

## GRANULE MASS

## Technical field

The present invention relates to a granule mass  
5 suitable as a plastic additive.

## Background art

It is known that, by adding a phenol-based antioxidant  
to polyolefin such as polyethylene and polypropylene,  
10 oxidation deterioration of a molded polyolefin article  
generated by light or heat is remarkably decreased.

A phenol-based antioxidant is usually a powder having  
a melting point of around 100 °C and a median diameter of 5  
15 to 70 μm, is added to polyolefin with better flowability  
through a hopper without being melted, but dust-proof  
measure was necessary upon addition to polyolefin due to a  
dust generated from a powder of a phenol-based antioxidant.

20 Under such the circumstances, a process for preparing  
a pellet of mixing tetrakis[3-(3,5-di-t-butyl-4-  
hydroxyphenyl)propionyloxymethyl]methane which is one kind  
of a phenol-based antioxidant, and an antacid additive such  
as stearate, heating the mixture to 115 °C to melt a part  
25 of the phenol-based antioxidant, and mixing a 2.5mm pellet-

like phenol-based antioxidant and an antacid additive with an extruder is disclosed in JP-A No. 5-179056 (e.g. Example 1). It is disclosed that the pellet is dust-free even when a binder such as paraffin which is not desirable to  
5 polyolefin is not used, and there is no disorder upon addition to polyolefin.

However, polyolefin obtained by melting and kneading a pellet obtained by heating a phenol-based antioxidant to  
10 100 °C or higher in advance has a problem that heat stability is uneven, and it has also a problem that the polyolefin must be extrusion-molded using an expensive extruder.

#### 15 Disclosure of the invention

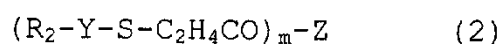
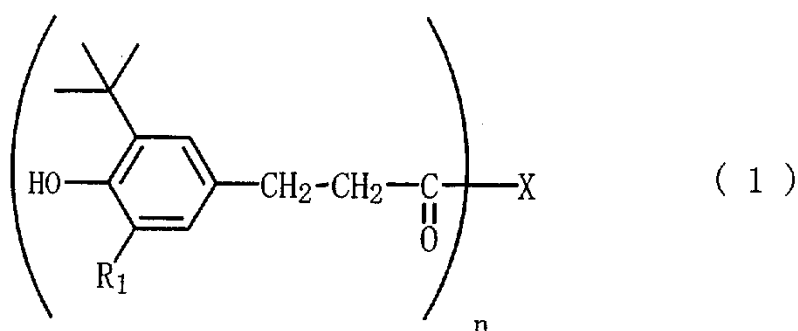
An object of the present invention is to provide a granule mass containing an antioxidant as a main component, which is excellent in flowability, produces little dust from an additive, and can be prepared by a simple facility  
20 when an additive such as an antioxidant is added to a plastic such as polyolefin, and affords a plastic having thermal stability which is hardly ununiformized, and a process for producing the same.

25 That is, the present invention provides the following

[1] to [12].

[1] A granule mass comprising a granule containing a phenol-based antioxidant represented by the following  
 5 formula (1) and a sulfur-based antioxidant represented by the following formula (2), wherein a content of the sulfur-based antioxidant (2) relative to a total of 100 parts by weight of the phenol-based antioxidant (1) and the sulfur-based antioxidant (2) is 3 to 70 parts by weight.

10



15 [in the formula (1),  $\text{R}_1$  represents an alkyl group of a carbon number of 1 to 8, X represents a n-hydric alcohol residue of a carbon number of 1 to 18 optionally containing a heteroatom and/or a cyclic group, and n represents an integer of 1 to 4,

20 in the formula (2),  $\text{R}_2$  represents an alkyl group of a carbon number of 12 to 18, Y represents a single bond or a

-C<sub>2</sub>H<sub>4</sub>CO<sub>2</sub>- group, Z represents a m-hydric alcohol residue of a carbon number of 5 to 18, and m represents an integer of 1 to 4]

5        [2] The granule mass according to [1], wherein a median diameter (based on weight) of a granule contained in the granule mass is 0.1 to 5 mm.

         [3] The granule mass according to [1] or [2], wherein  
10 a dust flying rate of the granule mass measured by a Heubach test is not more than 1% by weight.

         [4] The granule mass according to any one of [1] to [3], wherein the sulfur-based antioxidant represented by  
15 the formula (2) is at least one kind selected from the group consisting of 3,3'-thiodipropionic acid di-n-dodecyl ester, 3,3'-thiodipropionic acid di-n-tetradecyl ester and 3,3'-thiodipropionic acid di-n-octadecyl ester.

20        [5] The granule mass according to any one of [1] to [4], wherein the phenol-based antioxidant represented by the formula (1) is at least one kind selected from the group consisting of 3,9-bis[2-{3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-  
25 tetraoxaspiro[5·5]undecane, tetrakis[3-(3,5-di-t-butyl-4-

hydroxyphenyl)propionic acid] pentaerythrityl ester and bis{3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionic acid} triethyleneglycolyl ester.

5        [6] The granule mass according to any one of [1] to [5], which further contains at least one kind additive selected from the additive group consisting of a neutralizing agent, a lubricant, a phosphate antioxidant, a hindered amine-based light stabilizer, an ultraviolet  
10 absorbing agent, a metal soap, an antistatic agent, an anti-blocking agent, a pigment, a flame-retardant, a filler, and a phenol-based antioxidant other than the phenol-based antioxidant represented by the formula (1).

15        [7] A process for producing a granule mass, comprising stirring-granulating a mixture containing a sulfur-based antioxidant represented by the formula (2) and a phenol-based antioxidant represented by the formula (1) in a temperature range of 40 to 70 °C, wherein the content of  
20 the sulfur-based antioxidant (2) relative to a total of 100 parts by weight of phenol-based antioxidant (1) and the sulfur-based antioxidant (2) is 3 to 70 by weight.

      [8] The process according to [7], wherein stirring-  
25 granulation is performed with a stirring granulator having a stirring wing in the interior of the stirring granulator, and having a clearance between a tip of the stirring wing

and a wall surface of the interior of the stirring granulator, of not more than 30 mm.

[9] A plastic composition characterized in that 0.005  
5 to 5 parts by weight of a granule mass as defined in any  
one of [1] to [6] is incorporated into 100 parts by weight  
of a plastic.

[10] The composition according to [9], wherein the  
10 plastic is a thermoplastic resin.

[11] The composition according to [10], wherein the  
plastic is polyolefin.

15 [12] A method of stabilizing a plastic, comprising  
incorporating 0.005 to 5 parts by weight of a granule mass  
as defined in any one of [1] to [6] into 100 parts by  
weight of the plastic.

## 20 Brief Description of the drawings

Fig. 1 is a schematic cross-sectional view of a  
stirring granulator (high speed mixer) used in Examples.

Fig. 2 is an outline view of an extruder used in  
25 Comparative Example 2.

Explanation of symbols

- 1 Cylinder-type container
- 2 Stirring wing
- 3 Chopper
- 5 4 Motor
- 5 Bag filter
- 6 Granule discharge part
- (A) Adaptor part
- Position for measuring maximum temperature of mixture at
- 10 adaptor part
- (B) Extrusion port
- (C) Heat mixing part
- (C1) to (C4) Position for set temperature of heat mixing part
- 15 (D) Die part
- Position for set temperature of die part
- (E) Screw cylinder
- (H) Raw material charging part

20 Mode for carrying out the invention

The present invention will be described in detail below.

A phenol-based antioxidant used in the present

invention is a compound represented by the formula (1).

As  $R_1$  in the phenol-based antioxidant (1), a methyl group, a t-butyl group, a t-pentyl group or a t-octyl group is preferable, and a methyl group or a t-butyl group is particularly preferable.

X in the phenol-based antioxidant (1) represents a n-hydric alcohol residue of a carbon number of 1 to 18, and the alcohol residue refers to a group in which a hydrogen atom has left from a hydroxy group of an alcohol.

As X, a triethylene glycol residue, a pentaerythritol residue or a 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane residue is preferable and, particularly, a pentaerythritol residue or a 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane residue is preferable. And, n in the phenol-based antioxidant (1) is preferably 2 or 4.

A melting point of the phenol-based antioxidant (1) is usually around 70 to 220 °C, preferably 70 to 150 °C, further preferably 100 to 130 °C.

When a melting point of the phenol-based antioxidant

(1) is not higher than 220 °C, there is a tendency that dispersity in a plastic is improved and, when the melting point is not lower than 70 °C, there is a tendency that adhesion between the antioxidants themselves at storage  
5 under a high temperature is suppressed, being preferable.

Examples of the phenol-based antioxidant (1) include 3,9-bis[2-{3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-  
10 tetraoxaspiro[5.5]undecane, bis{3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionic acid} triethylene glycolyl ester, and tetrakis{3-(3,5-di-t-butyl-4-hydroxyphenyl)propionic acid} pentaerythrityl ester.

15 A median diameter based on weight of the phenol-based antioxidant (1) is usually around 1 to 100 µm, preferably around 5 to 70 µm. When a median diameter of the phenol-based antioxidant is not less than 1 µm, there is a tendency that a time for producing a granule is shortened,  
20 and a heating temperature is lowered and, on the other hand, when the median diameter is not more than 100 µm, a high fluidity index is exhibited in many cases, even when not granulated.

25 A fluidity index in the present invention is a Carr's

fluidity index, in which four kinds of values of a repose angle, compressibility, a spatula angle, and a uniformity degree or an aggregation degree of a granule mass are measured, each of them is scored using an index having a maximum of 25, which has been empirically obtained in many powders and particles, and the fluidity index is expressed by a total of these indices (maximum 100; minimum 0) [see "Terminology Dictionary For Powder Technology" edited by The Society of Powder Technology, Japan, 2nd edition, Nikkan Kogyo Shinbun, LTD, March 30, 2000, p.56-p.57].

A sulfur-based antioxidant used in the present invention is a compound represented by the formula (2).

In the sulfur-based antioxidant (2),  $R_2$  is preferably a dodecyl group, a tetradecyl group or an octadecyl group. And,  $m$  is preferably 1 or 4.

$Z$  in the sulfur-based antioxidant (2) represents a  $m$ -hydric alcohol residue of a carbon number of 5 to 18, and an alcohol residue refers to a group in which a hydrogen atom is left from a hydroxy group of an alcohol.

As  $Z$ , a dodecyl alcohol residue, a tetradecyl alcohol residue, an octadecyl alcohol residue or a pentaerythritol

residue is preferable.

In particular, when Y in the sulfur-based antioxidant (2) is a single bond, a compound in which  $R_2$  is a dodecyl group, m is 4, and Z is a pentaerythritol residue is preferable.

When Y is a  $-C_2H_4CO_2-$  group, it is preferable that  $R_2$  is a dodecyl group, a tetradecyl group or an octadecyl group, m is 1, and Z is an alcohol residue of a carbon number of 12 to 18 corresponding to  $R_2$ .

Specific examples of the sulfur-based antioxidant which can be used in the present invention include the following compounds:

3,3'-thiodipropionic acid di-n-dodecyl ester,  
3,3'-thiodipropionic acid di-n-tetradecyl ester,  
3,3'-thiodipropionic acid di-n-octadecyl ester,  
20 tetrakis(3-dodecylthiopropionic acid) pentaerythrityl ester

In the granule mass of the present invention, a content of the sulfur-based antioxidant (2) based on a total of 100 parts by weight of the phenol-based antioxidant (1) and the sulfur-based antioxidant (2) is 3

to 70 parts by weight, preferably 8 to 35 parts by weight. When a content of the sulfur-based antioxidant (2) is not less than 3 parts by weight, there is a tendency of shortening in a time for producing a granule, lowering of a heating temperature, and improvement in a fluidity index, being preferable. When the content is not more than 70 parts by weight, there is a tendency that production of a coarse granule is suppressed and this is preferable: When the content is not more than 35 parts by weight, there is a tendency that production of a coarse granule is further suppressed, a size of a granule is easily controlled, and this is particularly preferable.

In the case where the granule mass of the present invention contains an additive described later, when not less than 8 parts by weight of the sulfur-based antioxidant (2) is mixed, a time for producing a granule is shortened, a heating temperature is lowered, and this is particularly preferable.

20

In addition, in the granule mass of the present invention, a content of the phenol-based antioxidant (1) based on a total of 100 parts by weight of the phenol-based antioxidant (1) and the sulfur-based antioxidant (2) is usually 97 to 30 parts by weight.

In the present invention, it is not meant that the phenol-based antioxidant (1) and the sulfur-based antioxidant (2) are contained in each one granule at the above-mentioned weight ratio, but it is meant that a  
5 granule mass meaning all granules is constructed such that it contains the phenol-based antioxidant (1) and the sulfur-based antioxidant (2) at the above-mentioned weight ratio.

10 The granule mass of the present invention means a granule aggregate of an irregular shape described in JIS-Z 8841 (1993) Item 10, Explanation Table 1, Shape and Name of Granulated Material.

15 The granule mass of the present invention may further contain at least one additive selected from the following additive group in such the range that granulation property (granulation operability) is not influenced. Usually, a total content of the additives in the granule mass is  
20 around 0 to 90% by weight. As the additive, an organic additive or an inorganic additive having a melting point of not lower than 70 °C is preferable from a viewpoint of granulation property.

A median diameter based on weight of an additive used in the present invention is preferably in a range of 0.1 to 100  $\mu\text{m}$ , particularly preferably in a range of 0.5 to 70  $\mu\text{m}$ . When a commercially available additive is used as it is, it is preferable that the additive is adjusted to a preferable median diameter based on weight by the known method in advanced and, thereafter, it is used.

[Additive group: neutralizing agent, lubricant, phosphorus-based antioxidant, hindered amine-based light stabilizer, ultraviolet absorbing agent, filler, metal soap, antistatic agent, anti-blocking agent, pigment, flame-retardant, and phenol-based antioxidant other than the phenol-based antioxidant (1)]

Examples of the additive include the following compounds: neutralizing agents such as synthetic hydrotalcite, natural hydrotalcite, calcium hydroxide etc.; lubricants such as oleic acid amide, erucic acid amide, polyethylene wax etc.; phosphorus-based antioxidants such as 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, bis(2,4-di-cumylphenyl)pentaerythritol diphosphite, tetrakis(2,4-di-t-butylphenyl)-4,4'-diphenylene diphosphonite, 6-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propoxy]-2,4,8,10-tetra-t-

butyldibenz[d,f][1,3,2]dioxaphosphine etc.;

hindered amine-based light stabilizers such as bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, poly[{6-(1,1,3,3-tetramethylbutyl)amino-1,3,5-triazin-2,4-diyl}{(2,2,6,6-tetramethyl-4-piperidyl)imino}-1,6-hexamethylene{(2,2,6,6-tetramethyl-4-piperidyl)imino}] etc.;

ultraviolet absorbing agent such as 2-(2-hydroxy-5-methylphenyl)benzotriazole, 2-(3-t-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole, 2,4-di-t-butylphenyl  
 10 3,5-di-t-butyl-4-hydroxybenzoate etc.;

filler such as calcium carbonate, silicate, glass fiber, talc, kaolin, mica, barium sulfate, carbon black, carbon fiber, zeolite, metal powder, metal oxide etc.; metal soap containing a fatty acid metal salt such as a lithium salt,  
 15 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 palmitic acid, a lithium salt,  
 20 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, a calcium salt, a magnesium salt or a zinc salt of 12-hydroxystearic acid etc.;

25 the following antistatic agent;

cationic surfactant of quaternary ammonium salt-type,  
amphoteric surfactant of betaine-type, anionic surfactant  
of alkyl phosphate-type, cationic surfactant such as  
primary amine salt, secondary amine salt, tertiary amine  
5 salt, quaternary amine salt and pyridine derivative,  
anionic surfactant such as sulfated oil, soap, sulfated  
ester oil, sulfated amide oil, sulfated ester salt of  
olefin, fatty alcohol sulfate ester salt, alkyl sulfate  
ester salt, fatty acid ethyl sulfonate salt,  
10 alkyl naphthalenesulfonate salt, alkyl benzenesulfonate salt,  
succinic acid ester sulfonate salt and phosphate ester salt,  
antistatic agent such as nonionic surfactant such as  
polyhydric alcohol partial fatty acid ester, fatty alcohol  
ethylene oxide adduct, fatty acid ethylene oxide adduct,  
15 fatty amine or fatty acid amide ethylene oxide adduct,  
alkyl phenol ethylene oxide adduct, polyhydric alcohol  
partial fatty acid ester ethylene oxide adduct and  
polyethylene glycol, amphoteric surfactant such as  
carboxylic acid derivative and imidazoline derivative and,  
20 among them, antistatic agent having a melting point  
exceeding 70 °C,  
inorganic anti-blocking agent such as aluminum silicate,  
synthetic silica, natural silica, zeolite, kaolin and  
diatomaceous earth, or organic anti-blocking agent such as  
25 cross-linked polymethyl methacrylate;

- pigment such as carbon black, titanium oxide, phthalocyanine-based pigment, quinacridone-based pigment, isoindolinone-based pigment, perylene or perynine-based pigment, quinophthalone-based pigment, diketopyrrolo-
- 5 pyrrole-based pigment, dioxazine-based pigment, bisazofused-based pigment and benzimidazolone-based pigment; flame-retardant such as decabromobiphenyl, antimony trioxide, phosphate-based flame-retardant, aluminum hydroxide etc,;
- 10 phenol-based antioxidant other than the phenol-based antioxidant (1) such as 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-
- 15 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), 4,4'-thiobis(6-t-
- 20 butyl-3-methylphenol) etc.

The process of the present invention comprises stirring-granulating a mixture containing a sulfur-based antioxidant represented by the formula (2) and a phenol-

25 based antioxidant represented by the formula (1) in a temperature range of 40 to 70 °C, wherein the content of

the sulfur-based antioxidant (2) relative to a total of 100 parts by weight of phenol-based antioxidant (1) and the sulfur-based antioxidant (2) is 3 to 70 by weight.

5        Specifically, a phenol-based antioxidant (1), a sulfur-based antioxidant (2) and, if necessary, an additive other than (1) and (2) are placed into a stirring granulator, and the mixture is stirred at a temperature of the mixture measured with a thermometer disposed in the  
10 interior of the granulator, of 40 to 70 °C, preferably 45 to 55 °C. When a temperature of the mixture is not lower than 40 °C, since there is a tendency that a time for preparing a granule is shortened, this is preferable. When the temperature is not higher than 70 °C, since there is a  
15 tendency that the antioxidizing ability of a granule is improved, this is preferable.

Examples of a method of heating a stirring granulator include a method of setting utilizing heat production  
20 resulting from a shear force when an antioxidant and the like in a stirring granulator are stirred, a method of raising a temperature by passing a heating medium through a jacket or the like of a stirring granulator, and a method of combining of them.

25

Examples of a method of placing an additive such as an

antioxidant into a stirring granulator include a method of placing a phenol-based antioxidant (1), a sulfur-based antioxidant (2) and, if necessary, an additive at once, followed by stirring-granulation, a method of placing a  
5 phenol-based antioxidant (1) and, if necessary, an additive at once, stirring the mixture, raising a temperature to a desired temperature, placing a sulfur-based antioxidant (2), and stirring-granulating the mixture, and a method of similarly raising a temperature to a desired temperature  
10 while the mixture is stirred, spraying a sulfur-based antioxidant (2) which has been warmed to liquid, and stirring-granulating this.

In the process of the present invention, unlike the  
15 previous extrusion molding, mixing and granulating can be performed in one stirring granulator.

Among them, since a method of placing a phenol-based antioxidant (1), a sulfur-based antioxidant (2) and, if  
20 necessary, an additive at once, and stirring-granulating the mixture, if necessary, while warming the mixture is simple, it is preferable.

A stirring granulator used in the present invention is  
25 an internal stirring-type granulator usually having a

stirring wing in the interior thereof, and having a clearance between a tip of a stirring wing and a wall surface in the interior of a stirring granulator of usually not more than 30 mm, preferably around 0.1 to 5 mm (about 1 5 mm in Examples).

Examples of the stirring granulator include a vertical-type mixer such as a high speed mixer (stirring rolling granulator), a Henschel mixer (high speed stirring 10 granulator), a particle granulator, Pharma-Matrix, a supermixer, a GRAL-Gral, a Schugi mixer, a high speeder, a new speed kneader and the like, and a horizontal-type mixer such as a Lodige mixer, a Spartan granulator, a pin mixer and the like. The stirring granulator may be provided with 15 a stirring wing called chopper which is subjected to grinding and particle size adjustment of a coarse granulated particle, unlike a stirring wing for granulation.

A stirring wing of a high speed mixer used in Examples 20 will be explained in more detail. A cross-section of a stirring wing is inclined from a bottom at an angle of 10 to 50° (in Examples, 30 to 45° for a central part, and 20 to 25° for a tip), and a mixture containing an antioxidant, and a produced granule are scooped up from a bottom.

A shape of a wing end contacting with a wall surface in the interior of a stirring granulator may be conveniently designed. In the case of a high speed mixture used in Examples, there is inclination toward a central  
5 part, a mixture is scooped up to a central part, so that a mixture does not reside on a corner between a bottom and a wall surface.

A stirring rate is different depending on a shape of a  
10 selected stirring wing, but usually, a wing tip rate is around 2 to 40 m/s, preferably 4 to 20 m/s. When a wing tip rate is not higher than 40 m/s, since there is a tendency that grinding of a produced granule with a stirring wing is suppressed, this is preferable. When the  
15 rate is not lower than 2 m/s, since there is a tendency that flowability of the resulting granule is improved, this is preferable.

When mixed with a stirring granulator, from a  
20 viewpoint of suppression of deterioration in an antioxidant, it is preferable to mix under the inert gas atmosphere such as nitrogen.

After completion of mixing, from a viewpoint of  
25 suppression of deterioration in an antioxidant, it is

preferable to cool the mixture lower than a temperature of the interior of the granulator, more preferably at a temperature of about 40 °C to about 0 °C by passing the cold air, or retaining a granule in a refrigerator.

5

In addition, in order to stabilize quality of the resulting granule, a large granule (for example, 5 mm or more, preferably 3 mm or more) or a small granule (for example, 0.1 mm or less, preferably 0.3 mm or less, more  
10 preferably 0.5 mm or less) may be removed with a sieve.

The thus obtained granule mass of the present invention is the aforementioned granule aggregate, and the granule has a median diameter based on weight of 0.1 to 5  
15 mm. And, a granule mass having a dust flying rate in a Heubach test of not more than 1% by weight has a small dust flying amount at handling, and is preferable also from a viewpoint of working environment. Particularly, a granule mass consisting of granules having a median diameter based  
20 on weight of 0.1 to 2 mm is better in dispersity upon corporation into a plastic.

The granule mass of the present invention is suitable as a stabilizing agent for a plastic which easily undergoes  
25 deterioration due to heat or light.

Examples of the plastic include a thermoplastic resin. As the thermoplastic resin, polyolefin having MI (melt index), when a load 2.16 kg is applied at 230 °C, in a range of 0.01 to 100 is preferable. In addition, a plastic 5 having a median diameter based on weight in a range of 0.1 to 10 mm is preferable.

Examples of the plastic includes a polyolefin-based resin (polyethylene, polypropylene, ethylene-vinyl acetate 10 copolymer etc.), a polystyrene-based resin (GP-PS, HI-PS, styrene-butadiene copolymer, acrylonitrile-styrene-butadiene copolymer etc.), a polyamide based resin (6 nylon, 12 nylon etc.), cyclic polyolefin, chlorine-containing polymer (polyvinyl chloride, chlorinated rubber etc.), 15 polyester (polyethylene terephthalate, polybutylene terephthalate etc.), polyurethane, engineering plastic (polyphenylene ether, polycarbonate etc.) and the like.

As a plastic, a thermoplastic resin is preferable and, 20 inter alia, polyolefin is preferable.

These plastics can be stabilized by adding the granule mass of the present invention.

An addition amount of the granule mass is preferably in a range of 0.005 to 5 parts by weight, more preferably in a range of 0.01 to 1 part by weight based on 100 parts by weight of the plastic. When the amount is not less than  
5 0.005 part by weight, since there is a tendency that heat stability of a plastic is improved, this is preferable. When the amount is not more than 5 parts by weight, since there is a tendency that properties possessed by a plastic are not deteriorated, and bleeding of an additive is  
10 reduced, this is preferable.

Examples of a method of incorporating the granule mass of the present invention into a plastic include a method of mixing the granule mass and a plastic, and melting and  
15 kneading the mixture with an extruder, a method of feeding a solution obtained by dissolving or suspending a granule mass in a solvent in advance, to a solution after polymerization of a plastic and, thereafter, removing the solvent by a method such as evaporation, distillation and  
20 the like.

The thus stabilized plastic can be processed, for example, into a product such as a film, a molded material and a pipe by the known method.

The granule mass of the present invention produces little dust, and is excellent in flowability, and a plastic obtained by melting and kneading the granule mass of the present invention is excellent in heat stability and the  
5 heat stability is scarcely varied. In addition, according to the process for producing the granule mass of the present invention, it is possible to produce a granule mass with simple facilities.

#### 10 Examples

The present invention will be described in more detail based on Examples, but it is needless to say that the present invention is not limited by these Examples.

#### 15 (Stirring granulator)

In Examples, a high speed mixer was used in which a stirring wing 2 of three blades having a rotation axis was provided on a bottom of a vertical-type upwardly narrowed cylindrical-type container 1, and a chopper 3 was disposed  
20 from a side wall in a horizontal direction. A raw material such as antioxidant was placed therein through a charging inlet (not shown) disposed on an upper part of a container 1. In addition, nitrogen was supplied to a container 1 from a line (not shown) to prevent deterioration of an  
25 antioxidant, and a bag filter 5 was disposed so that a raw

material was not discharged from a container 1. A cooled granule was taken out through a granule discharging part 6.

(Determination of median diameter)

5        A median diameter based on weight was measured using a fully automatical sound-type sieving robot sifter RPS-85c manufactured by Seishin Enterprise Co. LTD.

(Dust flying rate)

10       A dust flying rate was measured using a dustmeter type I manufactured by Dr. Hans Heubach GmbH & Co. KG. As a measuring method, a test material was placed into a dust forming unit having a diameter of 277.2 mm and a volume of 2.2 L, the unit was rotated at 36 rpm, the air was passed  
15 at an airflow quantity of 15 L/min and, when an airflow quantity reached 500 L, an amount of fine powders produced on a filter was measured, and weight % relative to a test material used was obtained.

20 (Fluidity index)

A fluidity index was determined by measuring a bulk density, a repose angle, a spatula angle and a uniformity degree using a powder tester manufactured by Hosokawa Micron (see Chemical Technology Handbook, revision 5,  
25 p.254).

Raw materials used in the following Examples, Comparative Examples, Reference Examples are shown in the following Tables 1 to 3.

5 Table 1

| Phenol-based antioxidant |                                                                                                                          | Melting point (°C) | Median diameter |
|--------------------------|--------------------------------------------------------------------------------------------------------------------------|--------------------|-----------------|
| (1-1)                    | 3,9-Bis[2-{3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5·5]undecane | 110~120            | 30 μm           |
| (1-2)                    | Tetrakis{3-(3,5-di-t-butyl-4-hydroxyphenyl)propionic acid} pentaerythrityl ester                                         | 113~116            | 25 μm           |

Table 2

| Sulfur-based antioxidant |                                                 |
|--------------------------|-------------------------------------------------|
| (2-1)                    | 3,3'-Thiodipropionic acid di-n-tetradecyl ester |
| (2-2)                    | 3,3'-Thiodipropionic acid di-n-octadecyl ester  |

Table 3

| Other additive |                                      | Melting point (°C) |
|----------------|--------------------------------------|--------------------|
| (3)            | Tris(2,4-di-t-butylphenyl) phosphite | 183~187            |
| (4)            | Calcium stearate                     | 150~158            |

10

(Example 1: Production of granule mass a)

Into a high speed mixer (manufactured by Fukae Powtec

Co. LTD.; volume 10 L) were placed 751 g of a phenol-based antioxidant (1-1) and 751 g of a sulfur-based antioxidant (2-1). After placement, the materials were mixed for 3 minutes at a rotation number of a stirring wing of 240 rpm and a rotation number of a chopper blade of 2000 rpm. Thereafter, when the mixer was operated by increasing a rotation number of a stirring wing to 400 rpm, a temperature of the mixture was raised to 45 °C after 12 minutes. At this point, stirring was stopped, and the mixture was cooled to room temperature. The title additive granule mass a for a plastic was obtained at an amount of 1.5 kg.

(Examples 2 to 6: Production of granule masses b to f)

According to the same procedure as that of Example 1 except that a raw material corresponding to each of Examples 2 to 6 described in Table 4 was used in place of raw material antioxidants (1-1) and (2-1) used in Examples 1, granule masses b to f were produced. A granulation temperature is also described in Table 4.

Table 4

|                       | Granule mass | Phenol-based antioxidant |               |                | Sulfur-based antioxidant |               |                | Other additive |             |                | Granulation temperature<br>[°C] |
|-----------------------|--------------|--------------------------|---------------|----------------|--------------------------|---------------|----------------|----------------|-------------|----------------|---------------------------------|
|                       |              | (1-1),<br>[g]            | (1-2),<br>[g] | Content<br>(%) | (2-1),<br>[g]            | (2-2),<br>[g] | Content<br>(%) | (3),<br>[g]    | (4),<br>[g] | Content<br>(%) |                                 |
| Example 1             | a            | 751                      | -             | 50             | 751                      | -             | 50             | -              | -           | -              | 45                              |
| Example 2             | b            | 1400                     | -             | 92             | 130                      | -             | 8              | -              | -           | -              | 52                              |
| Example 3             | c            | 1430                     | -             | 95             | 72                       | -             | 5              | -              | -           | -              | 46                              |
| Example 4             | d            | 214                      | -             | 14             | 429                      | -             | 29             | 429            | 429         | 57             | 46                              |
| Example 5             | e            | -                        | 214           | 14             | 429                      | -             | 29             | 429            | 429         | 57             | 45                              |
| Example 6             | f            | 1200                     | -             | 80             | -                        | 301           | 20             | -              | -           | -              | 62                              |
| Comparative Example 1 | g            | 1500                     | -             | 100            | -                        | -             | 0              | -              | -           | -              | Granulation impossible          |
| Comparative Example 2 | a'           | 1000                     | -             | 50             | 1000                     | -             | 50             | -              | -           | -              | 47                              |

A content indicates a weight ratio of a phenol-based antioxidant, a sulfur-based antioxidant, or other additive letting a whole granule mass to be 100%.

(Comparative Example 1: Production of additive mixture g)

According to the same procedure as that of Example 1 except that a raw material described in Comparative Example 1 in Table 4 was mixed at a weight described in Table 4 in place of the raw material used in Example 1, granulation was tried, but an additive mixture g (powdery) was obtained without being granulated.

10 (Comparative Example 2: Production of additive cylindrical pellet mass a')

Into a 10 L Henschel mixer were placed 1000 g of a phenol-based antioxidant (1-1) and 1000 g of a sulfur-based antioxidant (2-1), and the materials were mixed for 30 seconds at a rotation number of a stirring wing of 2400 rpm to obtain a mixture. The mixture was placed into a 30 mmφ biaxial extruder (manufactured by Nakatani Machine Co. LTD.) through a hopper (H) described in Fig 2. As operation condition, C1 is 35 °C, C2 is 40 °C, C3 is 40 °C, 15 C4 is 40 °C, A is 47 °C, D is 47 °C, and a rotation number of a screw is 40 rpm. When extrusion granulation was performed under the above condition, a strand-like composition having a diameter of 4 mmφ was obtained. This composition was cut into a length of about 5 mm using a 20 cutter, to obtain an additive cylindrical pellet mass a'.  
25

C1 to C4 indicate a set heating temperature of a heat mixing part (cylinder part) of an extruder shown in Fig 2. D indicates a set heating temperature of a die part of an extruder shown in Fig 2.

5

Example 7 (Measurement of physical properties of granule masses a to f, mixture g and cylindrical pellet mass a')

A median diameter based on weight, and a dust flying rate in a Heubach test of granule masses, a mixture and a  
10 cylindrical pellet mass a to g and a' produced in Examples 1 to 6, Comparative Example 1 and Reference Example 1 were measured, and results are described in Table 5.

Since as a dust flying rate is smaller, dust flying at  
15 handling is reduced, this means that working environment was improved.

Therefore, granule masses a to f of the present invention have a small dust flying rate, and working  
20 environment is improved.

Table 5

|                       | Granule mass | Median diameter DP50 (mm) | Dust flying rate (%) | Fluidity index (%) |
|-----------------------|--------------|---------------------------|----------------------|--------------------|
| Example 1             | a            | 3.0                       | 0.6                  | 68                 |
| Example 2             | b            | 0.19                      | 1.0                  | 72                 |
| Example 3             | c            | 0.16                      | 0.1                  | Better flowability |
| Example 4             | d            | 0.51                      | 0.8                  | 82                 |
| Example 5             | e            | 0.42                      | 0.2                  | 81                 |
| Example 6             | f            | 0.49                      | 0.8                  | 78                 |
| Comparative Example 1 | g            | <0.1                      | >1.0                 | Not measured       |
| Comparative Example 2 | a'           | >2                        | <0.1                 | Better flowability |

(Example 8: Assessment of performance of granule masses a to f, mixture g, and cylindrical pellet mass a')

Dispersity in polypropylene of granule masses a to f, mixture g and cylindrical pellet mass a' produced in Examples 1 to 6, and Comparative Examples 1 and 2 was measured.

10

In addition, heat stability of a polypropylene composition with each of granule masses a to f, mixture g, and cylindrical pellet mass a' incorporated therein was measured.

15

<Preparation of pellet for assessment>

Polypropylene (1.4 kg) [MI=3 (230 °C, 2.16 kg·f)], 0.7

g of calcium stearate and 1.05 g of an additive granule mass (a) for a plastic were dry-blended. The resulting mixture was placed into a 30 mmφ monoaxial extruder (manufactured by Tanabe Plastic Machinery Co. LTD.) through a hopper. Then, the extruder was operated under the condition of an extrusion temperature of 220 °C and a rotation number of a screw of 50 rpm. Detailed operating conditions are described below.

Let a polypropylene pellet obtained until 5 to 10 minutes after placement into the extruder through a hopper represents PP-1, a pellet obtained until 10 to 15 minutes represent PP-2 and, similarly, let a pellet obtained until 15 to 20 minutes represent PP-3 and a pellet obtained until 20 to 25 minutes represent PP-4.

Retention MI values of pellets PP-1 to PP-4 were measured under the following condition.

Five gram of PP-1 was placed into a cylinder of a MI meter at a cylinder temperature of 280 °C, then this was made to reside for 20 minutes in the state where a piston was set, a load 2.16 kg was applied and a retention MI value at 280 °C was measured. Similarly, retention MI values of PP-2 to PP-4 at 280 °C were measured. And

results of measurements are described in Table 6.

According to the same manner except that a granule mass a was changed to b to f, g and a' regarding granule masses b to f, mixture g and cylindrical pellet a', a pellet was prepared, a retention MI value was measured and results are described in the following Table 6.

As a retention MI value is smaller, heat stability is excellent. In addition, as unevenness (standard deviation) of a retention MI value between PP-1 to PP-4 is smaller, dispersity in polypropylene is better, and this means a polypropylene composition having uniform heat stability.

Therefore, it is seen that granule masses a to f of the present invention are better in dispersity in polypropylene and are excellent in the heat stability effect on polypropylene. Further, it is seen that a polypropylene composition with each of granule masses a to f of the present invention incorporated therein is relatively uniform and is also excellent in heat stability.

Table 6

|                       | Granule mass | Addition amount * | Retention MI value (g/10 min) |      |      |      |         |                    |
|-----------------------|--------------|-------------------|-------------------------------|------|------|------|---------|--------------------|
|                       |              |                   | PP-1                          | PP-2 | PP-3 | PP-4 | Average | Standard deviation |
| Example 1             | a            | 0.075             | 18.9                          | 18.2 | 19.3 | 20.4 | 19.2    | 0.9                |
| Example 2             | b            | 0.075             | 16.5                          | 18.3 | 16.4 | 18.7 | 17.5    | 1.2                |
| Example 3             | c            | 0.075             | 19.6                          | 18.3 | 18.4 | 18.6 | 18.7    | 0.6                |
| Example 4             | d            | 0.3               | 11.6                          | 13.4 | 14.3 | 15.3 | 13.6    | 1.6                |
| Example 5             | e            | 0.3               | 16.8                          | 13.4 | 13.5 | 14.0 | 14.4    | 1.6                |
| Example 6             | f            | 0.075             | 16.5                          | 18.7 | 18.8 | 22.3 | 19.1    | 2.4                |
| Comparative Example 1 | g            | 0.075             | 17.3                          | 16.8 | 17.9 | 17.9 | 17.5    | 0.5                |
| Comparative Example 2 | a'           | 0.075             | 27.3                          | 33.0 | 22.6 | 28.0 | 28.3    | 5.3                |

\*An addition amount of each additive indicates the number of weight part per 100 parts by weight of polypropylene.

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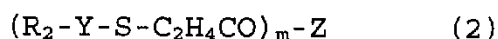
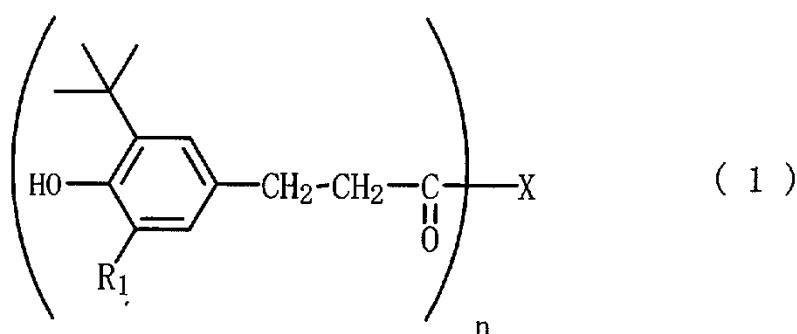
#### Industrial applicability

Since the granule mass of the present invention produces little dust, is excellent in flowability and is better in dispersity in a plastic such as polyolefin and the like, it becomes possible to produce a polyolefin resin composition excellent in heat stability.

10

WHAT IS CLAIMS IS:

1. A granule mass comprising a granule containing a phenol-based antioxidant represented by the following  
 5 formula (1) and a sulfur-based antioxidant represented by the following formula (2), wherein a content of the sulfur-based antioxidant (2) relative to a total of 100 parts by weight of phenol-based antioxidant (1) and the sulfur-based antioxidant (2) is 3 to 70 parts by weight, wherein the  
 10 granule mass is a granule aggregate of an irregular shape described in JIS-Z 8841 (1993) Item 10, and wherein a median diameter (based on weight) of a granule contained in the granule mass is 0.1 to 2 mm.



[in the formula (1), R<sub>1</sub> represents an alkyl group of a carbon number of 1 to 8, X represents a n-hydric alcohol residue of a carbon number of 1 to 18 optionally containing a heteroatom and/or a cyclic group, and n represents an

integer of 1 to 4,

in the formula (2),  $R_2$  represents an alkyl group of a carbon number of 12 to 18, Y represents a single bond or a  
5 -C<sub>2</sub>H<sub>4</sub>CO<sub>2</sub>- group, Z represents a m-hydric alcohol residue of a carbon number of 5 to 18, and m represents an integer of 1 to 4].

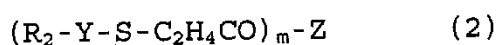
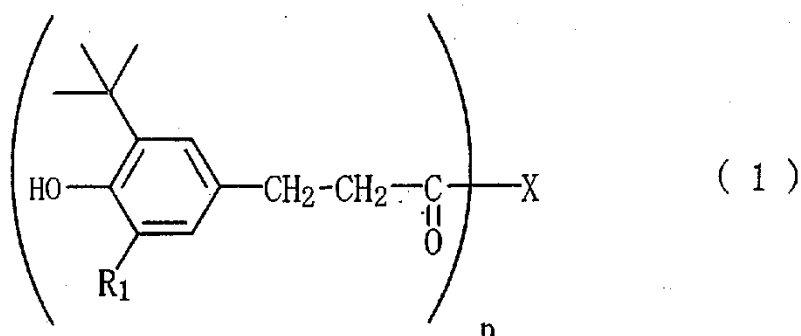
2. The granule mass according to claim 1, wherein a dust  
10 flying rate of the granule mass measured by a Heubach test is not more than 1% by weight.

3. The granule mass according to Claim 1 or 2, wherein the sulfur-based antioxidant represented by the formula (2)  
15 is at least one kind selected from the group consisting of 3,3'-thiodipropionic acid di-n-dodecyl ester, 3,3'-thiodipropionic acid di-n-tetradecyl ester and 3,3'-thiodipropionic acid di-n-octadecyl ester.

20 4. The granule mass according to any one of claims 1 to 3, wherein the phenol-based antioxidant represented by the formula (1) is at least one kind selected from the group consisting of 3,9-bis[2-{3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-  
25 tetraoxaspiro[5.5]undecane, tetrakis[3-(3,5-di-t-butyl-4-

hydroxyphenyl)propionic acid] pentaerythrityl ester and bis{3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionic acid} triethylene glycolyl ester.

- 5        5. The granule mass according to any one of claims 1 to 4, which further contains at least one kind additive selected from the group of an additive consisting of a neutralizing agent, a lubricant, a phosphorus-based antioxidant, a hindered amine-based light stabilizer, an ultraviolet  
10        absorbing agent, a metal soap, an antistatic agent, an anti-blocking agent, a pigment, a flame-retardant, a filler, and a phenol-based antioxidant other than the phenol-based antioxidant represented by the formula (1).
- 15        6. A process for producing a granule mass, comprising stirring-granulating 100 parts by weight of a mixture containing 3 to 70 parts by weight of a sulfur-based antioxidant represented by the formula (2) and a phenol-  
20        based antioxidant represented by the formula (1) at a temperature range of 40 to 70 °C, wherein the granule mass is a granule aggregate of an irregular shape described in JIS-Z 8841 (1993) Item 10, and wherein a median diameter (based on weight) of a granule contained in the granule mass is 0.1 to 2 mm.



[in the formula (1),  $\text{R}_1$  represents an alkyl group of a carbon number of 1 to 8, X represents a n-hydric alcohol residue of a carbon number of 1 to 18 optionally containing a heteroatom and/or a cyclic group, and n represents an integer of 1 to 4,

in the formula (2),  $\text{R}_2$  represents an alkyl group of a carbon number of 12 to 18, Y represents a single bond or a  $\text{---C}_2\text{H}_4\text{CO}_2\text{---}$  group, Z represents a m-hydric alcohol residue of a carbon number of 5 to 18, and m represents an integer of 1 to 4]

15

7. The process according to claim 6, wherein stirring-granulation is performed with a stirring granulator having a stirring wing in the interior of the stirring granulator, and having a clearance between a tip of the stirring wing and a wall surface of the interior of the stirring granulator, of not more than 30mm.

20

8. A plastic composition characterized in that 0.005 to 5 parts by weight of a granule mass as defined in any of claims 1 to 5 is incorporated into 100 parts by weight of a plastic.

5

9. The composition according to claim 8, wherein the plastic is a thermoplastic resin.

10

10. The composition according to claim 9, wherein the plastic is polyolefin.

15

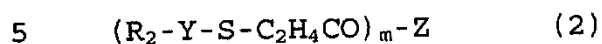
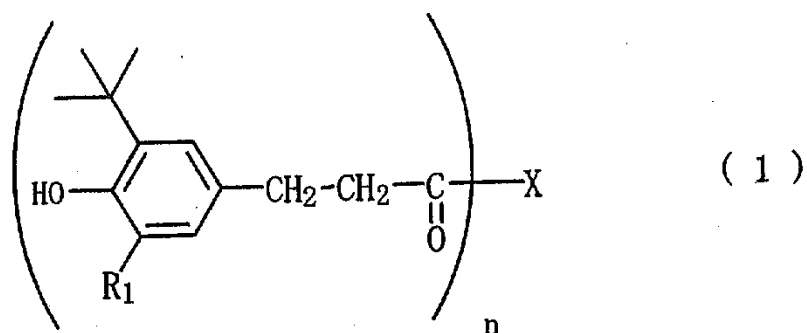
11. A method of stabilizing a plastic, comprising incorporating 0.005 to 5 parts by weight of a granule mass as defined in any one of claims 1 to 5 into 100 parts by weight of the plastic.

20

12. A granule mass comprising a granule containing a phenol-based antioxidant represented by the formula (1), a sulfur-based antioxidant represented by the following formula (2) and an additive wherein a content of the sulfur-based antioxidant (2) relative to a total of 100 parts by weight of the granule mass is 8 parts by weight or more, wherein the granule mass is a granule aggregate of an irregular shape described in JIS-Z 8841 (1993) Item 10, and wherein a median diameter (based on weight) of a

25

granule contained in the granule mass is 0.1 to 2 mm.



[in the formula (1),  $\text{R}_1$  represents an alkyl group of a carbon number of 1 to 8, X represents a n-hydric alcohol residue of a carbon number of 1 to 18 optionally containing a heteroatom and/or a cyclic group, and n represents an  
10 integer of 1 to 4,

in the formula (2),  $\text{R}_2$  represents an alkyl group of a carbon number of 12 to 18, Y represents a single bond or a  $\text{---C}_2\text{H}_4\text{CO}_2\text{---}$  group, Z represents a m-hydric alcohol residue of  
15 a carbon number of 5 to 18, and m represents an integer of 1 to 4]