

DESCRIPTION

GRANULAR STABILIZER PRODUCT

TECHNICAL FIELD

[0001]

This patent application claims the priority under the Paris Convention based on each of Japanese Patent Application No. 2014-263233 (filed on December 25, 2014) and Japanese Patent Application No. 2014-263239 (filed on December 25, 2014), and the entirety of these Applications is incorporated herein by reference.

The present invention relates to a granular stabilizer product and, more particularly, to a granular stabilizer product that tends to avoid any hydrolysis thereof even after being stored for a long time, that can achieve a stable function of suppressing any thermal degradation and any oxidation degradation when the granular stabilizer product is added to an organic material, and that is excellent in the workability.

BACKGROUND ART

[0002]

Organic materials such as thermoplastic resins and thermosetting resins such as polyolefin and polyester are each associated with degradation of the strength physical property, variation of the flowability, coloring, degradation of the surface physical property, and the like of the organic material originated from the phenomena such as cutting of molecules and cross-linking between molecules caused by the actions by heat, oxygen, and the like during its production, its processing, and, in addition, its use, and the value thereof as a commodity may therefore be significantly detracted. It is known that, for example, a phenol-based oxidation inhibitor, a phosphorus-based oxidation inhibitor, or the like is added to the organic material to solve the problems such as the thermal degradation and the oxidation degradation (Patent Document 1).

[0003]

Such an oxidation inhibitor acts as a stabilizer for the organic material and achieves an effect of suppressing any thermal degradation and any oxidation degradation during the production, the processing, and, in addition, the use of the organic material.

PRIOR ART DOCUMENT

PATENT DOCUMENT

[0004]

Patent Document 1: Japanese Laid-Open Patent Publication No. 10-273494

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005]

When the phosphorus-based oxidation inhibitor is stored for a long time, a hydrolysis reaction however occurs therein. When the oxidation inhibitor having the hydrolysis reaction occurring therein is added to an organic material, the processing stability becomes insufficient and the organic material having stable quality cannot be obtained. When the phosphorus-based oxidation inhibitor is added to an organic material, a bridge phenomenon may occur to cause uniform addition of the oxidation inhibitor to the organic material to be difficult and the function of suppressing the thermal degradation and the oxidation degradation may be dispersed.

[0006]

An object of the present invention is to provide a granular stabilizer product that tends to avoid any hydrolysis thereof even after being stored for a long time, that can achieve a stable function of suppressing any thermal degradation and any oxidation degradation when the granular stabilizer product is added to an organic material, and that is excellent in the workability.

MEANS FOR SOLVING PROBLEMS

[0007]

To solve the above problems, the inventors actively studied granular stabilizer

products in detail and completed the present invention.

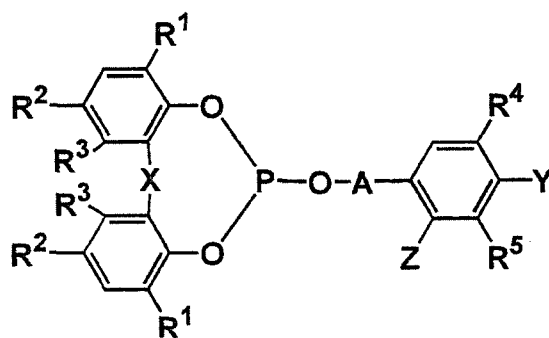
The present invention includes the following preferred embodiments.

[1] A granular stabilizer product containing:

a phosphite ester compound represented by

Formula (1):

[Ch. 1]



wherein

R^1 , R^2 , R^4 , and R^5 each independently represent a hydrogen atom, an alkyl group having 1 to 8 carbon atom(s), a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms, or a phenyl group;

R^3 represents a hydrogen atom or an alkyl group having 1 to 8 carbon atom(s);

X represents a single bond, a sulfur atom, or a $-CHR^6-$ group, wherein R^6 represents a hydrogen atom, an alkyl group having 1 to 8 carbon atom(s), or a cycloalkyl group having 5 to 8 carbon atoms;

"A" represents an alkylene group having 2 to 8 carbon atoms or a $^*-COR^7-$ group, wherein R^7 represents a single bond or an alkylene group having 1 to 8 carbon atom(s); $-CO-$ with * represents bonding with an oxygen atom of a phosphite structure in Formula (1);

as to Y and Z, either one thereof represents a hydroxyl group, an alkoxy group

having 1 to 8 carbon atom(s), or an aralkyloxy group having 7 to 12 carbon atoms, and another one thereof represents a hydrogen atom or an alkyl group having 1 to 8 carbon atom(s);

when Y is a hydroxyl group, either R^4 or R^5 represents an alkyl group having 3 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms, or a phenyl group;

two R^1 's in Formula (1) may be same as each other or may be different from each other;

two R^2 's in Formula (1) may be same as each other or may be different from each other;

two R^3 's in Formula (1) may be same as each other or may be different from each other, and
a metal oxide and/or a metal carbonate.

[2]The granular stabilizer product according to [1], wherein the granular stabilizer product contains 30 to 99.9% by mass of the phosphite ester compound, and 0.1 to 70% by mass of the metal oxide and/or the metal carbonate, relative to 100% by mass of the granular stabilizer product.

[3]The granular stabilizer product according to [1], wherein the granular stabilizer product contains 30 to 99% by mass of the phosphite ester compound, and 1 to 70% by mass of the metal oxide and/or the metal carbonate, relative to 100% by mass of the granular stabilizer product.

[4]The granular stabilizer product according to any one of [1] to [3], further containing a binder.

[5]The granular stabilizer product according to [4], wherein the granular stabilizer product contains 1 to 20% by mass of the binder, relative to 100% by mass of the total amount of the phosphite ester compound, and the metal oxide and/or the metal carbonate.

[6]The granular stabilizer product according to any one of [1] to [5], wherein a shape of the granular stabilizer product is a flake shape and/or pellet shape.

[7]The granular stabilizer product according to [6], wherein the granular stabilizer product having the flake shape has a flake length of 0.5 to 15 mm and a thickness of 0.5 to 5 mm, and wherein the granular stabilizer product having the pellet shape has a pellet diameter of 0.1 to 10 mm and a pellet length of 0.1 to 20 mm.

[8]The granular stabilizer product according to [6], wherein the granular stabilizer product having the flake shape has a flake length of 0.5 to 15 mm and a thickness of 0.5 to 5 mm, and wherein the granular stabilizer product having the pellet shape has a pellet diameter of 0.1 to 5 mm and a pellet length of 0.1 to 10 mm.

[9]A method for producing the granular stabilizer product according to any one of [1] to [8], wherein the granular stabilizer product is obtained from a mixture containing the phosphite ester compound represented by Formula (1), and the metal oxide and/or the metal carbonate using a compression granulator, an extrusion granulator, or a stirring granulator.

EFFECT OF THE INVENTION

[0009]

A granular stabilizer product can be provided that can achieve a stable function of suppressing any thermal degradation and any oxidation degradation when the granular stabilizer product is added to an organic material and that is excellent in the workability because the granular stabilizer product of the present invention tends to avoid any hydrolysis thereof even after being stored for a long time, tends to avoid any bridge phenomenon occurring therein, and can uniformly be added to the organic material.

MODES FOR CARRYING OUT THE INVENTION

[0010]

Embodiments of the present invention will be described.

A granular stabilizer product of the present invention contains a phosphite ester

compound represented by Formula (1), and a metal oxide and/or a metal carbonate.

[0011]

As to the phosphite ester compound represented by Formula (1) in the present invention, substituent groups R^1 , R^2 , R^4 , and R^5 each independently represent a hydrogen atom, an alkyl group having 1 to 8 carbon atom(s), a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms, or a phenyl group. Preferably, the substituent groups R^1 , R^2 , and R^4 are each independently an alkyl group having 1 to 8 carbon atom(s), a cycloalkyl group having 5 to 8 carbon atoms, or an alkylcycloalkyl group having 6 to 12 carbon atoms and, preferably, the substituent group R^5 is a hydrogen atom, an alkyl group having 1 to 8 carbon atom(s), or a cycloalkyl group having 5 to 8 carbon atoms. Representative examples of the alkyl group having 1 to 8 carbon atom(s) include, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, t-pentyl, isooctyl, t-octyl, 2-ethylhexyl, and the like. Representative examples of the cycloalkyl group having 5 to 8 carbon atoms include, for example, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, and the like. Representative examples of the alkylcycloalkyl group having 6 to 12 carbon atoms include, for example, 1-methylcyclopentyl, 1-methylcyclohexyl, 1-methyl-4-isopropylcyclohexyl, and the like. Representative examples of the aralkyl group having 7 to 12 carbon atoms include, for example, benzyl, α -methylbenzyl, α,α -dimethylbenzyl, and the like.

[0012]

Among these, preferably, the substituent groups R^1 and R^4 are each independently a t-alkyl group such as t-butyl, t-pentyl, t-octyl or the like, cyclohexyl, or a 1-methylcyclohexyl group. Preferably, the substituent group R^2 is an alkyl group having 1 to 5 carbon atom(s) such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, t-pentyl, or the like and, especially preferably, is methyl, t-butyl, or t-pentyl. Preferably, the substituent group R^5 is a hydrogen atom or an alkyl group

having 1 to 5 carbon atom(s) such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, t-pentyl, or the like.

[0013]

The substituent group R^3 represents a hydrogen atom or an alkyl group having 1 to 8 carbon atom(s). Examples of the alkyl group having 1 to 8 carbon atom(s) include, for example, alkyl groups same as above. Preferably, the substituent group R^3 is a hydrogen atom or an alkyl group having 1 to 5 carbon atom(s) and, especially preferably, is a hydrogen atom or a methyl group.

[0014]

The substituent group X represents a single bond, a sulfur atom, or a methylene group that may be substituted by an alkyl having 1 to 8 carbon atom(s) or a cycloalkyl having 5 to 8 carbon atoms. Examples of the alkyl having 1 to 8 carbon atom(s) and those of the cycloalkyl having 5 to 8 carbon atoms each substituting the methylene group are those of the alkyl group same as above and those of cycloalkyl group same as above. Preferably, X is a single bond, a methylene group, or a methylene group substituted by methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, or the like.

[0015]

The substituent group A represents an alkylene group having 2 to 8 carbon atoms or a $^*\text{-COR}^7\text{-}$ group (R^7 represents a single bond or an alkylene group having 1 to 8 carbon atom(s), and * represents bonding to the side of oxygen). Representative examples of the alkylene group having 2 to 8 carbon atoms include, for example, ethylene, propylene, butylene, pentamethylene, hexamethylene, octamethylene, 2,2-dimethyl-1,3-propylene, and the like. Preferably, propylene is used. * in the $^*\text{-COR}^7\text{-}$ group represents that carbonyl bonds to oxygen of phosphite. Representative examples of the alkylene group having 1 to 8 carbon atom(s) for R^7 include, for example, methylene, ethylene, propylene, butylene, pentamethylene, hexamethylene, octamethylene, 2,2-dimethyl-1,3-propylene, and the like. Preferably, R^7 is a single bond

or ethylene.

[0016]

As to Y and Z, either one thereof represents a hydroxyl group, an alkoxy group having 1 to 8 carbon atom(s), or an aralkyloxy group having 7 to 12 carbon atoms and the other one thereof represents a hydrogen atom or an alkyl group having 1 to 8 carbon atom(s). Examples of the alkyl group having 1 to 8 carbon atom(s) include, for example, the alkyl groups same as above, and examples of the alkoxy group having 1 to 8 carbon atom(s) include, for example, an alkoxy group whose alkyl portion is alkyl same as the above alkyl having 1 to 8 carbon atom(s). Examples of the aralkyloxy group having 7 to 12 carbon atoms include, for example, an aralkyloxy group whose aralkyl portion is aralkyl same as the above aralkyl having 7 to 12 carbon atoms.

[0017]

Specific examples of the phosphite ester compound represented by Formula (1) include, for example,

6-[3-(3-*t*-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-*t*-butyldibenzo[d,f][1,3,2]dioxaphosphin (Sumilizer (a registered trademark) GP, produced by Sumitomo Chemical Co., Ltd.),

2,10-dimethyl-4,8-di-*t*-butyl-6-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propoxy]-12H-dibenzo[d,g][1,3,2]dioxaphosphocin,

2,4,8,10-tetra-*t*-butyl-6-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propoxy]dibenzo[d,f][1,3,2]dioxaphosphin,

2,4,8,10-tetra-*t*-pentyl-6-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propoxy]-12-methyl-12H-dibenzo[d,g][1,3,2]dioxaphosphocin,

2,10-dimethyl-4,8-di-*t*-butyl-6-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionyloxy]-12H-dibenzo[d,g][1,3,2]dioxaphosphocin,

2,4,8,10-tetra-*t*-pentyl-6-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionyloxy]-12-methyl-12H-dibenzo[d,g][1,3,2]dioxaphosphocin,

2,4,8,10-tetra-*t*-butyl-6-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionyloxy]-dibenzo[d,f][1,3,2]dioxaphosphopin,
 2,10-dimethyl-4,8-di-*t*-butyl-6-(3,5-di-*t*-butyl-4-hydroxybenzoiloxy)-12H-dibenzo[d,g][1,3,2]dioxaphosphocin,
 2,4,8,10-tetra-*t*-butyl-6-(3,5-di-*t*-butyl-4-hydroxybenzoiloxy)-12-methyl-12H-dibenzo[d,g][1,3,2]dioxaphosphocin,
 2,4,8,10-tetra-*t*-butyl-6-[3-(3-methyl-4-hydroxy-5-*t*-butylphenyl)propoxy]dibenzo[d,f][1,3,2]dioxaphosphopin,
 2,10-dimethyl-4,8-di-*t*-butyl-6-[3-(3-methyl-4-hydroxy-5-*t*-butylphenyl)propoxy]-12H-dibenzo[d,g][1,3,2]dioxaphosphocin,
 2,4,8,10-tetra-*t*-butyl-6-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propoxy]-12H-dibenzo[d,g][1,3,2]dioxaphosphocin,
 2,10-diethyl-4,8-di-*t*-butyl-6-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propoxy]-12H-dibenzo[d,g][1,3,2]dioxaphosphocin,
 2,4,8,10-tetra-*t*-butyl-6-[2,2-dimethyl-3-(3-*t*-butyl-4-hydroxy-5-methylphenyl)propoxy]-dibenzo[d,f][1,3,2]dioxaphosphopin, and the like.

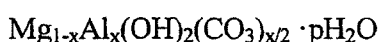
[0018]

The granular stabilizer product of the present invention contains the phosphite ester compound represented by Formula (1) by, for example, 30 to 99.9% by mass, preferably, 30 to 99% by mass, more preferably, 40 to 99% by mass, and, yet more preferably, 50 to 99% by mass, based on the total amount of the granular stabilizer product. When the content of the phosphite ester compound represented by Formula (1) is within any one of the above ranges, this is advantageous because the stabilizing effect is excellent when the granular stabilizer product of the present invention is added to an organic material.

[0019]

Examples of the metal oxide in the present invention include, for example,

silicon-containing oxides [for example, aluminosilicate (aluminum silicate), silica (synthetic silica and natural silica), diatomaceous earth, glass fiber, talc, kaolin, mica, zeolite, or the like], alumina, zinc oxide, titanium oxide, calcium oxide, magnesium oxide, iron oxide, tin oxide, antimony oxide, antimony trioxide, ferrite, and the like. Of these metal oxides, preferably, aluminosilicate, zinc oxide, and the like are used. Examples of the metal carbonate in the present invention include, for example, calcium carbonate, magnesium carbonate, zinc carbonate, barium carbonate, dawsonite, a layered double hydroxide, and the like. Examples of the layered double hydroxide include hydrotalcite. Each of these alone, or two or more thereof in combination may be used. Among these, preferably, hydrotalcite is used. Hydrotalcite is represented by a formula:



[Where x represents a value that is $0 < x \leq 0.5$ and p represents a value that is $0 \leq p$.]

Hydrotalcite may be a natural one or may be a synthesized one, and is usable regardless of its crystalline structure, its crystalline particle size, and the like. For example, DHT-4A (a registered trademark) produced by Kyowa Chemical Industry Co., Ltd., or the like is usable as hydrotalcite.

[0020]

The granular stabilizer product of the present invention contains the metal oxide and/or the metal carbonate by, for example, 0.1 to 70% by mass, preferably, 1 to 70% by mass, more preferably, 1 to 60% by mass, and, yet more preferably, 1 to 50% by mass, based on the total amount of the granular stabilizer product. When the content of the metal oxide and/or the metal carbonate is within any one of the above ranges, this is advantageous because the granular stabilizer product of the present invention tends to avoid any hydrolysis thereof and is excellent in the long-term stability.

[0021]

The granular stabilizer product of the present invention can effectively suppress any hydrolysis of the phosphite ester compound represented by Formula (1) even when

the rate of the metal oxide and/or the metal carbonate is small (or the amount of the metal oxide and/or the metal carbonate is small). Because the rate of the phosphite ester compound represented by Formula (1) can be set to be large, the granular stabilizer product of the present invention can effectively achieve its excellent function of suppressing any thermal degradation and any oxidation degradation for an organic material (for example, a resin or the like) suppressing the hydrolysis thereof. Due to this, for the granular stabilizer product of the present invention, the rate of the metal oxide and/or the metal carbonate can also be set to be, for example, 0.1 to 30% by mass (for example, 0.2 to 20% by mass), preferably, 0.5 to 10% by mass, and, more preferably, 1 to 9% by mass relative to the total amount of the granular stabilizer product. For the granular stabilizer product of the present invention, the rate of the phosphite ester compound represented by Formula (1) can also be set to be, for example, 70 to 99.9% by mass (for example, 80 to 99.8% by mass), preferably, 90 to 99.5% by mass, and, more preferably, 91 to 99% by mass relative to the total amount of the granular stabilizer product.

[0022]

The granular stabilizer product of the present invention may further contain a binder (a binding agent). Preferably, a binder having a melting point equal to or lower than the temperature for the granulation is used as the binder in the present invention, and examples of the binder include, for example, a binder having a melting point equal to or lower than 100°C. Preferably, the binder in the present invention is a low molecular weight binder, and the molecular weight of the binder may be, for example, equal to or lower than 1,000 g/mol (for example, 100 to 900 g/mol), preferably, equal to or lower than 800 g/mol (for example, 150 to 700 g/mol), and, more preferably, equal to or lower than 600 g/mol (for example, 200 to 600 g/mol). Examples of the binder include such agents each having a molecular weight equal to or smaller than 1,000 g/mol and/or a melting point equal to or lower than 100°C, as a phenol-based oxidation inhibitor, a

sulfur-based oxidation inhibitor, a phosphorus-based oxidation inhibitor, a hindered amine-based oxidation inhibitor, an ultraviolet absorbing agent, an antistatic agent, a lubricant, and the like.

[0023]

Examples of the phenol-based oxidation inhibitor used as the binder in the present invention include, for example, n-octadecyl-3-(4-hydroxy-3,5-di-t-butylphenyl)propionate (having a melting point of 50 to 55°C), 2,6-di-t-butyl-4-methylphenol (having a melting point of 69°C (the setting point)), 2,2-thio-di-ethylene-bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (having a melting point equal to or higher than 63°C), and tri-ethyleneglycol-bis-[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate] (having a melting point of 76 to 79°C).

[0024]

Examples of the sulfur-based oxidation inhibitor used as the binder in the present invention include, for example, 3,3'-thio-di-propionic acid di-n-dodecyl ester (having a melting point of 40 to 42°C), 3,3'-thio-di-propionic acid di-n-tetradecyl ester (having a melting point of 49 to 54°C), 3,3'-thio-di-propionic acid di-n-octadecyl ester (having a melting point of 65 to 67°C), and tetrakis(3-dodecyl thiopropionic acid)pentaerythritol ester (having a melting point of about 46°C).

[0025]

Examples of the phosphorus-based oxidation inhibitor used as the binder in the present invention include, for example, tetrakis(2,4-di-t-butylphenyl)-4,4'-biphenylene diphosphonite (having a melting point of 75 to 90°C), and bis-[2,4-di-t-butyl-6-methyl-phenyl]ethylphosphite (having a melting point of 89 to 92°C). The phosphorus-based oxidation inhibitor does not include the phosphite ester compound represented by Formula (1).

[0026]

Examples of the hindered amine-based oxidation inhibitor used as the binder in the present invention include, for example, sebacic acid bis(2,2,6,6-tetramethyl-4-piperidyl) ester (having a melting point of 81 to 86°C), and 2,2,6,6-tetramethyl-4-piperidylmethacrylate (having a melting point of 58°C).

[0027]

Examples of the ultraviolet absorbing agent used as the binder in the present invention include, for example, 2-hydroxy-4-n-octyloxybenzophenon (having a melting point equal to or higher than 45°C), 2-(2H-benzotriazole-2-yl)-4,6-di-t-pentylphenol (having a melting point equal to or higher than 77°C), and 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine-2-yl]-5-(octyloxy)phenol (having a melting point of 87 to 89°C).

[0028]

Examples of the antistatic agent used as the binder in the present invention include, for example, glycerin monostearate (having a melting point of 65 to 70°C), glycerin monocaprates (having a melting point of 46°C), glycerin monolaurate (having a melting point of 57°C), and citric acid fatty acid monoglyceride (having a melting point of 59°C).

[0029]

Examples of the lubricant used as the binder in the present invention include, for example, oleic amide (having a melting point of about 72 to about 77°C), erucamide (having a melting point of 79 to 81°C), propylene glycol monostearate (having a melting point of 42 to 48°C), stearyl stearate (having a melting point of 53 to 59°C), and sorbitan stearate (having a melting point of 52 to 58°C).

[0030]

Preferably, the granular stabilizer product of the present invention contains 1 to 20% by mass of the binder, relative to 100% by mass of the total amount of the phosphite ester compound represented by Formula (1), and the metal oxide and/or the metal

carbonate. When the content of the binder is within the above range, this is advantageous because a granular product having a stable shape can be produced.

[0031]

The granular stabilizer product of the present invention may contain optionally other additives in addition to the phosphite ester compound represented by Formula (1), the metal oxide and/or the metal carbonate, and the binder. Examples of the other additives include additives other than the binder, such as, for example, a phenol-based oxidation inhibitor, a phosphorus-based oxidation inhibitor, a hindered amine-based light stabilizer, an ultraviolet absorbing agent, a filler, a metallic soap containing a fatty acid metal salt and the like, an antistatic agent, an organic antiblocking agent, an inorganic antiblocking agent, a pigment, a flame retardant, and the like.

[0032]

Examples of the phenol-based oxidation inhibitor include, for example, 3,9-bis[2-{3-(3-*t*-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5·5]undecane, tetrakis{3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionic acid}pentaerythrityl ester, 2-*t*-butyl-6-(3-*t*-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate, 2-[1-(2-hydroxy-3,5-di-*t*-pentylphenyl)ethyl]-4,6-di-*t*-pentylphenyl acrylate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene, tris(3,5-di-*t*-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(4-*t*-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, 2,2'-methylenebis(6-*t*-butyl-4-methylphenol), 4,4'-butylidenebis(6-*t*-butyl-3-methylphenol), and 4,4'-thiobis(6-*t*-butyl-3-methylphenol)

[0033]

Examples of the phosphorus-based oxidation inhibitor include, for example, tris(2,4-di-*t*-butylphenyl)phosphite, bis(2,4-di-*t*-butylphenyl)pentaerythritol diphosphite, bis(2,6-di-*t*-butyl-4-methylphenyl)pentaerythritol diphosphite, and

bis(2,4-di-cumylphenyl)pentaerythritol diphosphite. The phosphorus-based oxidation inhibitor does not contain the phosphite ester compound represented by Formula (1).

[0034]

Examples of the hindered amine-based light stabilizer include, for example, poly[{6-(1,1,3,3-tetramethylbutyl)amino-1,3,5-triazine-2,4-diyl}{(2,2,6,6-tetramethyl-4-piperidyl)imino}-1,6-hexamethylene{(2,2,6,6-tetramethyl-4-piperidyl)imino}].

[0035]

Examples of the ultraviolet absorbing agent include, for example, 2-(2-hydroxy-5-methylphenyl)benzotriazole, 2-(3-t-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole, and 2,4-di-t-butylphenyl-3,5-di-t-butyl-4-hydroxybenzoate.

[0036]

Examples of the filler include, for example, barium sulfate, carbon black, carbon fiber, and metal powder.

[0037]

Examples of the metallic soap containing a fatty acid metal salt and the like include, for example, a lithium salt, a magnesium salt, a sodium salt, a calcium salt, a barium salt, an aluminum salt, a zinc salt, or an iron salt of stearic acid, a lithium salt, a magnesium salt, a sodium salt, a calcium salt, a barium salt, an aluminum salt, a zinc salt, or an iron salt of lauric acid, a calcium salt or a zinc salt of behenic acid, and a calcium salt, a magnesium salt, or a zinc salt of 12-hydroxystearic acid.

[0038]

The antistatic agent may be a cationic surface active agent, an anionic surface active agent, a non-ionic surface active agent, an ampholytic surface active agent, or the like. Examples of the cationic surface active agent include, for example, a quarternary ammonium salt-based cationic surface active agent, an amine salt (a primary amine salt, a secondary amine salt, a tertiary amine salt, or a quaternary amine salt), a piridine

derivative, and the like. Examples of the anionic surface active agent include, for example, an alkyl phosphate-based anionic surface active agent, a sulfated oil, a soap, a sulfated ester oil, a sulfated amide oil, sulfated ester salts of olefin, fatty alcohol sulfate ester salts, an alkyl sulfate ester salt, a fatty acid ethyl sulfonate, alkyl naphthalene sulfonate, alkyl benzene sulfonate, succinic acid ester sulfonate, a phosphoric ester salt, and the like. Examples of the non-ionic surface active agent include, for example, a betaine-based ampholytic surface active agent, a partial fatty acid ester of a polyhydric alcohol, an ethylene oxide adduct of a fatty alcohol, an ethylene oxide adduct of a fatty acid, an ethylene oxide adduct of a fatty amino or a fatty acid amide, an ethylene oxide adduct of alkyl phenol, an ethylene oxide adduct of a partial fatty acid ester of a polyhydric alcohol, polyethylene glycol, and the like. Examples of the ampholytic surface active agent include, for example, a carboxylic acid derivative, an imidazoline derivative, and the like. Examples of the antistatic agent also include an alkanolamine [such as, for example, a trialkanolamine (for example, triethanolamine, tripropanolamine, triisopropanolamine, or the like), a dialkanolamine (for example, diethanolamine, dipropanolamine, diisopropanolamine, tetraethanoethylenediamine, tetraisopropanoethylenediamine, or the like), or a monoalkanolamine (for example, dibutylisopropanolamine or the like)].

[0039]

Examples of the organic antiblocking agent include, for example, polymethylmethacrylic acid cross-linked product and the like.

[0040]

Examples of the pigment include, for example, carbon black, a phthalocyanine-based pigment, a quinacridone-based pigment, an isoindolinone-based pigment, a perylene- or a perinin-based pigment, a quinophthalone-based pigment, a diketopyrrolo-pyrrole-based pigment, a dioxazine-based pigment, a disazo condensation-based pigment, and a benzimidazolone-based pigment.

[0041]

Examples of the flame retardant include, for example, decabromobiphenyl, a phosphorus-based flame retardant, and aluminum hydroxide.

[0042]

The granular stabilizer product of the present invention contains preferably 0 to 70% by mass and, more preferably, 0 to 50% by mass of the other additives based on the total amount of the granular stabilizer product. For the granular stabilizer product of the present invention, the total of the contents of the constituent components, that is, the total of the contents of the phosphite ester compound represented by Formula (1), the metal oxide and/or the metal carbonate, and optionally the binder and the other additives is 100% by mass.

[0043]

The granular stabilizer product of the present invention is obtained by granulating a mixture that contains, for example, the phosphite ester compound represented by Formula (1), the metal oxide and/or the metal carbonate, and optionally the binder. The granular stabilizer product of the present invention has a low acid value and tends to avoid any hydrolysis thereof even after being stored for a long time, and its function of suppressing any thermal degradation and any oxidation degradation therefore tends to avoid any dispersion. Examples of the shape of the granular stabilizer product of the present invention include a pellet shape, a ring shape, a flake shape, a tube shape, a hollow shape, a honeycomb shape, and the like. Preferably, the shape of the granular stabilizer product of the present invention is a flake shape or a pellet shape. In the case where the shape of the granular stabilizer product is the flake shape and/or the pellet shape, no bridge phenomenon further tends to occur and the flowing-down property is further high when the granular stabilizer product is added to an organic material. The granular stabilizer product is therefore further excellent in the workability and, at the same time, can be blended more uniformly in the organic material, and its function of

suppressing any thermal degradation and any oxidation degradation therefore further tends to avoid any dispersion.

In the present invention, the flake-shaped granular product refers to a granular product having a shape such as a thin leaf shape (or a thin plate shape), or a scale shape, and the front face or the back face thereof may be a flat face or a curved face. The pellet-shaped granular product refers to a fixed shaped granular product whose thickness is substantially constant, such as a spherical shape, a circular column shape, an elliptical column shape, a polygonal column (for example, a triangle column, a square column, a pentagonal column, a hexagonal column, or the like), or the like, and the cross-section thereof is a circular shape, an elliptical shape, a polygonal shape, or the like. The pellet-shaped granular product may have recesses and protrusions on its surface, and may have a substantially spherical shape, a substantially circular column shape, a substantially elliptical column shape, a substantially polygonal column shape, or the like.

[0044]

When the shape of the granular stabilizer product of the present invention is the flake shape, from the viewpoint of the handling property, the granular stabilizer product of the present invention has a flake length of, preferably, 0.5 to 15 mm and, more preferably, 0.5 to 10 mm, and has a thickness of, preferably, 0.5 to 5 mm and, more preferably, 0.5 to 4 mm. The flake length of the granular stabilizer product refers to the length on the long axis side based on the aspect ratio of the flake-shaped granular product. The thickness of the granular stabilizer product refers to the length between the front face and the back face of the granular product.

In the present invention, the flake length and the thickness can each be measured by, for example, arbitrarily extracting 100 granular stabilizer product flakes, measuring the flake length and the thickness for each one thereof using a ruler, a slide caliper, a micrometer, or the like, and taking the average value.

When the shape of the granular stabilizer product of the present invention is the

pellet shape, from the viewpoint of the handling property, the granular stabilizer product of the present invention has a pellet diameter of, for example, 0.1 to 10 mm (for example, 0.1 to 8 mm), preferably, 0.1 to 5 mm, and, more preferably, 0.5 to 3 mm, and has a pellet length of, for example, 0.1 to 20 mm (for example, 0.1 to 15 mm), preferably, 0.1 to 10 mm and, more preferably, 0.5 to 5 mm. When the granular stabilizer product has the pellet shape, the pellet diameter is the average value of the short diameter and the long diameter of the cross-section (for example, the cross-section having a circular shape or an elliptical shape) and the pellet length is the maximal length of the pellet in a direction perpendicular to the cross-section.

In the present invention, the pellet diameter and the pellet length can be obtained by measuring the short diameter and the long diameter using the same method as that for the flake length and the thickness.

[0045]

The granular stabilizer product of the present invention can be produced to have a predetermined shape (for example, the above shape) using, for example, a commonly used granulation method (for example, a compression granulation method, an extrusion granulation method, a stirring granulation method, a rolling granulation method, a spraying granulation method, a fluid-bed granulation method, or the like) and using a granulator that supports the method (for example, a compression granulator, an extrusion granulator, a stirring granulator, a rolling granulator, a spraying granulator, a fluid-bed granulator, or the like). Examples of an advantageous production method include the compression granulation method, the stirring granulation method, and the extrusion granulation method. The granulation may be dry granulation or may be wet granulation (granulation including the binder and the like).

[0046]

When the granular stabilizer product of the present invention is produced using the compression granulation method, in the present invention, the dry compression

granulation can be conducted and this granulation can be conducted using a known compression granulator (a roller compactor).

When the granular stabilizer product of the present invention is granulated using the dry compression granulation method, this is advantageous because the granulation can be conducted without containing any undesired component such as a solvent. In the dry compression granulation method, for example, a mixture containing the phosphite ester compound represented by Formula (1), and the metal oxide and/or the metal carbonate is kneaded using a single- or a twin-screw extruder. The kneaded mixture is caused to pass through two rolls therebetween that are rotated relatively to each other, to be shaped into a sheet by the pressure generated between the rolls, and the sheet is processed into pieces each having a proper size using a crushing machine. The flake-shaped granular stabilizer product can thereby be obtained. Examples of the compression granulator include, for example, FT160 manufactured by Freund-Turbo Corporation and the like. The size of the granular stabilizer product can be controlled by adjusting the number of rotations of the screw(s) of the compression granulator, the roll compression pressure, the number of rotations of the rolls, the number of rotations of the crushing machine, and the like.

[0047]

When the granular stabilizer product of the present invention is produced using the stirring granulation method, for example, a mixture containing the phosphite ester compound represented by Formula (1), the metal oxide and/or the metal carbonate, and, optionally a binder (the binder is especially advantageously used) is mixed and granulated in the stirring granulator at an increasing temperature. The granular stabilizer product of the present invention can thereby be produced. The stirring granulator includes therein a rotary stirring blade. When the binder is used, preferably, the temperature during this process is equal to or higher than the melting point of the binder. Examples of the stirring granulator include, for example, a high-speed mixer manufactured by

EarthTechnica Co., Ltd., a vertical granulator manufactured by Powrex Corporation, and the like. The size of the granular stabilizer product can be controlled by adjusting the number of rotations of each of the agitator and the chopper of the stirring granulator.

[0048]

When the granular stabilizer product of the present invention is produced using the extrusion granulation method, for example, a mixture containing the phosphite ester compound represented by Formula (1), the metal oxide and/or the metal carbonate, and, optionally a binder is put in the extrusion granulator at an increasing temperature and the extruded mixture is cut into, for example, pellets. The granular stabilizer product can thereby be produced. When the binder is used, preferably, the temperature during the granulation is equal to or higher than the temperature at which the binder is melted, from the viewpoint of the moldability of the granular stabilizer product.

[0049]

Examples of the extrusion granulator include a screw extrusion granulator, a roll extrusion granulator, a disc pelletor extrusion granulator, a pellet mill extrusion granulator, a basket extrusion granulator, a blade extrusion granulator, an oscillating extrusion granulator, a gear extrusion granulator, a ring dice extrusion granulator, and the like. Specific examples of the extrusion granulator include, for example, Disc Pelletor, Twin Dome Gran, Basket Ryuza, and Pelletor Double manufactured by Dalton Corporation, Hata Granulator manufactured by Hata Corporation, and the like. The size of the granular stabilizer product can be controlled by adjusting the various parameters of the extrusion granulator and, for example, for the disc pelletor extrusion granulator, the size can be controlled by adjusting the number of rotations of the disc, and the like. The extrusion granulator (the screw extrusion granulator) may be a single-screw extrusion granulator or may be a twin-screw extrusion granulator. Preferably, the twin-screw extrusion granulator is used especially from the viewpoint of the kneading property (or the mixing property) and, for example, using this, the granular stabilizer product having a

predetermined shape can be highly likely to be obtained even without any binder.

When the granular stabilizer product of the present invention is granulated using the stirring granulation method or the extrusion granulation method as above, this is advantageous because the granulation efficiency is further high and the economic efficiency can be improved.

[0050]

Examples of the organic material to have the granular stabilizer product of the present invention blended therein include, for example, a thermoplastic resin and a thermosetting resin, and include, for example, a polyolefin [for example, a propylene-based resin, an ethylene-based resin (a high density polyethylene (HD-PE), a low density polyethylene (LD-PE), a linear low density polyethylene (LLDPE), an ethylene-ethyl acrylate copolymer, an ethylene-vinyl acetate copolymer, ethylene-vinyl alcohol copolymer, ethylene-methyl methacrylate copolymer, and the like), a cyclic polyolefin, and a methylpentene polymer], a polystyrene [poly(p-methylstyrene), poly(α -methylstyrene), an acrylonitrile-styrene copolymer, a special acrylic rubber-acrylonitrile-styrene copolymer, an acrylonitrile-chlorinated polyethylene-styrene copolymer, and the like], a chlorinated resin (for example, chlorinated polyethylene, polychloroprene, a chlorinated rubber, polyvinyl chloride, polyvinylidene chloride), a methacryl resin, a fluorine resin, polyacetal, a grafted polyphenylene ether resin, a polyphenylene sulfide resin, polyurethane, polyamide, a polyester resin (for example, polyethylene terephthalate, polybutylene terephthalate, polylactic acid, and the like), a polycarbonate, a polyacrylate, a polysulfone, a polyether ether ketone, poly ether sulfone, an aromatic polyester resin, a diallylphthalate prepolymer, a silicone resin, polyisoprene, a butadiene polymer, and the like. Preferably, the ethylene-based resin, the propylene-based resin, the polystyrene, and the butadiene polymer are especially used and, especially preferably, the ethylene-based resin, the propylene-based resin, or the butadiene polymer is used. Any one of these resins alone, or two or more thereof in

combination may be used.

The ethylene-based resin means a polyolefin that contains a structural unit originated from ethylene and that contains no propylene structural unit, and examples thereof include the above exemplified resins.

The propylene-based resin means a polyolefin that contains a structural unit originated from propylene, and examples thereof include resins each containing both of an ethylene structural unit and a propylene structural unit. For example, examples thereof include a crystalline propylene monopolymer, a propylene-ethylene random copolymer, a propylene- α -olefin random copolymer, a propylene-ethylene- α -olefin copolymer, a polypropylene-based block copolymer that includes: a propylene monopolymer component or a copolymer component mainly including propylene; and a copolymer component of propylene, and ethylene and/or α -olefin, and the like.

[0051]

When the propylene-based resin(s) is/are used as the organic material(s) in the present invention, any one of the propylene-based resins alone, or two or more thereof in a blend form may be used.

[0052]

The α -olefin is usually an α -olefin having 4 to 12 carbon atoms and examples thereof include, for example, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, and the like and, more preferably, 1-butene, 1-hexene, and 1-octene are used.

[0053]

Examples of the propylene- α -olefin random copolymer include, for example, a propylene-1-butene random copolymer, a propylene-1-hexene random copolymer, a propylene-1-octene random copolymer, and the like.

[0054]

Examples of the propylene-ethylene- α -olefin copolymer include, for example, a propylene-ethylene-1-butene copolymer, a propylene-ethylene-1-hexene copolymer, a

propylene-ethylene-1-octene copolymer, and the like.

[0055]

Examples of the copolymer component mainly including propylene of the polypropylene-based block copolymer that includes: a propylene monopolymer component or a copolymer component mainly including propylene; and a copolymer component of propylene, and ethylene and/or α -olefin, include, for example, a propylene-ethylene copolymer component, a propylene-1-butene copolymer component, a propylene-1-hexene copolymer component, and the like, and examples of the copolymer component of propylene, and ethylene and/or α -olefin include, for example, a propylene-ethylene copolymer component, a propylene-ethylene-1-butene copolymer component, a propylene-ethylene-1-hexene copolymer component, a propylene-ethylene-1-octene copolymer component, a propylene-1-butene copolymer component, a propylene-1-hexene copolymer component, a propylene-1-octene copolymer component, and the like. The content of the ethylene and/or α -olefin having 4 to 12 carbon atoms in the copolymer component of propylene, and ethylene and/or α -olefin is usually 0.01 to 20% by mass.

[0056]

Examples of the polypropylene-based block copolymer that includes: a propylene monopolymer component or a copolymer component mainly including propylene; and a copolymer component of propylene, and ethylene and/or α -olefin include, for example, a propylene-ethylene block copolymer, a (propylene)-(propylene-ethylene) block copolymer, a (propylene)-(propylene-ethylene-1-butene) block copolymer, a (propylene)-(propylene-ethylene-1-hexene) block copolymer, a (propylene)-(propylene-1-butene) block copolymer, a (propylene)-(propylene-1-hexene) block copolymer, a (propylene-ethylene)-(propylene-ethylene-1-butene) block copolymer, a (propylene-ethylene)-(propylene-ethylene-1-hexene) block copolymer, a

(propylene-ethylene)-(propylene-1-butene) block copolymer, a
(propylene-ethylene)-(propylene-1-hexene) block copolymer, a
(propylene-1-butene)-(propylene-ethylene) block copolymer, a
(propylene-1-butene)-(propylene-ethylene-1-butene) block copolymer, a
(propylene-1-butene)-(propylene-ethylene-1-hexene) block copolymer, a
(propylene-1-butene)-(propylene-1-butene) block copolymer, a
(propylene-1-butene)-(propylene-1-hexene) block copolymer, and the like.

[0057]

When the propylene-based resin is used as the organic material in the present invention, preferably, the propylene-based resin is the crystalline propylene monopolymer, or the polypropylene-based block copolymer that includes: a propylene monopolymer component or a copolymer component mainly including propylene; and a copolymer component of propylene, and ethylene and/or an α -olefin having 4-12 carbon atoms. More preferably, the propylene-based resin is the polypropylene-based block copolymer that includes: a propylene monopolymer component or a copolymer component mainly including propylene; and a copolymer component of propylene, and ethylene and/or an α -olefin having 4-12 carbon atoms.

[0058]

The butadiene polymer in the present invention is a polymer containing a structural unit originated from butadiene, or a hydrogenated product of this polymer. Examples of the butadiene polymer include, for example, a styrene-butadiene copolymer such as a styrene-butadiene rubber (SBR), a styrene-butadiene-styrene copolymer (SBS), or a styrene-butadiene block copolymer (SB), polybutadiene that is a monopolymer of butadiene, an acrylonitrile-butadiene copolymer, an acrylonitrile-butadiene-styrene copolymer (ABS), and the like. The butadiene polymer can be produced using an ordinary method such as, for example, a solution polymerization method, an emulsion polymerization method or a bulk polymerization method. The butadiene polymer may

be a resin or may be a rubber. When the butadiene polymer is polybutadiene, this polybutadiene may be a polybutadiene rubber produced using the solution polymerization method, or may be a polybutadiene rubber produced using the emulsion polymerization method.

[0059]

The granular stabilizer product of the present invention is usually blended by, preferably, 0.0001 to 5 parts by mass, more preferably, 0.0005 to 3 parts by mass, and, yet more preferably, 0.01 to 2 parts by mass relative to 100 parts by mass of the organic material.

[0060]

The granular stabilizer product of the present invention can be blended into the organic material using a wide range of known methods and any one(s) of a wide range of known apparatuses to obtain a uniform mixture. For example, when the organic material is a solid polymer, the granular stabilizer product of the present invention can also be directly dry-blended into the solid polymer. When the organic material is a liquid polymer, the granular stabilizer product of the present invention in the form of a solution or a dispersion liquid can also be blended into a polymer solution in the course of the polymerization or immediately after the polymerization, in addition to the above addition methods. On the other hand, when the organic material is mixed with a fluid medium such as an oil, the granular stabilizer product of the present invention can be directly added to the mixture of the organic material and the fluid medium to be melted therein, or the granular stabilizer product of the present invention can also be added thereto after being melted or suspended in the fluid medium, in addition to the above addition methods.

[0061]

The granular stabilizer product of the present invention has excellent performance as a stabilizer for various types of organic material including a thermoplastic

resin such as a polyolefin. The granular stabilizer product of the present invention tends to avoid any hydrolysis thereof and tends to avoid any bridge phenomenon occurring therein when the granular stabilizer product is added to the organic material. The granular stabilizer product can therefore be uniformly contained in the organic material and can therefore achieve a stable performance without any dispersion generated in its function of suppressing any thermal degradation and any oxidation degradation.

Examples

[0062]

The present invention will be described in more detail with reference to Examples and Comparative Examples while the present invention is not limited at all by Examples and Comparative Examples.

[0063]

(Example 1)

3,789 g of 6-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-t-butylidibenzophosphine (Sumilizer (a registered trademark) GP, produced by Sumitomo Chemical Co., Ltd.) and 211 g of hydrotalcite (DHT-4A (a registered trademark) produced by Kyowa Chemical Industry Co., Ltd.) were mixed with each other using a Henschel mixer. The mixture was thereafter put in a dry granulator (a roller compactor, FT160 manufactured by Freund-Turbo Corporation) to conduct roller compression therefor at a roll pressure of 5.0 MPa, at a powder supply screw rotation rate of 35.0 rpm, and at a roll rotation number of 15.0 rpm. The obtained compressed mixture was crushed using a crushing machine to obtain 4,000 g of a stabilizer "a" that was a flake-shaped dry granular product (having a flake length: 2.0 to 4.0 mm and a thickness: 2.5 mm).

[0064]

(Example 2)

4,000 g of a stabilizer "b" that was a flake-shaped dry granular product (having a flake length: 2.0 to 4.0 mm and a thickness: 3.0 mm) was obtained similarly to Example 1 except the fact that 2,815 g of 6-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-t-butyl-dibenzo[d,f][1,3,2]dioxaphosphin (Sumilizer (a registered trademark) GP, produced by Sumitomo Chemical Co., Ltd.), 296 g of hydrotalcite (DHT-4A (a registered trademark) produced by Kyowa Chemical Industry Co., Ltd.), and 889 g of tris(2,4-di-t-butylphenyl)phosphite were mixed with each other.

[0065]

(Example 3)

4,750 g of 6-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-t-butyl-dibenzo[d,f][1,3,2]dioxaphosphin (Sumilizer (a registered trademark) GP, produced by Sumitomo Chemical Co., Ltd.) and 250 g of zinc oxide (one type, produced by Honjo Chemical Corporation) were mixed with each other using a Henschel mixer. The mixture was thereafter put in a twin-screw extrusion granulator (SET-180 manufactured by Nanjing SUNUP Granulation Equipment Co., Ltd.) and was extruded therefrom at a jacket temperature of 55°C at the screw rotation frequency of 15 Hz to be cooled. The strand-like substance obtained after the cooling was crushed using a crushing machine to obtain 5,000 g of a pellet-shaped stabilizer "c" (having a pellet length: 3.0 to 15.0 mm and a pellet diameter: 3.0 to 5.0 mm).

[0066]

(Example 4)

5,000 g of a pellet-shaped stabilizer "d" (having a pellet length: 3.0 to 15.0 mm and a pellet diameter: 3.0 to 5.0 mm) was obtained similarly to Example 3 except the fact that 4,750 g of 6-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-t-butyl-dibenzo[d,f][1,

3,2]dioxaphosphopin (Sumilizer (a registered trademark) GP, produced by Sumitomo Chemical Co., Ltd.), 125 g of zinc oxide (one type, produced by Honjo Chemical Corporation), and 125 g of hydrotalcite (DHT-4C produced by Kyowa Chemical Industry Co., Ltd.) were mixed with each other.

[0067]

(Example 5)

5,000 g of a pellet-shaped stabilizer "e" (having a pellet length: 3.0 to 15.0 mm and a pellet diameter: 3.0 to 5.0 mm) was obtained similarly to Example 3 except the fact that 4,750 g of

6-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-t-butyl-dibenzo[d,f][1,3,2]dioxaphosphopin (Sumilizer (a registered trademark) GP, produced by Sumitomo Chemical Co., Ltd.) and 250 g of aluminosilicate (JC-50 produced by Mizusawa Industrial Chemicals, Ltd.) were mixed with each other.

[0068]

(Example 6)

5,000 g of a pellet-shaped stabilizer "f" (having a pellet length: 3.0 to 15.0 mm and a pellet diameter: 3.0 to 5.0 mm) was obtained similarly to Example 3 except the fact that 4,750 g of

6-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-t-butyl-dibenzo[d,f][1,3,2]dioxaphosphopin (Sumilizer (a registered trademark) GP, produced by Sumitomo Chemical Co., Ltd.), 125 g of aluminosilicate (JC-50 produced by Mizusawa Industrial Chemicals, Ltd.), and 125 g of hydrotalcite (DHT-4C produced by Kyowa Chemical Industry Co., Ltd.) were mixed with each other.

[0069]

(Example 7)

5,000 g of a pellet-shaped stabilizer "g" (having a pellet length: 3.0 to 15.0 mm and a pellet diameter: 3.0 to 5.0 mm) was obtained similarly to Example 3 except the fact

that 4,750 g of

6-[3-(3-*t*-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-*t*-butyldibenzo[d,f][1,3,2]dioxaphosphopin (Sumilizer (a registered trademark) GP, produced by Sumitomo Chemical Co., Ltd.), 125 g of triisopropanolamine (TIPA produced by Tokyo Chemical Industry Co., Ltd.), and 125 g of hydrotalcite (DHT-4C produced by Kyowa Chemical Industry Co., Ltd.) were mixed with each other.

[0070]

(Example 8)

5,000 g of a pellet-shaped stabilizer "h" (having a pellet length: 3.0 to 15.0 mm and a pellet diameter: 3.0 to 5.0 mm) was obtained similarly to Example 3 except the fact that 4,950 g of

6-[3-(3-*t*-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-*t*-butyldibenzo[d,f][1,3,2]dioxaphosphopin (Sumilizer (a registered trademark) GP, produced by Sumitomo Chemical Co., Ltd.) and 50 g of hydrotalcite (DHT-4C produced by Kyowa Chemical Industry Co., Ltd.) were mixed with each other.

[0071]

(Example 9)

5,000 g of a pellet-shaped stabilizer "i" (having a pellet length: 3.0 to 15.0 mm and a pellet diameter: 3.0 to 5.0 mm) was obtained similarly to Example 3 except the fact that 4,750 g of

6-[3-(3-*t*-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-*t*-butyldibenzo[d,f][1,3,2]dioxaphosphopin (Sumilizer (a registered trademark) GP, produced by Sumitomo Chemical Co., Ltd.) and 250 g of hydrotalcite (DHT-4C produced by Kyowa Chemical Industry Co., Ltd.) were mixed with each other.

[0072]

(Example 10)

1,548 g of

6-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-t-butyl-dibenzo[d,f][1,3,2]dioxaphosphepin (Sumilizer (a registered trademark) GP, produced by Sumitomo Chemical Co., Ltd.), 871 g of hydrotalcite (DHT-4A (a registered trademark) produced by Kyowa Chemical Industry Co., Ltd.), 194 g of tris(2,4-di-t-butylphenyl)phosphite, and 387 g of n-octadecyl-3-(4-hydroxy-3,5-di-t-butylphenyl)propionate (Irganox 1076 produced by BASF) were mixed with each other using a Henschel mixer. The mixture was thereafter put in a disc pelletor (model F-5 manufactured by Dalton Corporation). The material temperature therein was set to be 65 to 75° and a rotary roller was driven at the number of rotations of 132 rpm for the mixture to be extruded from a disc die under the rollers. The extruded mixture was cut immediately thereafter to obtain 3,000 g of a pellet-shaped stabilizer "j" (having a pellet diameter: 3.0 mm and a pellet length: 2.0 to 6.0 mm).

[0073]

(Comparative Example 1)

Only

6-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-t-butyl-dibenzo[d,f][1,3,2]dioxaphosphepin was used as a stabilizer "k" to be Comparative Example.

[0074]

(Comparative Example 2)

947 g of

6-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-t-butyl-dibenzo[d,f][1,3,2]dioxaphosphepin and 53 g of hydrotalcite were dry-blended with each other to obtain a stabilizer "l" as Comparative Example.

[0075]

The hydrolysis resistance was evaluated for each of the stabilizers "a" to "l" produced as above and the flowing-down property was evaluated for each of the stabilizers "a" to "l". The evaluation methods were as follows. The results thereof are

shown in Table 1.

[0076]

(Evaluation of Hydrolysis Resistance)

Each of the stabilizers was stored in a constant temperature and humidity bath at a temperature of 50°C and a humidity of 80%RH for 4 weeks and the acid value thereof was thereafter calculated according to JIS 0070 1992 (a KOH titration method using the color change of phenolphthalein). A lower acid value means higher hydrolysis resistance. The result thereof is shown in Table 1.

[0077]

(Evaluation of Flowing-down Property)

Each of the stabilizers "a" to "f" was stored in a constant temperature and humidity bath at a temperature of 50°C and a humidity of 80%RH for 4 weeks and 100 g of the stabilizer was thereafter put in an infundibulum (with a stopcock) having an aperture of 100 mm and an outer foot diameter of 25 mm. The time period was measured from the time when the stopcock was removed to the time when the overall stabilizer fell down. A shorter falling-down time period means a higher flowing-down property. The result thereof is shown in Table 1.

[0078]

[Table 1]

	Acid Value (mg KOH/g)	Falling-down Time Period (second)
Example 1 (Stabilizer a)	1.66	2.90
Example 2 (Stabilizer b)	1.33	2.14
Example 3 (Stabilizer c)	0.85	2.30
Example 4 (Stabilizer d)	0.34	2.40
Example 5 (Stabilizer e)	1.03	2.41
Example 6 (Stabilizer f)	0.29	2.48

Example 7 (Stabilizer g)	0.29	2.54
Example 8 (Stabilizer h)	0.57	2.63
Example 9 (Stabilizer i)	0.20	2.70
Example 10 (Stabilizer j)	0.66	3.08
Comparative Example 1 (Stabilizer k)	2.30	— *
Comparative Example 2 (Stabilizer l)	2.18	— *

*:The stabilizer did not flow down due to a bridge phenomenon.

INDUSTRIAL APPLICABILITY

[0079]

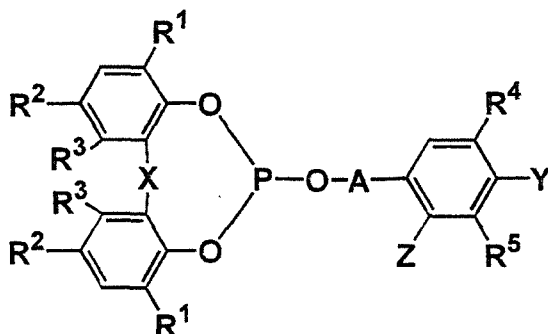
The granular stabilizer product of the present invention tends to avoid any hydrolysis thereof even after being stored for a long time, tends to avoid any bridge phenomenon occurring therein, and can uniformly be added to an organic material. A granular stabilizer product can therefore be provided that can achieve a stable function of suppressing any thermal degradation and any oxidation degradation when the granular stabilizer product is added to an organic material, and that is excellent in the workability.

CLAIMS

1. A granular stabilizer product containing:
a phosphite ester compound represented by

Formula (1):

[Ch. 1]



wherein

R^1 , R^2 , R^4 , and R^5 each independently represent a hydrogen atom, an alkyl group having 1 to 8 carbon atom(s), a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms, or a phenyl group;

R^3 represents a hydrogen atom or an alkyl group having 1 to 8 carbon atom(s);

X represents a single bond, a sulfur atom, or a $-CHR^6-$ group, wherein R^6 represents a hydrogen atom, an alkyl group having 1 to 8 carbon atom(s), or a cycloalkyl group having 5 to 8 carbon atoms;

"A" represents an alkylene group having 2 to 8 carbon atoms or a $^*-COR^7-$ group, wherein R^7 represents a single bond or an alkylene group having 1 to 8 carbon atom(s); $-CO-$ with * represents bonding with an oxygen atom of a phosphite structure in Formula (1);

as to Y and Z, either one thereof represents a hydroxyl group, an alkoxy group having 1 to 8 carbon atom(s), or an aralkyloxy group having 7 to 12 carbon atoms, and another one thereof represents a hydrogen atom or an alkyl group having 1 to 8 carbon

atom(s);

when Y is a hydroxyl group, either R⁴ or R⁵ represents an alkyl group having 3 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms, or a phenyl group;

two R¹s in Formula (1) may be same as each other or may be different from each other;

two R²s in Formula (1) may be same as each other or may be different from each other;

two R³s in Formula (1) may be same as each other or may be different from each other, and

a metal oxide and/or a metal carbonate.

2. The granular stabilizer product according to claim 1, wherein the granular stabilizer product contains 30 to 99.9% by mass of the phosphite ester compound, and 0.1 to 70% by mass of the metal oxide and/or the metal carbonate, relative to 100% by mass of the granular stabilizer product.

3. The granular stabilizer product according to claim 1, wherein the granular stabilizer product contains 30 to 99% by mass of the phosphite ester compound, and 1 to 70% by mass of the metal oxide and/or the metal carbonate, relative to 100% by mass of the granular stabilizer product.

4. The granular stabilizer product according to any one of claims 1 to 3, further containing a binder.

5. The granular stabilizer product according to claim 4, wherein

the granular stabilizer product contains 1 to 20% by mass of the binder, relative to 100% by mass of the total amount of the phosphite ester compound, and the metal oxide and/or the metal carbonate.

6. The granular stabilizer product according to any one of claims 1 to 5, wherein

a shape of the granular stabilizer product is a flake shape and/or a pellet shape.

7. The granular stabilizer product according to claim 6, wherein the granular stabilizer product having the flake shape has a flake length of 0.5 to 15 mm and a thickness of 0.5 to 5 mm, and wherein

the granular stabilizer product having the pellet shape has a pellet diameter of 0.1 to 10 mm and a pellet length of 0.1 to 20 mm.

8. The granular stabilizer product according to claim 6, wherein the granular stabilizer product having the flake shape has a flake length of 0.5 to 15 mm and a thickness of 0.5 to 5 mm, and wherein

the granular stabilizer product having the pellet shape has a pellet diameter of 0.1 to 5 mm and a pellet length of 0.1 to 10 mm.

9. A method for producing the granular stabilizer product according to any one of claims 1 to 8, wherein

the granular stabilizer product is obtained from a mixture containing the phosphite ester compound represented by Formula (1), and the metal oxide and/or the metal carbonate using a compression granulator, an extrusion granulator, or a stirring granulator.