

DESCRIPTION

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PROCESS FOR PRODUCING STABILIZED
OXYMETHYLENE COPOLYMER

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to an economical process for producing an oxymethylene copolymer having an excellent thermal stability.

Description of the Related Art:

Since a polyoxymethylene copolymer (which may hereinafter be abbreviated as "POM copolymer") has excellent mechanical properties, heat resistance, chemical resistance, electrical properties and sliding properties and at the same time has excellent moldability or formability, it is used as an engineering plastic for a wide variety of applications such as machine parts, automobile parts or electrical-electronic parts.

It is known that a stabilized POM copolymer provided for practical use is generally produced in

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accordance with a process as described below.

First, a crude POM copolymer is obtained by using, as a principal monomer, a cyclic acetal such as trioxane and, as a comonomer, a cyclic acetal or cyclic ether having an adjacent carbon atom; adding thereto, depending upon the purpose, a chain transfer agent for the regulation of the polymerization degree; and then copolymerizing the resulting mixture in the presence of a cationic active catalyst. In general, such a crude POM copolymer contains a large amount of unstable terminals. When heat is applied to the copolymer with the polymerization catalyst contained therein being still active, depolymerization of the copolymer or an increase in unstable terminals occurs.

Accordingly, the crude POM copolymer, which is a polymerization product, is provided for a decomposition and removal step of the unstable terminals after the catalyst contained in the copolymer is neutralized or deactivated with an organic or inorganic basic compound such as alkylamine, alkoxyamine or hindered amine, or a hydroxide of an alkali metal or alkaline earth

metal. Then, the copolymer so treated is heated in the presence of a basic compound, for example, the above-exemplified compound, and water or an alcohol which is used in combination with the basic compound as needed, whereby unstable terminals are removed by decomposition.

To the POM copolymer from which unstable terminals have been removed by decomposition, various additives are then added to impart the copolymer with thermal stability, long-term stability and the like besides, various additives or reinforcing agents are added as needed to impart the copolymer with desired properties, followed by melt kneading, whereby a stabilized POM copolymer suitable for practical use is prepared.

Various investigations have been carried out to prepare a stabilized POM copolymer more economically. Examples of the known measures for the economical production include improvement of a polymerizer, polymerization catalyst or the like in a polymerization step, an improvement in a deactivator, deactivating method or the like in a catalyst deactivation step and an improvement in a decomposition accelerator, a decomposition and

removal apparatus or the like in a decomposition and removal step of unstable terminals.

Any one of the above measures is only for a specific step so that improvements brought by it have limitations. There is accordingly a demand for the provision of a more economical process for the production of a POM copolymer in consideration of the whole step from polymerization until stabilization of a POM copolymer. Particularly, among the above-described steps, the step for decomposition and removal of unstable terminals requires a cumbersome operation and needs much energy for the treatment. If a POM copolymer can be provided to the final stabilization step substantially without the decomposition and removal step, economically advantageous production can be carried out. For this purpose, it is necessary to prepare a high-quality crude POM copolymer in the polymerization step and/or catalyst deactivation step.

The applicants of the present invention previously proposed a process for stabilizing the POM copolymer, which comprises adding, prior to the polymerization in the polymerization step, a

sterically hindered phenol to a monomer mixture in an amount of 0.001 to 2.0 % by weight based on all monomers, polymerizing the resulting mixture and then heating and melting the POM copolymer so obtained (JP-B-62-13369). It has been found that the addition of the sterically hindered phenol in the polymerization step brought about certain effects for the suppression of oxidation decomposition of the POM copolymer in the melt stabilization step owing to an improvement in the dispersibility of the sterically hindered phenol compared with that added at the time of melt stabilization treatment, however, the decomposition products of POM appearing at the melt stabilization step cannot be removed sufficiently.

As a method for improving the deactivation of a catalyst, it is known to pulverize the crude POM copolymer, which is a polymerization product, prior to deactivation from the viewpoint of heightening a catalyst deactivation efficiency and also a decomposition and removal efficiency of unstable terminals. From such viewpoints, the pulverized copolymer with a shorter particle diameter has been regarded to be preferable (JP-A-57-80414 and JP-A-

58-34819).

As a result of the investigation, however, the prevent inventors have found that such deactivation treatment of the crude POM copolymer subsequent to pulverization improves the quality of the resulting POM copolymer, but if the resulting POM copolymer is fed to a subsequent stabilization step, in which the resulting copolymer is added with a stabilizer and then the resulting mixture is melt-kneaded, without a decomposition and removal step of unstable terminals, the resulting POM copolymer inevitably has markedly inferior operability.

JP-A-7-233230 has proposed a method in which a crude POM copolymer having a limited amount of

unstable terminals is used as raw material and a stabilizer, water and the like are added thereto in a terminal stabilization zone, in an extruder equipped with a melting zone, terminal stabilization zone and degassing zone. As a result of investigation of the above method, it has been found that the method permits the smooth production of a stabilized POM but is accompanied with the economical problem, because the extruder should be elongated to meet the requirement for the terminal stabilization zone having a sufficient length.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an economically-advantageous and simple process for producing a stabilized POM copolymer which can be provided for practical use in order to overcome the above-described problems. Described specifically, an object of the present invention is to provide a process for producing a stabilized POM copolymer which can be provided for practical use without the conventionally-employed decomposition and removal step of unstable terminals. Another

object of the present invention is to provide a process for suppressing the oxidation of a POM copolymer having unstable terminals, which is the raw material in the stabilization step, thereby producing a stabilized PMO copolymer which can be provided for practical use, in the case where the raw material POM copolymer requires a certain time to be fed to the stabilization step owing to transportation, storage or the like.

With a view to attaining the above objects, the present inventors have carried out a total investigation on the process from a polymerization step until a stabilization step of a POM copolymer. As a result, it has been found that the unstable-end-having POM copolymer, which is the raw material in the stabilization step, is added with a hindered phenol in the polymerization step; the particle diameter distribution is controlled properly at the time of the pulverization of the polymer; and by the addition of a small amount of water to the raw material or addition of water after the raw material is melt plasticated in the stabilization step, the oxidation and decomposition of POM copolymer as the raw material are suppressed, the problem in the

operability such as biting neck in the stabilization step is overcome, and the decomposition product of the POM copolymer which is formed by the thermal decomposition at the melting time can be removed easily by degassing in a vacuum, leading to the completion of the present invention.

It has also been found that in the case where an unstable-terminal-having POM copolymer which is the raw material in the stabilization step has a fixed amount of unstable terminals and has a particle diameter distribution properly controlled, the addition of a small amount of water to the raw material or addition of water after the raw material is melt plasticated in the stabilization step can suppress the oxidation and decomposition of POM copolymer as the raw material and moreover, overcome the problem in the operability such as biting neck in the stabilization step, whereby the decomposition product of the POM copolymer which is formed by the thermal decomposition at the melting time can be removed easily by degassing in a vacuum, leading to the completion of the present invention.

In the present invention, there are thus provided:

1. a process for producing a stabilized copolyoxymethylene by stabilizing a copolyoxymethylene having unstable terminals characterized by:

(A) using as the copolyoxymethylene having unstable terminals a copolymer obtained by adding a sterically hindered phenol to a monomer mixture in an amount of 0.001 to 2.0 % by weight based on all monomers, polymerizing the monomer mixture, pulverizing the crude polyoxymethylene resulting from the polymerization into a powder having a particle diameter distribution satisfying the following items (1) to (4), and deactivating the polymerization catalyst contained in the crude polyoxymethylene, and

(B) adding a stabilizer to the copolyoxymethylene as the raw material together with water and degassing the mixture in a molten state in a vacuum:

- (1) an average particle diameter of 0.3 to 0.7 mm,
- (2) a content of particles having diameters larger than 1.0 mm of 3 to 20% by weight,
- (3) a content of particles having diameters

not smaller than 0.18 mm and not larger than 1.0 mm of 50 to 97% by weight, and

(4) a content of particles having diameters smaller than 0.18 mm of 0 to 30% by weight (provided that the sum of 100% by weight);

2. a process for producing a stabilized copolyoxymethylene by stabilizing a copolyoxymethylene having unstable terminals, characterized by:

(A) using as the copolyoxymethylene having unstable terminals a powdered copolymer containing 0.3 to 0.8% by weight of unstable terminals (based on the copolymer) and having a particle diameter distribution satisfying the following items (1) to (4), and

(B) adding a stabilizer to the copolyoxymethylene as the raw material together with water and degassing the mixture in a molten state in a vacuum:

- (1) an average particle diameter of 0.3 to 0.7 mm,
- (2) a content of particles having diameters larger than 1.0 mm of 3 to 20% by weight,
- (3) a content of particles having diameters

not smaller than 0.18 mm and not larger than 1.0 mm of 50 to 97% by weight, and

(4) a content of particles having diameters smaller than 0.18 mm of 0 to 30% by weight (provided that the sum of 100% by weight);

3. a process for producing a stabilized copolyoxymethylene as described in 1 or 2, wherein the water is premixed with the copolyoxymethylene feedstocks having unstable terminals;

4. a process for producing a stabilized copolyoxymethylene as described in 1 or 2, wherein the water is added after the copolyoxymethylene feedstocks having unstable terminals is melt plasticated;

5. a process for producing a stabilized copolyoxymethylene as described in any one of 1 to 3, wherein the water and the stabilizer are premixed with the copolyoxymethylene feedstocks having unstable terminals;

6. a process for producing a stabilized copolyoxymethylene as described in 1, 2 or 4, wherein the stabilizer is premixed with the copolyoxymethylene feedstocks having unstable terminals, and the water is added after the

copolyoxymethylene raw material having unstable terminals is melt plasticated; and

7. a process for producing a stabilized copolyoxymethylene as described in 1, 2 or 4, wherein the water and the stabilizer are added after the copolyoxymethylene feedstocks having unstable terminals is melt plasticated.

According to the process of the present invention, a stabilized POM copolymer can be prepared economically, which can be seen from the results of examples which will be described later.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will hereinafter be described more specifically.

The (crude) oxymethylene copolymer (POM copolymer) to which the present invention is applied is available by the copolymerization of, as a principal monomer, a cyclic acetal such as trioxane and, as a comonomer, a cyclic ether or cyclic formal in the presence of a cationic active catalyst.

The cyclic ether or cyclic formal employed here as the comonomer is a cyclic compound

containing at least a pair of coupling carbon atom and oxygen atom. Examples include ethylene oxide, 1,3-dioxolane, 1,3,5-trioxetane, diethylene glycol formal, 1,4-butanediol formal, 1,3-dioxane and propylene oxide. Among them, preferred comonomers are ethylene oxide, 1,3-dioxolane, diethylene glycol formal and 1,4-butanediol formal. The comonomer is used in an amount of 0.1 to 20 mole%, preferably 0.2 to 10 mole%, based on the trioxane which is a principal monomer.

Upon the production of the (crude) POM copolymer by the copolymerization of such a monomer and a comonomer, an ordinarily employed cationic catalyst is used as a polymerization catalyst. Examples of the cationic catalyst include Lewis acids such as halides of boron, tin, titanium, phosphorus, arsenic and antimony, for example, boron trifluoride, tin tetrachloride, titanium tetrachloride, phosphorus pentachloride, phosphorus pentafluoride, arsenic pentafluoride and antimony pentafluoride, compounds such as complex or salt thereof, a protonic acid such as trifluoromethanesulfonic acid and perchloric acid, esters of a proton acid such as an ester of

perchloric acid and a lower aliphatic alcohol (ex. a tertiary butyl ester of perchloric acid), anhydrides of a proton acid, particularly a mixed acid anhydride of perchloric acid and a lower aliphatic carboxylic acid (ex. acetyl perchlorate), isopoly acid, heteropoly acid (for example, phosphomolybdic acid), triethyloxonium hexafluorophosphate, triphenylmethyl hexafluoroarsenate and acetyl hexafluoroborate.

Among them, boron trifluoride and a coordination compound between boron trifluoride and an organic compound (for example, an ether) are most commonly used as catalysts. Since a proton acid such as heteropoly acid or isopoly acid has high activity as a catalyst, it easily provides a high-quality crude POM copolymer in a small amount and is easily deactivated. It is therefore preferred to prepare a crude POM copolymer by polymerizing in the presence of a catalyst selected from such catalysts or a mixture of two or more of them. When a Lewis acid such as boron trifluoride is used as a catalyst, it is preferably added in an amount of 15 to 25 ppm based on the feedstocks monomers. It is desired to use a monomer having a water content not

higher than 10 ppm in order to obtain a high-quality crude POM copolymer.

For the adjustment of the molecular weight of the crude POM copolymer available by copolymerization, it is also possible to carry out polymerization by adding a proper amount of a suitable chain transfer agent, for example, an acetal compound such as methylal or dioxymethylene dimethyl ether.

The crude POM copolymer can be copolymerized by using a conventionally known equipment and process, for example, either of a batch or continuous process, or either of melt polymerization or melt bulk polymerization. From the industrial viewpoint, generally-employed and preferred is the continuous bulk method in which a liquid monomer is used and a polymer is obtained in the form of a solid powdery mass with the progress of the polymerization. In this case, the polymerization can also be conducted in the presence of an inert liquid medium as needed. Examples of the polymerization apparatus usable in the present invention include co-kneader, twin-screw continuous extrusion mixer and twin-puddle type continuous

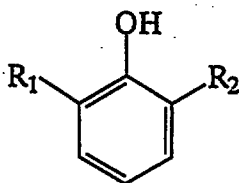
mixer.

The present invention provides a process for producing a stabilized POM copolymer, which is characterized by using a POM copolymer having unstable terminals as the raw materials, said copolymer having been obtained by pulverizing a crude POM copolymer available by the addition of a sterically hindered phenol into a powder having a specific particle diameter distribution and then deactivating the polymerization catalyst contained in the powdery copolymer; adding a stabilizer to the feedstocks POM copolymer together with water; and then degassing the mixture in a molten state in a vacuum substantially without the terminal stabilization treatment by decomposition and removal of the unstable terminals.

It is necessary that the crude POM copolymer available by such copolymerization is produced in the presence of a sterically hindered phenol (hindered phenol compound) which is an antioxidant. Since the sterically hindered phenol suppresses the oxidation decomposition of the resulting POM copolymer during polymerization and also oxidation decomposition of the POM copolymer at high

temperatures in the subsequent step, thereby permitting the provision of a high quality POM copolymer to a final stabilization step, the crude POM copolymer obtained by such a method is suitable as a crude POM copolymer to which the present invention is applied.

As the sterically hindered phenol usable in the present invention, preferred are those having a structure represented by the following formula:



wherein R_1 and R_2 may be the same or different from each other and each represents a group having at least 4 carbon atoms. Examples include 2,2'-methylenebis(4-methyl-6-t-butylphenol), hexamethyleneglycol-bis(3,5-di-t-butyl-4-hydroxyhydrocinnamate), tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]methane, triethyleneglycol-bis-3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxy-benzyl)benzene, n-

octadecyl-3-(4'-hydroxy-3',5'-di-t-butylphenol)propionate, 4,4'-methylenebis(2,6-di-t-butylphenol), 4,4'-butylidene-bis-(6-t-butyl-3-methylphenol), 2,2'-thiodiethyl-bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, di-stearyl-3,5-di-t-butyl-4-hydroxybenzylphosphonate, 2-t-butyl-6-(3-t-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenylacrylate. The above-exemplified sterically hindered phenols may be used either singly or in combination. Examples are not limited to them but the same kind of sterically hindered phenols are all usable. Among them, hexamethyleneglycol-bis(3,5-di-t-butyl-4-hydroxyhydrocinnamate) such as "Irganox 259" (trade name; product of Ciba Geigy), tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]methane such as "Irganox 1010" (trade name; product of Ciba Geigy) and triethyleneglycol-bis-3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate such as "Irganox 245" (trade name; product of Ciba Geigy) are particularly effective. On the other hand, when any one of the antioxidants other than the sterically hindered phenol, for example, amines, amidines and substances

generally employed as a stabilizer for polyacetal is added to a monomer, no polymerization reaction occurs.

The sterically hindered phenol to be added to a monomer prior to polymerization is effective even in a trace amount. It is used in an amount within a range of from 0.001 to 2.0 % by weight based on all monomers, with 0.005 to 1.0 % by weight being particularly preferred. Amounts smaller than the above range bring about less effects for the prevention of the oxidation and decomposition, while those exceeding the above range tend to decrease the polymerization reaction rate and are therefore not economical. Amounts outside the above range are therefore not desired.

As a method of adding such a sterically hindered phenol to a monomer, it is added to a liquid monomer to dissolve the former in the latter, or is added in the form of a solution dissolved in a small amount of solvent inert to the polymerization. In the case of continuous polymerization, it is possible to supply a fixed amount of the sterically hindered phenol a monomer line to be fed to a polymerizer and after mixing and dissolving it in

the monomer, to supply the resulting solution the polymerizer; or to add and dissolve it in advance in the monomer layer under storage.

The crude POM copolymer thus polymerized is then pulverized into powders which are required to satisfy the particle diameter distribution prescribed in the following items (1) to (4):

- (1) an average particle diameter of 0.3 to 0.7 mm,
- (2) a content of particles having diameters larger than 1.0 mm of 3 to 20% by weight,
- (3) a content of particles having diameters not smaller than 0.18 mm and not larger than 1.0 mm of 50 to 97% by weight, and
- (4) a content of particles having diameters smaller than 0.18 mm of 0 to 30% by weight (provided that the sum of 100% by weight).

The above particle diameter distribution is found by the present inventors after an extensive investigation with a view to satisfying both the quality, particularly the amount of unstable terminals, of the POM copolymer obtained by pulverization and deactivation of the catalyst and operability of the stabilization step in which the

pulverized POM copolymer, together with water and a stabilizing agent, is degassed in a molten state in a vacuum, followed by stabilization.

Among the above requirements, the upper limit (0.7 mm) of the average particle diameter in (1) and the upper limit of the ratio of the particles having a diameter exceeding 1.0 mm in (2) are important requirements mainly for determining the quality of the POM copolymer. On the other hand, the lower limit (0.3 mm) of the average particle diameter in (1), the lower limit of the ratio of the particles having a diameter exceeding 1.0 mm in (2) and the upper limit of the ratio of the particles having a diameter smaller than 0.18 mm in (4) are important requirements mainly for determining the operability in the stabilizing step by a stabilizer.

When the particle diameter exceeds the above particle diameter distribution, for example, the average particle diameter exceeds its upper limit or the ratio of the particles having a particle diameter larger than 1.0 mm exceeds its upper limit, the resulting pulverized POM copolymer becomes deteriorated in its quality, particularly the amount of unstable ends increases, and it becomes difficult

to obtain a POM copolymer stable enough to be provided on the market only by stabilization with a stabilizer without a stabilizing treatment of terminals by decomposition and removal of unstable terminals. When the particle diameter is below the above particle diameter distribution, on the other hand, for example, the average particle diameter is below its lower limit, the ratio of the particles having a particle diameter larger than 1.0 mm is below its lower limit, or the ratio of the particles smaller than 0.18 mm exceeds its upper limit, the operability in the stabilization step by kneading with a stabilizer becomes markedly inferior instead of satisfactory quality of the POM copolymer so that it becomes difficult to economically produce a stabilized POM copolymer.

With the forgoing in view, the preferred particle diameter distribution which can satisfy both the better quality of the POM copolymer and operability of the stabilization step is as follows:

- (1)' an average particle diameter of 0.4 to 0.7 mm,
- (2)' a content of particles having diameters larger than 1.0 mm of 5 to 15% by weight,

(3)' a content of particles having diameters not smaller than 0.18 mm and not larger than 1.0 mm of 60 to 95% by weight, and

(4)' a content of particles having diameters smaller than 0.18 mm of 0 to 25% by weight (the total being 100% by weight).

Upon pulverization as described above, no particular limitation is imposed on the pulverizer to be employed. Examples include rotary mill, hammer mill, jaw crusher, feather mill, rotary cutter mill, turbo mill and classifying type impact pulverizer. The particle diameter distribution can be controlled by the rotation frequency or clearance of a pulverizer, or screen mesh attached to a pulverizer and/or a shift attached separately as needed.

Upon deactivation of the catalyst contained in the crude POM copolymer, a conventionally known method can be employed. In the present invention, it is preferred that deactivation is effected by using an aqueous solution of an organic or inorganic basic compound typified by triethylamine, triethanolamine, sodium carbonate or calcium hydroxide; and at the same time, the crude POM

copolymer is pulverized by wet pulverization into powder having the above-described particle diameter distribution. Above all, it is preferred to add the deactivator on the way from the position immediately before the outlet of the polymerizer to the inlet of the pulverizer, whereby a high quality POM copolymer can be obtained. After deactivation of the catalyst and pulverization, the POM copolymer is subjected to washing, drying and the like as needed. The crude POM copolymer so treated can be used as the raw material for the stabilization step.

The present invention provides another method for producing a stabilized polyoxymethylene copolymer in the stabilization of a polyoxymethylene copolymer having unstable terminals, characterized by using as the raw material a POM copolymer which has unstable terminals in an amount of 0.3 to 0.8% by weight (based on the copolymer) and having a specific particle diameter distribution; adding a stabilizer to the resulting POM copolymer together with water; and degassing the mixture in a molten state in a vacuum.

Incidentally, the term "unstable terminal amount" of the POM copolymer as used herein means an

amount of formaldehyde in % by weight relative to the copolymer, said amount being determined by charging 1 g of a POM copolymer to a closed pressure bottle together with 100 ml of a 50% aqueous methanol solution containing 0.5% of ammonium hydroxide, heating the resulting mixture at 180°C for 45 minutes, cooling and taking the liquid out from the bottle, then analyzing the amount of formaldehyde decomposed and eluted in the liquid.

The amount of the unstable terminals is controlled to fall within a range of from 0.3 to 0.8 % by weight by the polymerization method including the step of adding a sterically hindered phenol; or by dissolving, in the deactivation step after polymerization, the polymerization product in a methanol solution of an organic or inorganic basic compound such as triethylamine, triethanolamine, sodium carbonate or calcium hydroxide and then precipitating the POM copolymer again, in the case where the sterically hindered phenol is not added. The crude POM copolymer so obtained is formed into a powder which can satisfy the particle diameter distribution prescribed in the following items (1) to (4) and is therefore provided as the raw

material.

- (1) an average particle diameter of 0.3 to 0.7 mm,
- (2) a content of particles having diameters larger than 1.0 mm of 3 to 20% by weight,
- (3) a content of particles having diameters not smaller than 0.18 mm and not larger than 1.0 mm of 50 to 97% by weight, and
- (4) a content of particles having diameters smaller than 0.18 mm of 0 to 30% by weight (provided that the sum is 100% by weight).

To the raw material crude POM copolymer so prepared, a stabilizer and water are added and the resulting mixture is degassed in a molten state in a vacuum, whereby a stabilized POM copolymer is obtained.

The present invention features that the crude POM copolymer so prepared is used as the raw material; and a stabilized POM copolymer is obtained by adding water to the raw material during its stabilization step and then mixing a stabilizer and the like in the resulting mixture while removing a volatile component such as the decomposition product of the POM polymer (formaldehyde gas) which has

remained in the raw material or has been generated during the stabilization step.

Water is added in an amount of 0.05 to 5.0 % by weight based on the weight of the raw material, with 0.5 to 3.0 % by weight being preferred. Amounts smaller than the above range do not bring about effects for the removal of volatile components, while those exceeding the above range are not preferred because the water content remains in the kneaded mixture. Water may be added after premixed with the raw material or after the raw material is melt plasticated. In the former method, water can be dispersed in advance, which makes it possible to sufficient dispersion of water after melt plastication. The addition of water during the melt plastication of the raw material is not preferred, because a large amount of water exists locally, thereby inhibiting the plastication of the raw material or there is a fear of the unplasticated portion being mixed in the raw material.

No particular limitation is imposed on the stabilizer usable here and any known stabilizer can be used. In general, however, an antioxidant and a thermal stabilizer are used in combination.

Examples of the antioxidant include 1,6-hexanediol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], pentaerythritoltetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], triethyleneglycol-bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate] and N,N'-hexamethylenebis(3,5-di-t-butyl-4-hydroxy-cyannamide).

Examples of the thermal stabilizer include triazine compounds such as melamine and melamine-formaldehyde condensate, polyamides such as nylon 12 and nylon 6·10; hydroxides, carbonates, phosphates, acetates and oxalates of an alkali metal or alkaline earth metal; and metallic salts of a higher fatty acid such as stearic acid or a higher fatty acid having a substituent such as a hydroxyl group.

To the POM copolymer of the present invention, various additives can be added depending upon the purpose. Examples include weather-resistant (light) stabilizer, lubricant, nucleating agent, mold release agent, antistatic, dye, pigment, other organic high-molecular materials, and inorganic or organic fibrous, plate or powdery fillers.

Examples of the apparatus usable for the stabilization step of the present invention include continuous extruders such as twin-screw extruder equipped with a vent and a monoaxial screw extruder equipped with a vent. The volatile components are removed from the vent under reduced pressure.

The present invention will hereinafter be described by examples and comparative examples, but it should however be borne in mind that the present invention is not limited to or by the following examples.

(Evaluation Method)

• Extrudability (Biting property of raw materials)

Observed are the biting condition of the raw materials into an extruder and discharged condition of a stabilized POM from the extruder at the time when a stabilizer is incorporated in the powdery POM copolymer and the resulting mixture is melt-kneaded in an extruder. They are evaluated in accordance with the following three ranks A to C:

A: Both biting condition and discharged strands are stable.

B: Inferior biting condition sometimes occurs and fluctuations in the thickness of the strands

appear.

C: Fluctuations in the biting condition are slightly large, fluctuations in the thickness of strands are large and strand break sometimes occurs.

• Amount of Unstable Terminals of the POM
Copolymer

In a closed pressure bottle, 1 g of a POM copolymer was charged together with 100 ml of a 50% aqueous methanol solution containing 0.5% of ammonium hydroxide, followed by heating at 180°C for 45 minutes. The reaction mixture was then cooled and taken out from the bottle. The amount of formaldehyde decomposed and dissolved in the liquid was determined by analysis and was indicated as % by weight based on the copolymer.

• The monomer (formaldehyde) content (extracted amount of formaldehyde) in the polymer

In 40 ml of distilled water, 2 g of a POM copolymer were charged, followed by reflux under boiling for 1.5 hours. Then, the amount of formaldehyde extracted in the water was determined by analysis and it was indicated by weight parts relative to the polymerized product.

Examples 1 to 5, Comparative Examples 1 to 5

[Preparation of Crude POM Copolymer Feedstocks (POM copolymer having unstable terminals)]

In each example, a twin-puddle type continuous polymerizer was continuously fed with trioxane added with 2.5 % by weight (based on all the monomers) of 1,3-dioxolane and polymerization was effected in the presence of boron trifluoride or phosphomolybdic acid as a catalyst. In some of the examples, tetrakis[methylene(3,5-di-t-butyl-4-hydroxycinnamate)]methane ("Irganox 1010", trade name; product of Ciba Geigy) was added in an amount of 0.05% (based on all the monomers), and in other examples, it was not added, which is shown in Tables 1 and 2. The crude POM copolymer discharged from the outlet at the end of the polymerizer was dehydrated and dried, after wet pulverization and deactivation treatment of the catalyst, whereby a powdery POM copolymer having a particle diameter distribution as shown in Table 1 or 2 was obtained. The particle diameter was controlled by changing the rotational frequency of the pulverizer or the size or shape of the screen mesh.

[Stabilization Treatment]

The powdery POM copolymer so obtained was mixed with 0.45 % by weight of tetrakis[methylene(3,5-di-t-butyl-4-hydroxycinnamate)]methane ("Irganox 1010", trade name; product of Ciba Geigy) and 0.1 % by weight of calcium stearate, followed by melt kneading in a monoaxial or biaxial extruder equipped with a vent. At that time, water was (1) added after premixed with the feedstocks, (2) added after the melt plastication of the feedstocks and (3) not added.

The results are shown in Tables 1 and 2.

In the tables described below, abbreviations have the following meanings.

Particle diameter distribution:

within a range: within a range of the particle diameter distribution as prescribed in claim 1

Outside a range 1: outside a range of the particle diameter distribution as prescribed in claim 1 and a content of the particles having a particle diameter less than 0.18 mm exceeds 30 % by weight.

Outside a range 2: outside a range of the
particle diameter
distribution as prescribed in
claim 1 and a content of the
particles having a particle
diameter of at least 1.00 mm
exceeds 20 % by weight.

Method of Addition:

Injection: addition of water to an extruder
after the melt plastication of the
feedstocks

Premixing: addition of water after the water is
mixed with the raw material

Kind of Catalyst:

BF₃: boron trifluoride

HPA: phosphomolybdic acid

Table 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Preparation of raw material					
• Addition of "Irganox 1010"	yes	yes	yes	yes	Yes
• Kind of catalyst	BF ₃	BF ₃	BF ₃	BF ₃	HPA
Amount added (ppm)	20	20	20	20	5
• Particle diameter distribution	within a range	within a range	within a range	within a range	within a range
Stabilization step					
• Extruder	monoaxial	Monoaxial	biaxial	biaxial	biaxial
Amount of water added (%)	2	2	2	2	2
• Addition Method	injection	premixing	injection	premixing	injection
• Extrudability	A	A	A	A	A
Evaluation (after extrusion)					
• Amount of unstable terminals (%)	0.41	0.49	0.40	0.45	0.50
• Amount of formaldehyde extracted (ppm)	65	78	63	70	80

Table 2

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5
Preparation of raw material					
• Addition of "Irganox 1010"	no	yes	yes	yes	Yes
• Kind of catalyst	BF ₃	BF ₃	BF ₃	BF ₃	BF ₃
• Amount added (ppm)	20	20	20	20	20
• Particle diameter distribution	within a range	outside a range 1	outside a range 2	within a range	within a range
Stabilization step					
• Extruder	Monoaxial	monoaxial	monoaxial	monoaxial	monoaxial
• Amount of water added (%)	2	2	2	-	5.5
• Addition Method	injection	premixing	injection	-	injection
• Extrudability	A	C	A	A	B
Evaluation (after extrusion)					
• Amount of unstable terminals (%)	0.59	0.50	0.92	0.61	0.83
• Amount of formaldehyde extracted (ppm)	152	96	182	253	70

Examples 6 to 8, Comparative Examples 6 to 9

[Preparation of Crude POM Copolymer Feedstocks (POM copolymer having unstable terminals)]

In each example, a twin-puddle type

continuous polymerizer was continuously fed with trioxane added with 2.5 % by weight (based on all the monomers) of 1,3-dioxolane and polymerization was effected in the presence of 20 ppm of boron trifluoride as a catalyst. The crude POM copolymer discharged from the outlet at the end of the polymerizer was dissolved under heating at 180°C in a methanol solution containing 0.25 % by weight of triethylamine, followed by cooling, whereby a POM copolymer was precipitated. The resulting precipitate was subjected to solvent removal and drying, followed by dry pulverization, whereby a powdery POM copolymer having a predetermined particle diameter distribution was obtained. The amount of the unstable terminal groups of the raw material POM copolymer was controlled by changing the retention time in a methanol solution at 180°C.

[Stabilization Treatment]

The powdery POM copolymer so obtained was mixed with 0.5 % by weight of tetrakis[methylene(3,5-di-t-butyl-4-hydroxycinnamate)]methane ("Irganox 1010", trade name; product of Ciba Geigy) and 0.1 % by weight of calcium stearate, followed by melt kneading in a

monoaxial or biaxial extruder equipped with a vent. At that time, water was (1) added after premixed with the feedstocks, (2) added after the melt plastication of the feedstocks and (3) not added.

The results are shown in Tables 3 and 4.

In the tables described below, abbreviations have the following meanings.

Particle diameter distribution:

within a range: within a range of the particle diameter distribution as prescribed in claim 1

outside a range 1: outside a range of the particle diameter distribution as prescribed in claim 1 and a content of particles having a particle diameter less than 0.18 mm exceeds 30 % by weight.

outside a range 2: outside a range of the particle diameter distribution as prescribed in claim 1 and a content of the particles having a particle diameter of at least 1.00 mm exceeds 20 %

by weight.

Method of addition:

Injection: addition of water to an extruder after
the melt plastication of the
feedstocks

Premixing: addition of water after the water is
premixed with the raw material

Table 3

	Ex. 6	Ex. 7	Ex. 8
Preparation of raw material			
• Amount of unstable terminals (%)	0.45	0.45	0.45
• Particle diameter distribution	within a range	within a range	within a range
Stabilization step			
• Extruder	monoaxial	monoaxial	biaxial
• Amount of water added (%)	2	2	2
• Addition Method	injection	premixing	injection
• Extrudability	A	A	A
Evaluation (after extrusion)			
• Amount of unstable terminals (%)	0.25	0.31	0.20
• Amount of formaldehyde extracted (ppm)	63	75	50

Table 4

	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9
Preparation of raw material				
• Amount of unstable terminals (%)	0.45	0.44	0.46	0.70
• Particle diameter distribution	within a range	outside a range 1	outside a range 2	within a range
Stabilization step				
• Extruder	monoaxial	monoaxial	monoaxial	monoaxial
• Amount of water added (%)	-	2	2	2
• Addition Method	-	injection	injection	injection
• Extrudability	A	C	A	A
Evaluation (after extrusion)				
• Amount of unstable terminals (%)	0.38	0.35	0.50	0.61
• Amount of formaldehyde extracted (ppm)	110	76	110	300

CLAIMS



1. A process for producing a stabilized copolyoxymethylene by stabilizing a copolyoxymethylene having unstable terminals, characterized by

(A) using as the copolyoxymethylene having unstable terminals a copolymer obtained by adding a sterically hindered phenol to a monomer mixture in an amount of 0.001 to 2.0% by weight based on all monomers, polymerizing the monomer mixture, pulverizing the crude polyoxymethylene resulting from the polymerization into a powder having a particle diameter distribution satisfying the following items (1) to (4), and deactivating the polymerization catalyst contained in the crude polyoxymethylene, and

(B) adding a stabilizer to the copolyoxymethylene as the raw material together with water and degassing the mixture in a molten state in a vacuum:

- (1) an average particle diameter of 0.3 to 0.7 mm,
- (2) a content of particles having diameters



larger than 1.0 mm of 3 to 20% by weight,
(3) a content of particles having diameters
not smaller than 0.18 mm and not larger than
1.0 mm of 50 to 97% by weight, and
(4) a content of particles having diameters
smaller than 0.18 mm of 0 to 30% by weight
(provided that the sum is 100% by weight).

2. A process for producing a stabilized
copolyoxymethylene by stabilizing a
copolyoxymethylene having unstable terminals,
characterized by

(A) using as the copolyoxymethylene having
unstable terminals a powdered copolymer containing
0.3 to 0.8% by weight of unstable terminals (based
on the copolymer) and having a particle diameter
distribution satisfying the following items (1) to
(4), and

(B) adding a stabilizer to the
copolyoxymethylene as the raw materials together
with water and degassing the mixture in a molten
state in a vacuum:

(1) an average particle diameter of 0.3 to
0.7 mm,



- (2) a Content of particles having diameters larger than 1.0 mm of 3 to 20% by weight,
- (3) a content of particles having diameters not smaller than 0.18 mm and not larger than 1.0 mm of 50 to 97% by weight, and
- (4) a content of particles having diameters smaller than 0.18 mm of 0 to 30% by weight (provided that the sum is 100% by weight).

3. The process for producing a stabilized copolyoxymethylene as claimed in Claim 1 or 2, wherein the water is premixed with the copolyoxymethylene feedstocks having unstable terminals.

4. The process for producing a stabilized copolyoxymethylene as claimed in Claim 1 or 2, wherein the water is added after the copolyoxymethylene feedstocks having unstable terminals is melt plasticated.

5. The process for producing a stabilized copolyoxymethylene as claimed in any of Claims 1 to 3, wherein the water and the stabilizer are premixed



with the copolyoxymethylene feedstocks having unstable terminals.

6. The process for producing a stabilized copolyoxymethylene as claimed in Claim 1, 2 or 4, wherein the stabilizer is premixed with the copolyoxymethylene feedstocks having unstable terminals, and the water is added after the copolyoxymethylene raw material having unstable terminals is melt plasticated.

7. The process for producing a stabilized copolyoxymethylene as claimed in Claim 1, 2 or 4, wherein the water and the stabilizer are added after the copolyoxymethylene feedstocks having unstable terminals is melt plasticated.