is not particularly limited as long as the crystalline polyamide resin (A) is a polymer having an amide bond ($-\text{NHCO}-$) in its main chain. The polyamide resin (A) is preferably crystalline, and examples thereof include, but are not limited to, crystalline polyamide resins such as polyamide 6 (PA6), polyamide 66 (PA66), polyamide 46 (PA46), polyamide 11 (PA11), polyamide 12 (PA12), polyamide 610 (PA610), polyamide 612 (PA612), polymethaxylylene adipamide (PAMXD6), hexamethylenediamine-terephthalic acid polymer (PA6T), a copolymer of hexamethylenediamine-terephthalic acid and adipic acid (PA6T/66), a copolymer of

hexamethylenediamine-terephthalic acid and ϵ -caprolactam (PA6T/6), a trimethylhexamethylenediamine-terephthalic acid polymer (PATMD-T), a copolymer of m-xylylenediamine with adipic acid and isophthalic acid (PAMXD6/MXDI), a copolymer of trihexamethylenediamine with terephthalic acid and ϵ -caprolactam (PATMDT/6), and a copolymer of diaminodicyclohexylenemethane with isophthalic acid and lauryllactam, and blends thereof.

[0014]

The blending amount (content) of the polyamide resin (A) is 97.5 to 94 parts by mass based on the total of 100 parts by mass of the polyamide resin (A) and the melamine cyanurate (B). When the blending amount of the polyamide resin (A) is within this range, it is possible to suppress the bleeding of a flame retardant and to apply the retention of high flame retardancy to a composition. The blending amount (content) of the polyamide resin (A) is preferably 97 to 94.5 parts by mass, and more preferably 97 to 95 parts by mass. In a flame-retardant polyamide resin composition of the present invention, the blending amount of each component is the content as it is.

[0015]

The flame-retardant polyamide resin composition in the present invention can be obtained by a production method including the step of melt-kneading the polyamide

resin (A), the melamine cyanurate (B), and the metal hypophosphite (C). It is preferable that 45 to 75% by mass of a polyamide 66 resin (A1), 10 to 40% by mass of a polyamide 6 resin (A2), and 0 to 8% by mass of an amorphous polyamide resin (A3) are mixed based on the total amount of the polyamide resin (A).

[0016]

Examples of the polyamide 66 resin (A1) in the present invention include a polyamide 66 resin obtained by the polycondensation of adipic acid and hexamethylenediamine as raw materials. The relative viscosity of the polyamide 66 resin (A1) is a value measured at a concentration of 1% in 98% sulfuric acid and a temperature of 25°C according to JIS K6810, and is preferably 2.2 to 3.5. When the relative viscosity of the polyamide 66 resin (A1) is less than 2.2, mechanical characteristics are apt to be deteriorated, and when the relative viscosity of the polyamide 66 resin (A1) is more than 3.5, melt fluidity is apt to be insufficient. The relative viscosity of the polyamide 66 resin (A1) is more preferably 2.3 to 3.0.

[0017]

The terminal amino group concentration of the polyamide 66 resin (A1) is preferably 10 to 50 eq/ton, and more preferably 10 to 40 eq/ton from the viewpoint of hinge

durability and heat discoloration resistance.

[0018]

The blending amount of the polyamide 66 resin (A1) is preferably 45 to 75 parts, and more preferably 50 to 70 parts by mass based on 100 parts by mass of all polyamide resin from the viewpoint of hinge durability. When the blending amount of the polyamide 66 resin (A1) is more than 75 parts by mass, hinge properties (snap-fit properties) are deteriorated, and when the blending amount is less than 45 parts by mass, molding processability is apt to be deteriorated.

[0019]

The polyamide 6 resin (A2) in the present invention is a polyamide 6 resin obtained by the polycondensation of ϵ -caprolactam as a raw material. The relative viscosity of the polyamide 6 resin (A2) is a value measured at a concentration of 1% in 98% sulfuric acid and a temperature of 25°C according to JIS K6810, and is preferably 2.0 to 4.0. When the relative viscosity of the polyamide 6 resin (A2) is less than 2.0, mechanical characteristics are apt to be deteriorated, and when the relative viscosity of the polyamide 6 resin (A2) is more than 4.0, flame retardancy and fluidity are apt to be impaired. The relative viscosity of the polyamide 6 resin (A2) is more preferably 2.2 to 3.0.

[0020]

The terminal amino group concentration of the polyamide 6 resin (A2) is preferably 5 to 50 eq/ton, and more preferably 10 to 40 eq/ton from the viewpoint of hinge durability and heat discoloration resistance.

[0021]

The blending amount of the polyamide 6 resin (A2) is preferably 10 to 40 parts by mass based on 100 parts by mass of all polyamide resin. When the blending amount of the polyamide 6 resin (A2) is less than 10 parts by mass, hinge properties (snap-fit properties) are apt to be deteriorated, and when the blending amount is more than 40 parts by mass, molding processability is apt to be deteriorated. The blending amount of the polyamide 6 resin (A2) is more preferably 20 to 40 parts by mass from the viewpoint of a balance between snap-fit properties and molding processability.

[0022]

The amorphous polyamide resin (A3) is a compound that the melting peak of a crystal is not observed in a thermogram during DSC measurement, and includes polymers, copolymers obtained by the polycondensation of diamines such as 4,4'-diamino-3,3'-dimethyldicyclohexylmethane (CA), 4,4'-diaminodicyclohexylmethane (PACM), meta-xylylenediamine (MXD), trimethylhexamethylenediamine (TMD),

isophoronediamine (IA), 4,4'-diaminodicyclohexylpropane (PACP), and hexamethylenediamine with dicarboxylic acids such as terephthalic acid, isophthalic acid, adipic acid, sebacic acid, and dodecanedicarboxylic acid and lactams such as caprolactam and lauryllactam, or blends thereof.

[0023]

Among them, a polyamide resin having an aromatic component is preferable from the viewpoint of lowering the Tc2 to easily suppress the cracks of the hinge part. As the polyamide resin containing an aromatic component, polyamide 6T/6I containing terephthalic acid, isophthalic acid, and adipic acid as raw materials, and polyamide 6T/66 containing terephthalic acid, adipic acid, and hexamethylenediamine as raw materials, and the like are preferable, and polyamide 6T/6I is particularly preferable from the viewpoint of the moldability of the polyamide resin.

[0024]

[Melamine cyanurate (B)]

Preferred examples of the melamine cyanurate (B) in the present invention include an equimolar reactant of cyanuric acid and melamine. Some of amino groups or hydroxyl groups in the melamine cyanurate may be substituted with other substituents. The melamine cyanurate can be obtained, for example, by mixing an

aqueous solution of cyanuric acid and an aqueous solution of melamine, reacting them under stirring at 90 to 100°C, and filtering the generated precipitate. The obtained solid can be used as it is, but it is preferable to use the pulverized solid as necessary. The particle diameter of the pulverized solid is not particularly limited, but from the viewpoint of flame retardancy and toughness, the average particle diameter of the pulverized solid is preferably 0.5 to 20 μm , and more preferably 1 to 15 μm .

[0025]

The blending amount (content) of the melamine cyanurate (B) is 2.5 to 7 parts by mass based on the total of 100 parts by mass of the polyamide resin (A) and the melamine cyanurate (B). The blending amount is 2.5 parts by mass or more from the viewpoint of flame retardancy, and 7 parts by mass or less from the viewpoint of toughness. The blending amount is more preferably 2.5 to 6 parts by mass, and still more preferably 3 to 5 parts by mass. In the present invention, the toughness is a characteristic related to snap-fit property.

[0026]

[Metal hypophosphite (C)]

The metal hypophosphite (C) in the present invention is a salt of hypophosphorous acid with Group 1, 2, 3, 4, 5, 6, 7, 8, 11, 12, or 13 element of the periodic table of

elements and a metal such as tin or lead, and one kind or two or more kinds thereof may be used in combination.

Among them, sodium hypophosphite (NaH_2PO_2) and calcium hypophosphite ($\text{Ca}(\text{H}_2\text{PO}_2)_2$) are preferable from the viewpoint that the effect of delaying a crystallization rate by an amide exchange reaction can be more remarkably achieved. The metal hypophosphite may be a hydrate, and examples thereof include sodium hypophosphite monohydrate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$).

[0027]

The blending amount of the metal hypophosphite (C) is 0.001 to 2 parts by mass, preferably 0.05 to 1.5 parts by mass, and more preferably 0.1 to 1.0 parts by mass, based on 100 parts by mass of a total of the polyamide resin (A) and the melamine cyanurate (B). When the amount of the metal hypophosphite is within a specific range, an amide exchange reaction between the polyamide resins is promoted, which is preferable for stabilizing resin properties.

[0028]

In order to improve the moldability, discoloration resistance, and thermal stability and the like of the resin composition of the present invention, the resin composition preferably contains a lubricant (D), a phosphorus-based antioxidant (E), and a hindered phenol-based antioxidant (F) and the like.

[0029]

[Lubricant (D)]

Examples of the lubricant (D) in the present invention include esters and metal salts of long-chain fatty acids, amide-based compounds such as ethylene bisterephthalamide and methylene bisstearylamide, waxes such as aliphatic hydrocarbon-based and polyethylene-based waxes, and polysiloxane-based silicone oils. These lubricants may be used singly or as a mixture. The optimum amount of the lubricant to be added may be selected in consideration of moldability and flame retardancy, but fatty acid metal salt-based or fatty acid ester-based lubricants are preferable from the viewpoint of the balance between moldability and flame retardancy.

[0030]

Examples of the fatty acid metal salt include metal salts of fatty acids having 12 to 40 carbon atoms such as stearic acid, palmitic acid, behenic acid, erucic acid, oleic acid, lauric acid, and montanic acid. Among them, metal salts of aliphatic carboxylic acids having 18 to 30 carbon atoms are preferable, and alkali metal or alkaline earth metal salts of stearic acid, behenic acid, lignoceric acid, and montanic acid and the like are more preferable from the viewpoint of the releasability of the polyamide resin composition. Examples of the alkali metal or

alkaline earth metal include lithium, sodium, magnesium, and calcium salts.

[0031]

Examples of the fatty acid ester-based compound include a mixture mainly composed of myricyl palmitate, stearyl stearate, behenyl behenate, stearyl behenate, glycerin monopalmitate, glycerin monostearate, glycerin distearate, glycerin tristearate, pentaerythritol monopalmitate, pentaerythritol monostearate, pentaerythritol distearate, pentaerythritol tristearate, and pentaerythritol tetrastearate.

[0032]

The blending amount (content) of the lubricant (D) is 0.01 to 1 parts by mass based on 100 parts by mass of the polyamide resin composition. When the blending amount is less than 0.01 parts by mass, the releasability of the polyamide resin composition may be deteriorated, and when the blending amount is more than 1 part by mass, the flame retardancy of the polyamide resin composition may be deteriorated. The blending amount of the lubricant (D) is preferably 0.1 to 0.9 parts by mass.

[0033]

[Phosphorus-based antioxidant (E)]

A phosphorus-based antioxidant (E) in the present invention may be an inorganic compound or an organic

compound, and is not particularly limited. Preferred examples of the phosphorus-based compound include inorganic phosphates such as monosodium phosphate, disodium phosphate, trisodium phosphate, sodium phosphite, calcium phosphite, magnesium phosphite and manganese phosphite; triphenyl phosphite, trioctadecyl phosphite, tridecyl phosphite, triisodecyl phosphite, trinonylphenyl phosphite, diphenyl isodecyl phosphite, diphenyl alkyl phosphite, phenyl dialkyl phosphite, tris(nonylphenyl)phosphite, trilauryl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl)phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite, diisodecyloxypentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl))pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylenediphosponite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g]-1,3,2-dioxaphosine, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenzo[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methyl phosphite, and bis(2,4-di-tert-butyl-6-methylphenyl)ethyl phosphite, and these compounds are

blended in order to enhance heat discoloration resistance.

[0034]

As the phosphorus-based antioxidant (E), phosphite compounds are preferably used. Among the phosphite compounds, the compounds having a pentaerythritol diphosphite skeleton are preferable. Specifically, those having a pentaerythritol diphosphite skeleton such as bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite ("ADK STAB PEP-36", molecular weight: 633), bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite ("ADK STAB PEP-24G", molecular weight: 604), distearyl pentaerythritol diphosphite ("ADK STAB PEP-8", molecular weight: 733), or bis(nonylphenyl)pentaerythritol diphosphite ("ADK STAB PEP-4C", molecular weight: 633) and having a molecular weight of about 600 to 800 are particularly preferable in terms of being capable of further improving releasability without reducing flame retardancy and also being suitable for snap-fit properties.

[0035]

The blending amount (content) of the phosphorus-based antioxidant (E) is 0.01 to 1 part by mass based on 100 parts by mass of the non-halogen-based flame-retardant polyamide resin composition. When the blending amount of the phosphorus-based antioxidant (E) is within this range, discoloration during extrusion processing can be

suppressed, and secondary oxidative degradation due to phosphorus-derived radicals can be prevented from being induced. The blending amount of the phosphorus-based antioxidant (E) is preferably 0.1 to 0.5 parts by mass.

[0036]

[Hindered phenol-based antioxidant (F)]

Examples of a hindered phenol-based antioxidant (F) in the present invention include N,N'-hexamethylene-bis-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionamide, bis(3,3-bis-(4'-hydroxy-3'-tert-butylphenyl)butanoic acid)glycol ester, 2,1'-thioethylbis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), and triethylene glycol-3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionate "SONGNOX 2450", molecular weight: 633), and mixtures of two or more thereof can also be used.

[0037]

The blending amount (content) of the hindered phenol-based antioxidant (F) is 0.01 to 1 part by mass based on 100 parts by mass of the non-halogen-based flame-retardant polyamide resin composition. When the blending amount of the hindered phenol-based antioxidant (F) is within this range, oxidation degradation over time can be prevented with an appropriate formulation amount according to the coordination bond of the polyamide composition. The

blending amount of the hindered phenol-based antioxidant (F) is preferably 0.1 to 0.5 parts by mass.

[0038]

[Other components]

In addition to the above-described (A), (B), (C), (D), (E), and (F) other components, for example, colorants such as pigments and dyes, additives such as heat stabilizers, weather resistance improvers, nucleating agents, plasticizers, release agents, and antistatic agents, and other resin polymers and the like can be added to the flame-retardant polyamide resin composition of the present invention as long as the object of the present invention is not impaired. The flame-retardant polyamide resin composition of the present invention preferably occupies 80% by mass or more, more preferably 90% by mass or more, and still more preferably 95% by mass or more in the total of the above-mentioned components (A), (B), (C), (D), (E) and (F).

[0039]

Specific examples of suitable molded parts obtained using the flame-retardant polyamide resin composition of the present invention include moldings having hinges, especially molded parts having thin hinge portion, such as connectors, coil bobbins, circuit breakers, electromagnetic switches, holders, plugs, sockets, switches, cases, and

covers used in fields of electric and electronic parts, automobile parts and the like, and more specific examples thereof include parts required to have heat discoloration resistance and snap-fit properties, such as ferrite core covers, binding bands, and electric wiring protection members.

[0040]

A method for producing the flame-retardant polyamide resin composition of the present invention is not particularly limited, and a general single screw extruder, twin-screw extruder, pressure kneader and the like can be used as a kneader, but a twin-screw extruder is particularly preferable in the present invention. As one aspect, the above (A), (B), (C), (D), (E) and (F), and a pigment and the like depending on the application are mixed, and the mixture is charged into a twin-screw extruder. The polyamide-based resin composition having excellent toughness and flame retardancy can be produced by uniform kneading with the twin-screw extruder. The kneading temperature of the twin-screw extruder is preferably 220 to 300°C, and the kneading time thereof is preferably about 2 to 15 minutes.

EXAMPLES

[0041]

Hereinafter, the present invention will be described in more detail with reference to Examples, but the present invention is not limited to these Examples at all.

[0042]

The following components were used.

Polyamide resin (A);

A1-1: Polyamide 66 (RV=2.8), Vydyne 21Z (manufactured by Ascend), melting point: 265°C

A1-2: Polyamide 66 (RV=2.4), EPR24 (manufactured by Shanghai Shenma Plastics Technology Co., Ltd.), melting point 265°C

A2-1: Polyamide 6 (RV=2.0), M2000 (manufactured by MEIDA), melting point: 225°C

A2-2: Polyamide 6 (RV=2.6), ZISAMIDE TP4208 (manufactured by ZIG SHENG INDUSTRIAL CO., LTD.), melting point: 225°C

A2-3: Polyamide 6 (RV=3.6), ZISAMIDE TP6603 (manufactured by ZIG SHENG INDUSTRIAL CO., LTD.), melting point: 225°C

A3: Polyamide 6T6I (RV=1.9), Grivory (R) G16 (manufactured by EMS LTD.), glass-transition temperature: 130°C

[0043]

Melamine cyanurate (B);

B: MC6000 (manufactured by Nissan Chemical

Corporation)

[0044]

Metal hypophosphite (C);

C: Sodium hypophosphite (manufactured by TAIHEI
CHEMICAL INDUSTRIAL CO., LTD.)

[0045]

Lubricant (D);

D1: Calcium montanate, CS-8-CP (manufactured by
Nitto Chemical Industry Co., Ltd.)

D2: Aliphatic ester, Licolub WE-40 (manufactured by
Clariant Japan Co., Ltd.)

[0046]

Phosphorus-based antioxidant (E);

E: ADK STAB PEP-36 (manufactured by ADEKA
Corporation)

[0047]

Hindered phenol-based antioxidant (F);

F: SONGNOX2450 (manufactured by Songwon
International Japan K.K.)

[0048]

[Examples 1 to 6, Comparative Examples 1 to 4]

The production of evaluation samples

Raw materials were weighed in blending ratios for
polyamide resin compositions shown in Table 1 and mixed in
a tumbler. The mixture was then charged into a twin-screw

extruder, then pellets of polyamide resin compositions were obtained. The set temperature of the twin-screw extruder was set to 250°C to 300°C, and the kneading time thereof was set to 5 to 10 minutes. Various evaluation samples were molded from the obtained pellets using an injection molding machine. The cylinder temperature and mold temperature of the injection molding machine were respectively set to 250°C to 280°C and 80°C.

[0049]

Various evaluation methods are as follows. The evaluation results are shown in Table 1.

1. Relative viscosity [RV] of polyamide resin (98% sulfuric acid solution method)

Measurement was performed using an Ubbelohde's viscometer at a polyamide resin concentration of 1 g/dl at 25°C in a 98% by mass sulfuric acid solution.

2. Terminal amino group concentration (AEG) of polyamide resin

A sample was dissolved in heavy benzene/HFIP-d (1/1: volume ratio) (temperature: 35°C, 1 hour), and the solution was then centrifuged. To the supernatant, 0.2 M triethylamine/CDCl₃ (CDCl₃ containing 0.2 M triethylamine) was added, followed by performing ¹H-NMR measurement. The sample was cut out from the vicinity of the central portion of a 100 mm × 100 mm × 3 mm resin flat plate prepared by an

injection molding method with a molding temperature set to 270°C and a mold temperature set to 80°C. From the analysis of the obtained ¹H-NMR, an amino group amount was calculated from CH₂ peak intensity at an amino group α-position based on the weight of the polyamide resin.

Note, HFIP is hexafluoro-2-propanol.

[NMR measurement]

Device: Fourier transform nuclear magnetic resonance device (AVANCE-NEO manufactured by Bruker)

¹H resonance frequency: 600.13 MHz

Flip angle of detected pulse: 45°

Incorporation time of data: 4 seconds

Retardation time: 1 second

3. Temperature lowering crystallization temperature (Tc2)

Using a differential scanning calorimeter (EXSTAR6000 manufactured by Seiko Instruments Inc.), the temperature was raised to 305°C at a temperature raising rate of 20°C/min under a nitrogen stream, and held for 5 minutes. Thereafter, measurement was performed at a temperature lowering rate of 10°C/min. The exothermic peak temperature of the polyamide resin composition at the time of temperature lowering was determined, and taken as a temperature lowering crystallization temperature (Tc2).

4. Melt flow rate

In accordance with the test method (Method A) described in ISO1133, a melt flow rate (MFR: g/10 min) was measured at a measurement temperature of 275°C and a load of 1000 g. For the measurement, a polyamide resin composition having a moisture content of 0.1% by mass or less was used.

5. Hinge durability

When 20 molded articles each having a hinge part and obtained by an injection molding method were left under an environment of 5°C for 15 minutes, and the hinge part was then bent once under the environment, the number of cracks and fractures generated in the hinge part was defined as "hinge part cracks (5°C)" and tabulated. When a molded article left for at least 6 hours in an oven at 85°C after molding was left for 15 minutes in an environment at 5°C in the same manner, and the hinge part was then bent once in the same environment, the number of cracks and fractures generated in the hinge part was defined as "hinge part cracks (85°C annealing, 5°C)" and tabulated.

6. Combustibility:

Measurement was performed according to UL 94, vertical combustion test. V-0 represents the highest flame retardancy.

[0050]

[Table 1]

			Examples						Comparative examples			
Blending composition	(RV, AEG)		1	2	3	4	5	6	1	2	3	4
	A1-1: PA66 (2.8, 43)	parts by mass				67		33	67	60	72	67
	A1-2: PA66 (2.4, 36)	parts by mass	67	67	67		60	34				
	A2-1: PA6 (2.0, 25)	parts by mass	24			24		24		36	12	26
	A2-2: PA6 (2.6, 40)	parts by mass		24			36		24			
	A2-3: PA6 (3.6, 36)	parts by mass			24							
	A3: PA6T6I (1.9, 15)	parts by mass	5	5	5	5		5	5			5
	B: melamine cyanurate	parts by mass	4	4	4	4	4	4	4	4	4	2
	C: metal hypophosphite	parts by mass	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	
	D1: Ca montanite	parts by mass	0.4	0.4	0.4	0.4	0.4		0.4	0.4	0.4	0.4
	D2: fatty acid ester	parts by mass						0.8				
	Average AEG of PA	eq/ton	31	35	34	36	36	33	39	40	36	36
Composition characteristics	Tc2 of composition	°C	240	240	240	240	239	240	239	238	243	241
	MFR (275°C, 1 kgf)	g/10 min	80	62	50	48	110	69	23	38	40	43
	Hinge part cracks (5°C)		⊙	⊙	⊙	⊙	⊙	⊙	△	×	×	×
	Hinge part cracks (Annealing at 85°C, 5°C)		○	○	○	○	○	⊙	×	×	×	×
	Flame retardancy: UL94; 0.4 mm		V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-2

(Note 1) Number of hinge part cracks(⊙: 0, ○: 1 to 2, △: 3 to 4, ×: 5 ≤)

(Note 2) Blending of 0.2 parts by mass of phosphorus-based antioxidant (E) and 0.2 parts by mass of hindered phenol-based antioxidant (F) in all compositions

[0051]

In Examples 1 to 6, both hinge part cracks (5°C) and hinge part cracks (85°C annealing, 5°C) achieve the number of cracks of 2 or less, to obtain good hinge durability. Examples 1 to 6 achieve V-0 evaluation also for flame retardancy at a thickness of 0.4 mm. It can be confirmed that the temperature Tc2 and melt flow rate of the polyamide resin composition satisfy the requirements. The comparison of Examples 1 to 6 using the metal hypophosphite (C) with Comparative Example 4 using only the phosphorus compound (only the phosphorus-based antioxidant) shows that the former is more excellent in hinge durability.

[0052]

Meanwhile, Comparative Examples 1 to 4 partially satisfy the characteristics, but none of them satisfies good hinge durability. The melt flow rate of Comparative Examples 1 and 2 cannot satisfy the requirements, resin orientation is formed in the vicinity of the mold, and cracks are apt to occur in the hinge part, which is not preferable. In addition, in Comparative Example 2, the terminal amino group concentration (eq/ton) of the polyamide resin (A) exceeds the upper limit of the requirements, and it becomes difficult to promote the effect of delaying a crystallization rate by an amide exchange reaction, which is not preferable. In Comparative

Example 3, the Tc2 of the composition cannot satisfy the requirements, and therefore the relaxation of resin orientation is less likely to occur in the vicinity of the mold and cracks are apt to occur in the hinge part, which is not preferable. Finally, in Comparative Example 4, the content ratio of the composition cannot satisfy the requirements, the relaxation of resin orientation is less likely to occur in the vicinity of the mold, and cracks are apt to occur in the hinge part, which is not preferable. In addition, the flammability is evaluated as V-2, and the flame retardancy cannot be secured, which is not preferable.

INDUSTRIAL APPLICABILITY

[0053]

The flame-retardant polyamide resin composition of the present invention is suitable for molded articles having a hinge part. The obtained molded article can be suitably used for electric and electronic parts, automobile parts and the like in which bending durability of the hinge part is desired.

CLAIMS

Claim 1. A flame-retardant polyamide resin composition comprising:

97.5 to 93 parts by mass of a polyamide resin (A);

2.5 to 7 parts by mass of a melamine cyanurate (B);

and 0.01 to 2 parts by mass of a metal hypophosphite (C) based on 100 parts by mass of a total of the components (A) and (B), wherein

the flame-retardant polyamide resin composition satisfies requirements described in the following (a) to (c):

(a) $10 \leq$ terminal amino group concentration (eq/ton) of polyamide resin (A) ≤ 39

(b) melt flow rate (275°C, 1 kgf) ≥ 40

(c) $236^{\circ}\text{C} \leq$ temperature lowering crystallization temperature (Tc2) $\leq 242^{\circ}\text{C}$.

Claim 2. A method for producing a flame-retardant polyamide resin composition according to claim 1, the method comprising the step of melt-kneading a polyamide resin (A), melamine cyanurate (B) and a metal hypophosphite (C), wherein the polyamide resin (A) comprises 45 to 75% by mass of a polyamide 66 resin (A1), 10 to 40% by mass of a polyamide 6 resin (A2), and 0 to 8% by mass of an amorphous

polyamide resin (A3) based on a total amount of the polyamide resin (A).

Claim 3. The flame-retardant polyamide resin composition according to claim 1 or 2, further comprising 0.01 to 1 parts by mass of a lubricant (D), 0.01 to 1 parts by mass of a phosphorus-based antioxidant (E), and 0.01 to 1 parts by mass of a hindered phenol-based antioxidant (F) based on 100 parts by mass of the flame-retardant polyamide resin composition.

Claim 4. The flame-retardant polyamide resin composition according to any one of claims 1 to 3, wherein the phosphorus-based antioxidant (E) is a compound having a pentaerythritol diphosphite skeleton.

Claim 5. The flame-retardant polyamide resin composition according to any one of claims 1 to 4, wherein the flame-retardant polyamide resin composition is used for a hinge member.

Claim 6. A molded article having a hinge part, the molded article comprising the flame-retardant polyamide resin composition according to any one of claims 1 to 4.

Claim 7. The molded article according to claim 5,
wherein the molded article having a hinge part is any one
of a ferrite core cover, a binding band, and an electric
wiring protection member.