

REPLACED SHEETS SG

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DESCRIPTION

PROCESS FOR DEACTIVATING CATALYST CONTAINED IN
OXYMETHYLENE COPOLYMER AND PROCESS FOR PRODUCING
STABILIZED OXYMETHYLENE COPOLYMER

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to an efficient process for deactivating a catalyst contained in an oxymethylene copolymer obtained by polymerization and also an economical process for producing an oxymethylene copolymer having 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.

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It is known that a stabilized POM copolymer provided for practical use is generally produced in 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 in the presence of a cationic active catalyst. In general, such a crude POM copolymer contains a large amount of unstable end parts. 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 end parts occurs.

Accordingly, the crude POM copolymer, which is a polymerization product, is provided for a decomposition and removal step of the unstable end parts 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 as needed, whereby unstable end parts are removed by decomposition.

To the POM copolymer from which unstable end parts have been removed by decomposition, suitable additives are added to impart the copolymer with thermal stability and long-term stability and besides, various additives or reinforcing agents are added 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 end parts.

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 the decomposition and removal of unstable end parts requires a cumbersome operation and needs much energy for the treatment. If a POM copolymer can be provided for the final stabilization step substantially without the decomposition and removal step, an economically advantageous production can be carried out. For exclusion of the decomposition and removal step, it is necessary to prepare a high-quality (crude) POM copolymer in the polymerization step and/or catalyst deactivation step.

Particularly, the deactivating step of a catalyst has an important meaning. If the POM copolymer contains less unstable end parts after the deactivation of the catalyst, the final product has

improved stability and furthermore, is accompanied with the advantage that the post-treatment step such as stabilization can be simplified.

As a method for the improvement of the catalyst deactivation, it is known to deactivate the crude POM copolymer, which is a polymerization product, by pulverization from the viewpoint of heightening a catalyst deactivation efficiency and also a decomposition and removal efficiency of unstable ends. From such viewpoints, the pulverized copolymer with a smaller particle size has been regarded to be preferable (JP-A-57-80414 and JP-A-58-34819). More specifically, disclosed in JP-A-58-34819 is a means for efficient deactivation of a catalyst by pulverizing the crude POM copolymer, which is a polymerization product, to 20 mesh or less, thereby deactivating the catalyst.

As a result of investigation, the present inventors have found that such deactivation treatment of the crude POM copolymer by pulverization improves the quality of the resulting POM copolymer, but if the resulting POM copolymer is provided for a subsequent stabilization step, in which the resulting copolymer is added with a

stabilizer and then melt-kneaded, without a decomposition and removal step of unstable end parts, the resulting POM copolymer inevitably has markedly inferior operability.

Described specifically, the particle size distribution of the pulverized material is important in the deactivation step with a view to satisfying both of (1) quality of the POM copolymer after the catalyst deactivation treatment and (2) operability upon melt-kneading with a stabilizer for stabilization substantially without an end stabilization treatment (decomposition and removal of unstable end parts). The operability of the stabilization step has remained unsolved when only by the particle size is decreased as the conventional method. Moreover, it is impossible to obtain a pulverized copolymer which can satisfy both of the above requirements by using a pulverizer known to date.

As described above, no effective and simplified process for economically producing a stabilized POM copolymer by providing a POM copolymer for a final stabilization step without a decomposition and removal step of unstable end parts

has so far been found.

SUMMARY OF THE INVENTION

The present invention has been completed with the forgoing in view. An object of the present invention is to provide an efficient process for deactivating a catalyst in order to obtain a high-quality POM copolymer and an economically advantageous and simple process for producing a stabilized POM copolymer suitable for practical use.

With a view to attaining the above object, the present inventors have carried out a total investigation on the process from a polymerization step of a POM copolymer until a stabilization step. As a result, it has been found that the pulverization of the crude POM copolymer, which is a polymerization product, is an important factor and the above-described object can be attained by pulverizing the crude POM copolymer by a suitable pulverizer, leading to the completion of the present invention.

In the present invention, there is thus provided a process for deactivating a catalyst

contained in an oxymethylene copolymer, which comprises pulverizing an oxymethylene copolymer discharged from a polymerizer with a pulverizer having the below-described structure and also deactivating the polymerization catalyst with a basic compound:

[Structure of Pulverizer]

a pulverizer having a stator-side element, a rotor-side element, rotation drive means, an inlet for the substance to be pulverized and an outlet provided with a screen mesh for the pulverized substance, each of the stator-side and rotor-side elements having projections intermittently arranged so as to form one or more concentric circles on a nearly circular base, and the projections arranged to form the concentric circle(s) on the rotor-side element being rotated at a predetermined clearance from the projections arranged to form the concentrated circle(s) on the rotor-side element upon the rotation of the rotor-side element to make the pulverization possible.

There is also provided a process for producing a stabilized oxymethylene copolymer, which



comprises melt-kneading an oxymethylene copolymer, the catalyst of which has been deactivated by the above method, together with a stabilizer, substantially without a treatment for stabilizing the ends by removing the unstable end parts by decomposition.

The invention provides, in addition, a process for producing a stable oxymethylene copolymer, which comprises the steps of polymerizing an oxymethylene copolymer, pulverizing the copolymer product mixture with the above shown pulverizer and adding a basic compound to the mixture to deactivate the polymerization catalyst.

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 at least one of 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 relative to the raw material.

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 metylal or dioxymethylene dimethyl ether.

Alternatively, it is possible to produce such a crude POM copolymer in the presence of a hindered phenol compound which is an antioxidant. The use of the hindered phenol compound is effective for controlling the oxidative destruction of the resulting POM copolymer during polymerization or suppressing the oxidative destruction of the POM copolymer caused by heating treatment in the subsequent step, thereby providing the final stabilization step with a high-quality-maintained POM copolymer. The crude POM copolymer so obtained is therefore preferably employed for the present invention.

The crude POM copolymer can be copolymerized

by using the 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 be conducted in the presence of an inert liquid medium as needed. Examples of the polymerization apparatus usable in the present invention include Ko-kneader, twin-screw continuous extrusion mixer and twin-puddle type continuous mixer.

The present invention is characterized by pulverizing a crude POM copolymer obtained as described above in a specific pulverizer and also deactivating the polymerization catalyst contained in the copolymer.

The pulverizer used in the present invention has a stator-side element, a rotor-side element, rotation drive means, an inlet for the substance to be pulverized and an outlet provided with a screen mesh for the pulverized substance, each of the

stator-side and rotor-side elements having projections intermittently arranged so as to form one or more concentric circles on a nearly circular base, and the projections arranged to form the concentric circle(s) on the rotor-side element being rotated at a predetermined clearance from the projections arranged to form the concentrated circle(s) on the rotor-side element upon the rotation of the rotor-side element to make the pulverization possible. The specific example of this pulverizer has a structure as illustrated in FIG. 1.

Brief Description of the Drawings:

FIG. 1 is a cross-sectional schematic view illustrating one example of a pulverizer usable in the present invention.

Description of Numerical Reference:

- 1 projection arranged so as to form a concentric circle on a rotor-side nearly circular base
- 2 other projection arranged so as to form the concentric circle on the rotor-side nearly circular base
- 3 another projection arranged so as to form the



- concentric circle on the rotor-side nearly circular base
- 4 rotor-side nearly circular base
 - 5 projection arranged so as to form a concentric circle on a stator-side nearly circular base
 - 6 other projection arranged so as to form the concentric circle on the stator-side nearly circular base
 - 7 stator-side nearly circular base constituting a portion of a housing
 - 8 screen mesh
 - 9 connecting port of a driving force transmission mechanism through rotation drive means (not illustrated)
 - 10 inlet of a substance to be pulverized
 - 11 outlet of pulverized substance

The pulverizer used in the present invention will hereinafter be described with reference to the accompanying drawing.

In FIG. 1, projections 1,2,3 are intermittently arranged so as to form one or more concentric circles on a rotor-side nearly circular base 4, while projections 5,6 are intermittently

arranged so as to form concentric circle(s) on the stator-side nearly circular base 7 which constitutes a portion of the housing of the pulverizer. The rotor-side nearly circular base 4 is connected with rotation drive means (not illustrated) through a driving force transmission mechanism 9. By the driving force transmitted, the rotor-side nearly circular base 4 rotates and the rotor-side projections rotate with a predetermined clearance against the stator-side projections, which cause impact blow at these projections, grinding between the rotor-side projections and stator-side projections, grinding between substances to be pulverized, whereby pulverization is performed. The substance to be pulverized which has been introduced from the inlet 10 is pulverized by such a pulverizing mechanism and then discharged from the outlet 11 through a screen mesh 8 which has been disposed in the cylindrical shape.

In such a pulverizer usable in the present invention, no particular limitation is imposed on the number of the rows of the projections arranged on the rotor-side and stator-side nearly circular bases and the number of the projections on the same

concentric circle. It is however preferred that the pulverizer has 4 to 20 projections on each of three rotor-side concentric circles and 15 to 40 projections on each of two stator-side concentric circles, each arranged intermittently. When a plural number of rows are arranged as described above, it is desired to arrange less projections on the inner peripheral side and more projections on the outer peripheral side. Also when a plural number of rows are arranged, it is not necessary to arrange the projections on the same axis extending from the center toward the outer periphery and it is possible to arrange them on different phases as needed.

Upon pulverization of a POM copolymer by using such a pulverizer, it is preferred, in the present invention, that the pulverized POM copolymer has a specific particle size distribution as described below. For this purpose, the screen mesh 8 preferably has a circular mesh opening having a diameter of 2 to 6 mm or an oblong mesh opening having a longer diameter of 10 to 30 mm and a shorter diameter of 2 to 6 mm. The oblong mesh opening which has its longer diameter arranged

perpendicularly to the circumferential direction of the rotor is preferred. On the control of the particle size of the substance to be pulverized, the clearance between the rotor-side projections arranged at the outermost circle and the screen mesh 8 contributes largely. The clearance of 8 to 15 mm is preferred.

From the viewpoints of deactivation efficiency of a catalyst, quality of the POM copolymer after the deactivation of the catalyst, simplification of the post treatment step and operability, the POM copolymer so pulverized is preferred to satisfy the particle size distribution prescribed below in (1) to (4). The pulverized copolymer having such a particle size distribution can easily be obtained by the pulverization in the above-described pulverizer.

- (1) the average particle diameter being 0.3 to 0.7 mm,
- (2) 3 to 20% by weight of the particles having a diameter of longer than 1.0 mm,
- (3) 50 to 97% by weight of the particles having a diameter of 0.18 to 1.0 mm,
- (4) 0 to 30% by weight of the particles having

a diameter of shorter than 0.18 mm
(the total being 100% by weight).

The above particle size distribution has been found by the present inventors, as a result of an extensive investigation with a view to satisfying both the quality, specifically the amount of unstable ends, of the POM copolymer available by the pulverization and deactivation of the catalyst; and operability of the stabilization step for melt-kneading the pulverized POM copolymer together with a stabilizer, thereby stabilizing the copolymer.

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 size exceeds the above particle size distribution, for example, the average particle size exceeds its upper limit or the ratio of the particles having a particle size longer 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 treatment for stabilizing the ends by removing the unstable end portions by decomposition. When the particle size is below the above particle size distribution, on the other hand, for example, the average particle size is below its lower limit, the ratio of the particles having a particle size longer than 1.0 mm is below its lower limit, or the ratio of the particles shorter 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 size distribution which can satisfy both the better quality of the POM copolymer and operability of the stabilization step is as follows:

- (1)' the average particle diameter being 0.4 to 0.7 mm,
- (2)' 5 to 15% by weight of the particles having a diameter of longer than 1.0 mm,
- (3)' 60 to 95% by weight of the particles having a diameter of 0.18 to 1.0 mm,
- (4)' 0 to 25% by weight of the particles having a diameter of shorter than 0.18 mm (the total being 100% by weight).

In the present invention, a method known to date can be adopted as a deactivation method when the POM copolymer discharged from the polymerizer is pulverized as described above and at the same time, the catalyst contained in the copolymer is deactivated.

For example, the deactivation can be effected either by using a large amount or small amount of an aqueous solution or solvent solution containing a basic compound, or by bringing into contact with a basic gas. Any known basic substance is effective as a deactivating agent usable in the form of an

aqueous solution or solvent solution. Examples include, ammonia, various amine compounds, oxides, hydroxides, organic acid salts or inorganic acid salts of an alkali metal or an alkaline earth metal and trivalent phosphorus compounds.

Examples of the amine compound include primary, secondary and tertiary aliphatic and aromatic amines, such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, butylamine, dibutylamine and tributylamine and alcohol amines corresponding thereto (for example, triethanolamine), aniline, diphenylamine, heterocyclic amines and hindered amines (various piperidine derivatives).

Examples of the alkali metal or alkaline earth metal compound include inorganic weak acid salts such as oxides, hydroxides, carbonates, bicarbonates, phosphates, borates and silicates of an alkali metal or an alkaline earth metal; organic acid salts such as acetates, oxalates, formates, benzoates, terephthalates, isophthalates, phthalates and fatty acid salts; alkoxides such as methoxide, ethoxide, n-butoxide, sec-butoxide and tert-butoxide and phenoxides. Among them, hydroxides, carbonates

and fatty acid salts are preferably employed. Examples of the alkali metal or alkaline earth metal component here include lithium, sodium, potassium, cesium, magnesium, calcium, strontium and barium, with lithium, sodium, potassium, magnesium and calcium being preferred. Specific examples of the particularly preferred compound include calcium hydroxide, magnesium hydroxide, sodium carbonate, calcium acetate, calcium stearate and calcium hydroxystearate.

As a solvent for preparing the deactivator, water or an organic solvent is used. Examples of organic solvents include alcohols such as methanol and ethanol; ketones such as ethylketone and acetone; aromatic compounds such as benzene, toluene and xylene; and saturated hydrocarbons such as cyclohexane, n-hexane and n-heptane. Particularly preferred is an aqueous solution.

As examples of a deactivator usable in the form of a basic gas, ammonia and amine compounds can be cited. Amine compounds having a boiling point not higher than 150°C and represented by the formula R_1NH_2 , R_1R_2NH or $R_1R_2R_3N$ (wherein R_1 , R_2 , R_3 each represents an alkyl or alcohol group having 4 or

below carbon atoms are preferred.

As the above-exemplified amine compound, those having a relatively low-molecular weight and a low boiling point are preferred in order to bring them into contact in the gaseous form with a resulting crude polymer, with those represented by the above formula wherein R_1 , R_2 , R_3 having carbon atoms not greater than 2 being particularly preferred. Even in the case of amines having a relatively high boiling point, it is also possible to bring them into contact in the gaseous form with the crude polymer after diluted with a carrier gas as described below.

Examples of such an amine compound include methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, butylamine, dibutylamine and tributylamine and alcohol amines corresponding thereto (for example, triethanolamine), with methylamine, dimethylamine and trimethylamine being particularly preferred.

The above-described basic gas may be used either singly or be brought into contact with the resulting polymer as a mixed gas diluted with another carrier gas. No particular limitation is

imposed on the carrier gas, however, an inert gas is preferred. Examples may include nitrogen gas and other organic gases.

Such a deactivator in the liquid or gaseous form may be added before and/or after the pulverization step of the above-described POM copolymer and according to the form of the deactivator, wet pulverization or dry pulverization can be employed. Among them, in the present invention, it is preferred to carry out deactivating treatment using an aqueous solution containing the above-described basic compound, and in addition it is preferred to add such a deactivator on the way from immediately before the outlet of the polymerizer to the inlet of the pulverizer, thereby conducting wet pulverization.

After the deactivating treatment of the catalyst and pulverization, the POM copolymer is washed and dried as needed.

In the present invention, a high-quality POM copolymer with less unstable ends can be obtained by pulverizing a crude POM copolymer, which is a polymerization product, by a specific pulverizer as described above and at the same time deactivating

the catalyst so that the post-treatment step can be simplified.

For example, when the catalyst-deactivated POM copolymer is subjected to an end treatment step, similar to the conventional process, to remove its stable ends by decomposition, it is possible to carry out the removal by a simple apparatus and economically advantageous method. By making use of the characteristic that a high-quality POM copolymer is available by the above-described catalyst deactivating treatment, it is also possible to melt-knead the POM copolymer together with a stabilizer, thereby obtaining a stabilized oxymethylene copolymer, substantially without a treatment for stabilizing the ends by removing the unstable end parts by decomposition. This method is particularly preferred and for this method, it is more preferred that the copolymer contains an unstable end amount of 0.3 to 0.8.

Incidentally, an unstable end amount of the POM copolymer as prescribed herein means an amount of formaldehyde in wt.% 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 the reaction mixture and then analyzing the amount of formaldehyde decomposed and dissolved in the liquid.

No particular limitation is imposed on the stabilizer usable in the present invention. Any known stabilizer can be employed, but generally, an antioxidant and thermal stabilizer are used in combination.

As a stabilizer, the addition of a conventionally known substance as a stabilizer for a polyacetal resin, for example, a hindered phenol antioxidant, is important. It is preferred to add a nitrogen-containing compound or an oxide or fatty acid salt of a metal in combination with the antioxidant.

Examples of the hindered phenol antioxidant include 2,6-di-t-butyl-4-methylphenol, triethyleneglycol-bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate], 1,6-hexanediol-bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], tetrakis[3-(3,5-di-t-butyl-4-

hydroxyphenyl)propionate]methane, N,N'-hexamethylenebis(3,5-di-t-butyl-4-hydroxy-hydrocyannamide), 2-t-butyl-6-(3'-t-butyl-5'-methyl-2'-hydroxybenzyl)-4-methylphenylacrylate, 3,9-bis[2-((3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy)-1,1'-dimethylethyl]-2,4,8,10-tetraoxaspiro[5,5]-undecane.

Examples of the nitrogen-containing compound include dicyandiamide, melamine and derivatives thereof, urea and derivatives thereof, benzotriazole compounds, piperidine compounds (hindered amines), various polyamides, copolymers thereof (ex. nylon 6, 12, 6/12, 6/66/610, 6/66/610/12).

As the metal oxide, oxides of an alkaline earth metal are preferred, while examples of the fatty acid salt of a metal include calcium salts and magnesium salts of a higher fatty acid.

Since the above-described stabilizers differ in their functions, it is preferred to select at least two of them depending on the purpose and use them in combination.

Moreover, it is possible to add, at this stage, various other additives such as filler, for example, glass fiber, crystallization accelerator

(nucleating agent) and mold releasing agent as needed.

The heating and melting treatment in the present invention is preferably carried out within a temperature range of from a melting point of the resulting polymer to 250°C, preferably a temperature range of from the melting point to 230°C.

Temperatures higher than 250°C cause decomposition and deterioration of the polymer and are therefore not preferred. No particular limitation is imposed on the heating and melting apparatus, however, that having a function of kneading the molten polymer and at the same time, having a venting function is required. Examples include a monoaxial or multiaxial continuous extrusion kneader and Ko-kneader having at least one vent hole.

In the present invention, this melt-kneading treatment makes it possible to carry out complete deactivation of the polymerization catalyst and the deactivator incorporated in the crude polymer accelerates the decomposition and removal of unstable end parts from the crude polymer and is then removed together with the other volatile substances from the vent portion, whereby a stable

polyacetal copolymer can be obtained in the pellet form. It is obvious that for the above purpose, the removal from the vent hole is conducted by suction by placing the vent hole under reduced pressure.

Examples

The present invention will now be described by examples and comparative examples. It is obvious that the present invention is not limited to or by the following examples.

Examples 1 to 8, Comparative Example 1

In each example, a twin-puddle type continuous polymerizer was continuously fed with trioxane (containing 15 ppm or 8 ppm of water) and 2.5 wt.% (based on the whole monomer) of 1,3-dioxolane and polymerization was effected in the presence of boron trifluoride or phosphomolybdic acid (supplied as a mixture with a comonomer) as a catalyst. At the outlet at the end of the polymerizer, an aqueous solution containing 500 ppm of triethylamine was supplied. While it was brought into contact with the crude POM copolymer just discharged from the outlet in order to effect the

deactivation of the catalyst, they were introduced into a pulverizer having the structure as shown in FIG. 1 and being equipped with a screen mesh and clearance (between the outermost projection at the rotor side and the screen mesh), whereby wet pulverization was carried out. The slurry discharged from the pulverizer, said slurry containing the powdery POM copolymer and the catalyst deactivator, was introduced in a storage tank and subjected to deactivation treatment of the catalyst, followed by dehydration and drying, whereby powdery POM copolymer having a particle size distribution and properties as shown in Table 1 was obtained. For comparison, a similar test was conducted using a stone mill type pulverizer which is called "refiner".

The powdery POM copolymer so obtained was not subjected to the conventional treatment for the decomposition and removal of unstable end portions but was melt-kneaded in an extruder after mixed with, as a stabilizer, 0.5 wt.% of pentaerythrityltetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] and 0.1 wt.% of calcium stearate, whereby a stabilized POM copolymer was

obtained in the pellet form. The evaluation results are shown in Table 1.

Incidentally, the evaluation method and standards are as follows:

[Thermal stability of stabilized POM]

The weight loss of 5 g of stabilized POM copolymer when heated at 220°C for 45 minutes in the air is weighed and it is indicated by a weight reduction ratio (%) per minute.

[Extrudability]

• Biting of raw materials

Observed are the biting condition of the raw materials into an extruder and discharged condition of 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 four ranks A to D:

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 breaking sometimes occurs.

D: Fluctuations in the biting condition are large and a biting amount is totally low and no strands are formed.

- Motor load amplitude

Difference between the maximum and minimum current values of the motor at the time of extrusion (unit: ampere)

- Difference in the fluctuations of the resin pressure

Difference between the maximum and minimum values indicated by the resin manometer disposed immediately after the tip of the screw of the extruder (unit: kg/cm^2).

	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Ex 7	Ex 8	Comp.Ex.1
Water content of monomer (ppm)	15	8	8	8	8	8	8	8	8
Catalyst Kind Concentration (ppm)	BF ₃ 30	BF ₃ 20	BF ₃ 20	BF ₃ 20	BF ₃ 20	BF ₃ 20	BF ₃ 20	HPA 5	BF ₃ 20
Screen mesh shape mesh size (mm)	circular 3	circular 3	oblong 3 x 25	circular 6.5	circular 3	circular 1.5	oblong 6.5 x 25	circular 3	refiner
Clearance (mm)	10	10	10	10	20	10	10	10	-
Particle size distribution (%)	Average particle size	0.46	0.49	0.59	0.74	0.22	0.81	0.40	0.85
	D > 1.0 mm	7	10	11	30	3	34	8	45
	1.0 mm ≥ D ≥ 0.18 mm	71	67	67	65	51	63	69	40
	0.18 mm > D	22	23	22	5	46	3	23	15
Amount of unstable ends after deactivation (%)	0.78	0.66	0.67	0.85	0.79	0.65	0.88	0.68	1.10
Thermal stability of stabilized POM	0.013	0.005	0.005	0.017	0.015	0.005	0.018	0.005	0.037
Biting condition of raw material Motor load amplitude Fluctuation difference of resin Pressure	A	A	A	A	A	C	A	A	A
	2	2	2	3	2	10	3	2	4
	3	3	2	3	3	10	4	3	5

BF₃: boron trifluoride HPA: phosphomolybdic acid



CLAIMS

1. A process for deactivating a catalyst contained in an oxymethylene copolymer, characterized by pulverizing the oxymethylene copolymer discharged from a polymerizer with a pulverizer having the below-described structure and also deactivating the polymerization catalyst with a basic compound:

[Structure of the pulverizer]

a pulverizer having a stator-side element, a rotor-side element, rotation drive means, an inlet for the substance to be pulverized and an outlet provided with a screen mesh for the pulverized substance, each of the stator-side and rotor-side elements having projections inter-mittently arranged so as to form one or more concentric circles on a nearly circular base, and the projections arranged to form the concentric circle(s) on the rotor-side element being rotated at a predetermined clearance from the projections arranged to form the concentrated circle(s) on the rotor-side element upon the rotation of the rotor-side element to make the pulverization possible.





2. The process for deactivating a catalyst contained in an oxymethylene copolymer according to claim 1, wherein the screen mesh of the pulverizer has circular mesh openings having a diameter of 2 to 6 mm or oval-shaped mesh openings having a major axis of 10 to 30 mm and a minor axis of 2 to 6 mm.

3. The process for deactivating a catalyst contained in an oxymethylene copolymer according to claim 1 or 2, wherein the clearance between the outermost side of the projections on the rotor-side element and the screen mesh is 8 to 15 mm in the pulverizer.

4. The process for deactivating a catalyst contained in an oxymethylene copolymer according to any of claims 1 to 3, wherein the oxymethylene copolymer pulverized with the pulverizer satisfies the following requirements (1) to (4) of the particle size distribution:

(1) the average particle diameter is 0.3 to 0.7 mm,

(2) 3 to 20% by weight of the particles have





a diameter of longer than 1.0 mm,

(3) 50 to 97% by weight of the particles have a diameter of 0.18 to 1.0 mm, and

(4) 0 to 30% by weight of the particles have a diameter of shorter than 0.18 mm

(the total being 100% by weight).

5. The process for deactivating a catalyst contained in an oxymethylene copolymer according to any of claims 1 to 4, wherein the oxymethylene copolymer is one obtained by the polymerization conducted in the presence of a proton acid as the catalyst.

6. The process for deactivating a catalyst contained in an oxymethylene copolymer according to any of claims 1 to 4, wherein the oxymethylene copolymer is one obtained by the polymerization conducted in the presence of 15 to 25 ppm, based on the starting monomer, of a Lewis acid as the catalyst.

7. The process for deactivating a catalyst contained in an oxymethylene copolymer according to





any of claims 1 to 6, wherein the oxymethylene copolymer is one obtained by the polymerization conducted in the presence of a hindered phenolic compound.

8. The process for deactivating a catalyst contained in an oxymethylene copolymer according to any of claims 1 to 7, wherein the oxymethylene copolymer is one obtained by the polymerization of a monomer having a water content of 10 ppm or below.

9. The process for deactivating a catalyst contained in an oxymethylene copolymer according to any of claims 1 to 8, wherein the pulverization is conducted by the wet pulverization method and the deactivation treatment is conducted with an aqueous solution of a basic compound.

10. The process for deactivating a catalyst contained in an oxymethylene copolymer according to any of claims 1 to 9, wherein the deactivation treatment is conducted by adding the aqueous solution of a basic compound between the point immediately before the outlet for the polymer of the





polymerizer and the inlet of the pulverizer.

11. A process for producing a stabilized oxymethylene copolymer, characterized by melt-kneading the oxymethylene copolymer, after the deactivation of the catalyst by the process according to any of claims 1 to 10, with a stabilizer substantially without any step of stabilizing the ends by removing an unstable end part by decomposition.

12. The process for producing a stabilized oxymethylene copolymer according to claim 11, wherein the oxymethylene copolymer has 0.3 to 0.8% by weight (based on the copolymer) of the unstable ends after the deactivation of the catalyst.



ABSTRACT

PROCESS FOR DEACTIVATING CATALYST CONTAINED IN OXYMETHYLENE COPOLYMER AND PROCESS FOR PRODUCING STABILIZED OXYMETHYLENE COPOLYMER

A process for deactivating a catalyst contained in an oxymethylene copolymer discharged from a polymerizer is pulverized with a pulverizer having the below-described structure and the polymerization catalyst is deactivated with a basic compound:

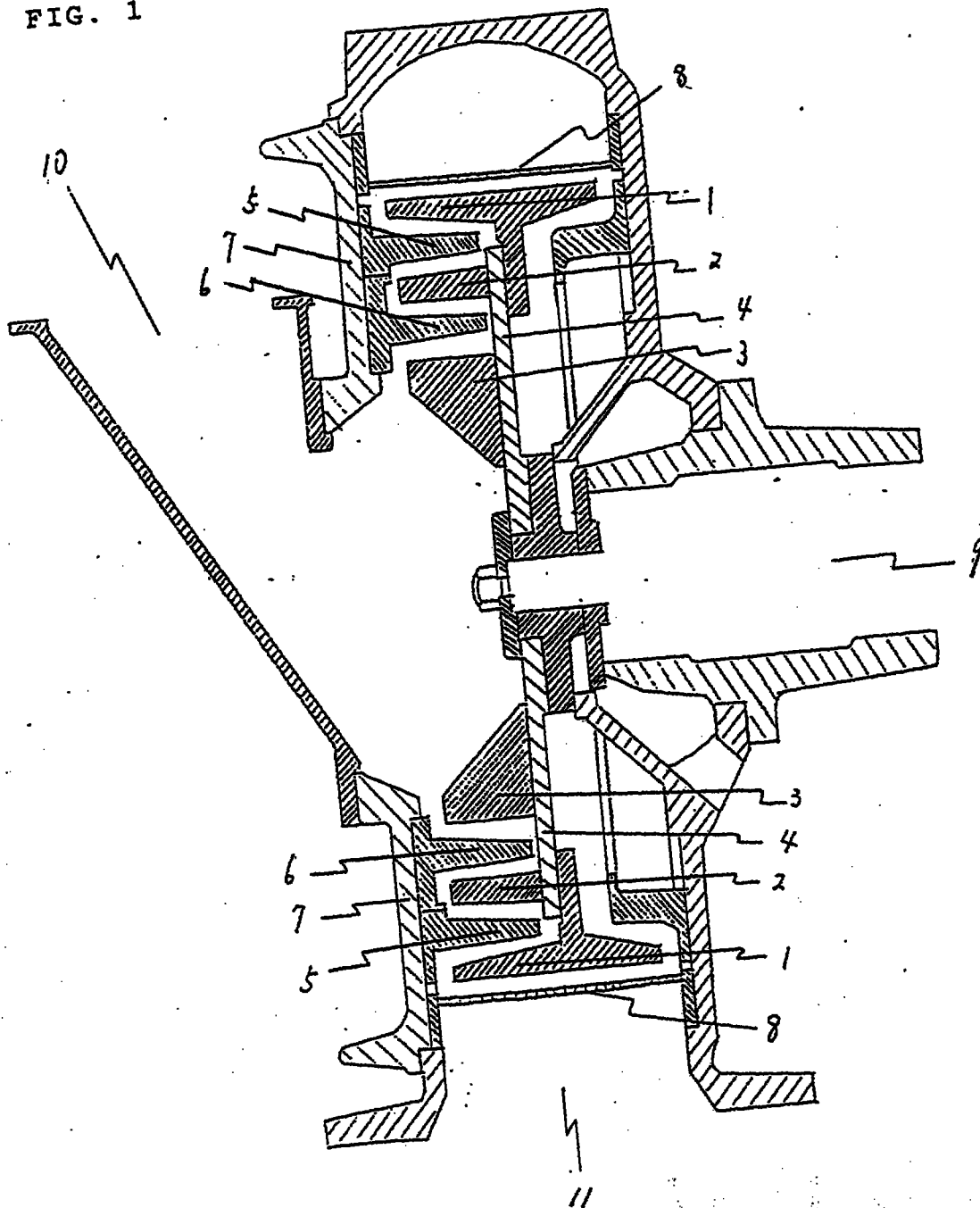
[Structure of the pulverizer]

a pulverizer having a stator-side element, a rotor-side element, rotation drive means, an inlet for the substance to be pulverized and an outlet provided with a screen mesh for the pulverized substance, each of the stator-side and rotor-side elements having projections intermittently arranged so as to form one or more concentric circles on a nearly circular base, and the projections arranged to form the concentric circle(s) on the rotor-side element being rotated at a predetermined clearance from the projections arranged to form the concentrated circle(s) on the rotor-side element upon the rotation of the rotor-side element to make the pulverization possible.



DRAWINGS

FIG. 1



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DESCRIPTION

PROCESS FOR DEACTIVATING CATALYST CONTAINED IN
OXYMETHYLENE COPOLYMER AND PROCESS FOR PRODUCING
STABILIZED OXYMETHYLENE COPOLYMER

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to an efficient process for deactivating a catalyst contained in an oxymethylene copolymer obtained by polymerization and also an economical process for producing an oxymethylene copolymer having excellent thermal stability.

Description of the Related Art:

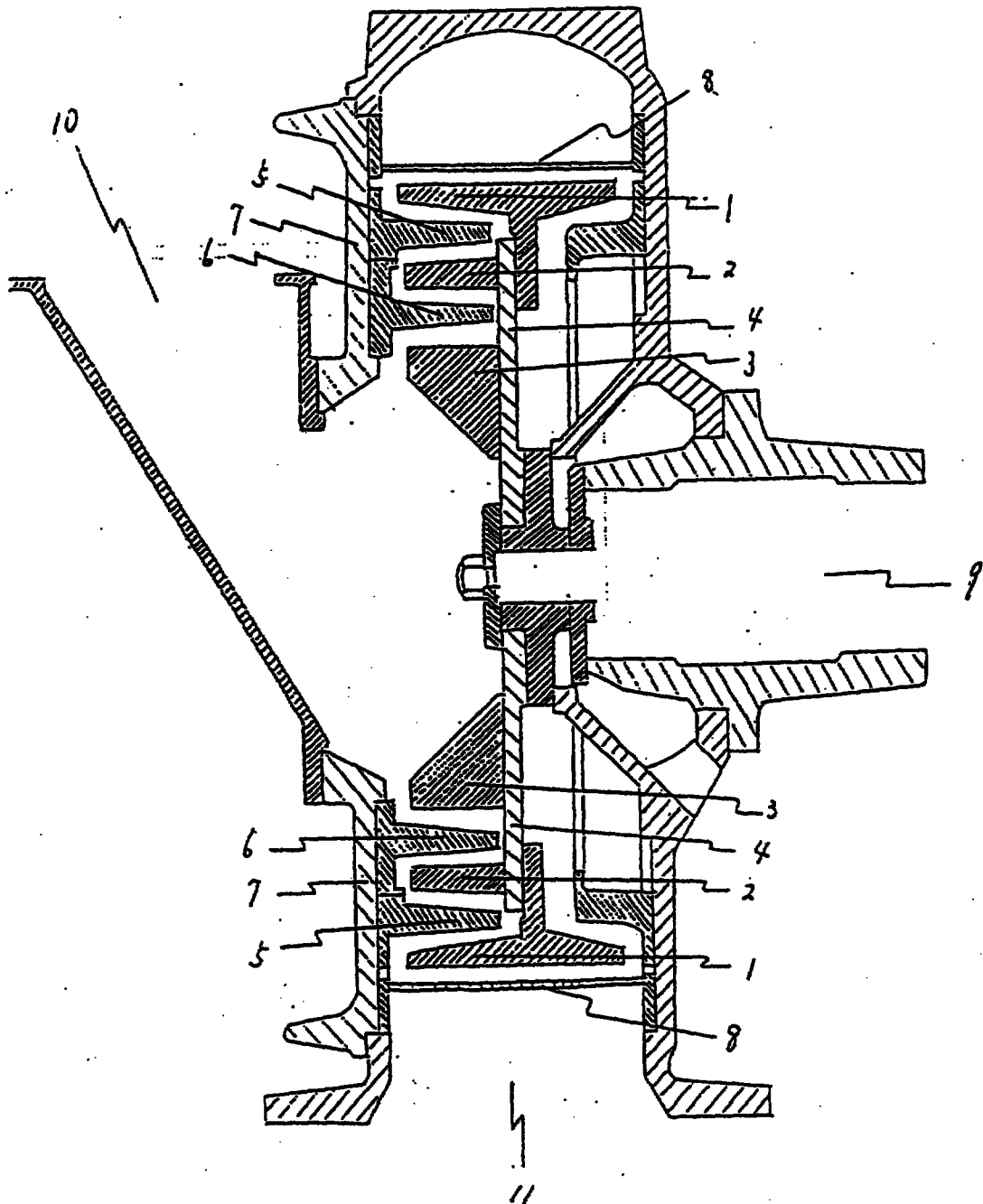
Since a polyoxymethylene copolymer (which may hereinafter be abbreviated as "POM copolymer") has excellent mechanical properties, heat resistance, chemical resistance, electrical properties and sliding properties and at the same time has excellent moldability or formability, it is used as an engineering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

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DRAWINGS

FIG. 1



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contained in an oxymethylene copolymer, which comprises pulverizing an oxymethylene copolymer discharged from a polymerizer with a pulverizer having the below-described structure and also deactivating the polymerization catalyst with a basic compound:

[Structure of Pulverizer]

a pulverizer having a stator-side element, a rotor-side element, rotation drive means, an inlet for the substance to be pulverized and an outlet provided with a screen mesh for the pulverized substance, each of the stator-side and rotor-side elements having projections intermittently arranged so as to form one or more concentric circles on a nearly circular base, and the projections arranged to form the concentric circle(s) on the rotor-side element being rotated at a predetermined clearance from the projections arranged to form the concentric ~~concentrated~~ circle(s) on the stator ~~rotor~~-side element upon the rotation of the rotor-side element to make the pulverization possible.

There is also provided a process for producing a stabilized oxymethylene copolymer, which

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stator-side and rotor-side elements having projections intermittently arranged so as to form one or more concentric circles on a nearly circular base, and the projections arranged to form the concentric circle(s) on the rotor-side element being rotated at a predetermined clearance from the concentric projections arranged to form the ~~concentric~~ stator circle(s) on the ~~rotor~~-side element upon the rotation of the rotor-side element to make the pulverization possible. The specific example of this pulverizer has a structure as illustrated in FIG. 1.

Brief Description of the Drawings:

FIG. 1 is a cross-sectional schematic view illustrating one example of a pulverizer usable in the present invention.

Description of Numerical Reference:

- 1 projection arranged so as to form a concentric circle on a rotor-side nearly circular base
- 2 other projection arranged so as to form the concentric circle on the rotor-side nearly circular base
- 3 another projection arranged so as to form the

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CLAIMS

1. A process for deactivating a catalyst contained in an oxymethylene copolymer, characterized by pulverizing the oxymethylene copolymer discharged from a polymerizer with a pulverizer having the below-described structure and also deactivating the polymerization catalyst with a basic compound:

[Structure of the pulverizer]

a pulverizer having a stator-side element, a rotor-side element, rotation drive means, an inlet for the substance to be pulverized and an outlet provided with a screen mesh for the pulverized substance, each of the stator-side and rotor-side elements having projections intermittently arranged so as to form one or more concentric circles on a nearly circular base, and the projections arranged to form the concentric circle(s) on the rotor-side element being rotated at a predetermined clearance from the projections arranged to form the concentric ~~concentrated~~ circle(s) on the stator ~~rotor~~-side element upon the rotation of the rotor-side element to make the pulverization possible.

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ABSTRACT

PROCESS FOR DEACTIVATING CATALYST CONTAINED IN
OXYMETHYLENE COPOLYMER AND PROCESS FOR PRODUCING
STABILIZED OXYMETHYLENE COPOLYMER

A process for deactivating a catalyst contained in an oxymethylene copolymer discharged from a polymerizer is pulverized with a pulverizer having the below-described structure and the polymerization catalyst is deactivated with a basic compound:

[Structure of the pulverizer]

a pulverizer having a stator-side element, a rotor-side element, rotation drive means, an inlet for the substance to be pulverized and an outlet provided with a screen mesh for the pulverized substance, each of the stator-side and rotor-side elements having projections intermittently arranged so as to form one or more concentric circles on a nearly circular base, and the projections arranged to form the concentric circle(s) on the rotor-side element being rotated at a predetermined clearance from the projections arranged to form the concentric stator ~~concentrated~~ circle(s) on the ~~rotor~~-side element upon the rotation of the rotor-side element to make the pulverization possible.

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ABSTRACT

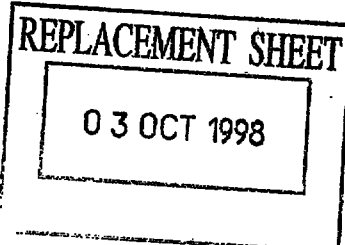
PROCESS FOR DEACTIVATING CATALYST CONTAINED IN OXYMETHYLENE COPOLYMER AND PROCESS FOR PRODUCING STABILIZED OXYMETHYLENE COPOLYMER

A process for deactivating a catalyst contained in an oxymethylene copolymer discharged from a polymerizer is pulverized with a pulverizer having the below-described structure and the polymerization catalyst is deactivated with a basic compound:

[Structure of the pulverizer]

a pulverizer having a stator-side element, a rotor-side element, rotation drive means, an inlet for the substance to be pulverized and an outlet provided with a screen mesh for the pulverized substance, each of the stator-side and rotor-side elements having projections intermittently arranged so as to form one or more concentric circles on a nearly circular base, and the projections arranged to form the concentric circle(s) on the rotor-side element being rotated at a predetermined clearance from the projections arranged to form the concentric ~~concentrated~~ circle(s) on the stator ~~rotor~~-side element upon the rotation of the rotor-side element to make the pulverization possible.

Figure to accompany Abstract : Figure 1



CLAIMS

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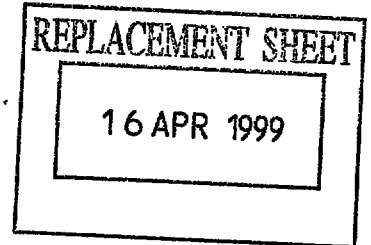
1. A process for deactivating a catalyst contained in an oxymethylene copolymer, characterized by pulverizing the oxymethylene copolymer discharged from a polymerizer with a pulverizer having the below-described structure and also deactivating the polymerization catalyst with a basic compound:

[Structure of the pulverizer]

a pulverizer having a stator-side element, a rotor-side element, rotation drive means, an inlet for the substance to be pulverized and an outlet provided with a screen mesh for the pulverized substance, each of the stator-side and rotor-side elements having projections inter-mittently arranged so as to form one or more concentric circles on a nearly circular base, and the projections arranged to form the concentric circle(s) on the rotor-side element being rotated at a predetermined clearance from the projections arranged to form the concentric ~~concentrated~~ circle(s) on the stator ~~rotor~~-side element upon the rotation of the rotor-side element to make the pulverization possible.



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CLAIMS

1. A process for deactivating a catalyst contained in an oxymethylene copolymer, characterized by pulverizing the oxymethylene copolymer discharged from a polymerizer with a pulverizer having the below described structure, such that the oxymethylene copolymer so pulverized satisfies the following requirements (1) to (4) of the particle size distribution:

(1) the average particle diameter being 0.3 to 0.7 mm.

(2) 3 to 20% by weight of the particles having a diameter of longer than 1.0 mm.

(3) 50 to 97% by weight of the particles having a diameter of 0.18 to 1.0 mm.

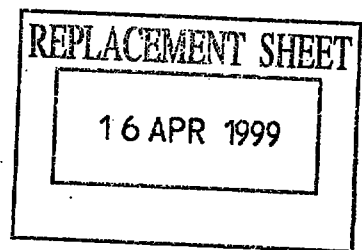
(4) 0 to 30% by weight of the particles having a diameter of shorter than 0.18 mm.

(the total being 100% by weight).

and also deactivating the polymerization catalyst with a basic compound:

[Structure of the pulverizer]

a pulverizer having a stator-side element, a rotor-side element, rotation drive means, an inlet for



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the substance to be pulverized and an outlet provided with a screen mesh for the pulverized substance, each of the stator-side and rotor-side elements having projections inter-mittently arranged so as to form one or more concentric circles on a nearly circular base, and the projections arranged to form the concentric circle(s) on the rotor-side element being rotated at a predetermined clearance from the projections arranged to form the concentric circles(s) on the stator-side element upon the rotation of the rotor-side element to make the pulverization possible.



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2. The process for deactivating a catalyst contained in an oxymethylene copolymer according to claim 1, wherein the screen mesh of the pulverizer has circular mesh openings having a diameter of 2 to 6 mm or oval-shaped mesh openings having a major axis of 10 to 30 mm and a minor axis of 2 to 6 mm.

3. The process for deactivating a catalyst contained in an oxymethylene copolymer according to claim 1 or 2, wherein the clearance between the outermost side of the projections on the rotor-side element and the screen mesh is 8 to 15 mm in the pulverizer.

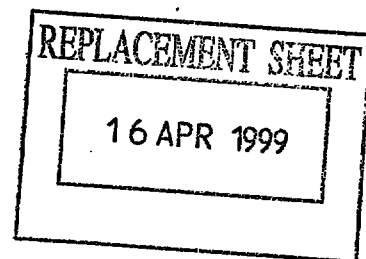
~~4. The process for deactivating a catalyst contained in an oxymethylene copolymer according to any of claims 1 to 3, wherein the oxymethylene copolymer pulverized with the pulverizer satisfies the following requirements (1) to (4) of the particle size distribution:~~

~~(1) the average particle diameter is 0.3 to 0.7 mm,~~

~~(2) 3 to 20% by weight of the particles have~~



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~~a diameter of longer than 1.0 mm,~~

~~(3) 50 to 97% by weight of the particles have
a diameter of 0.18 to 1.0 mm, and~~

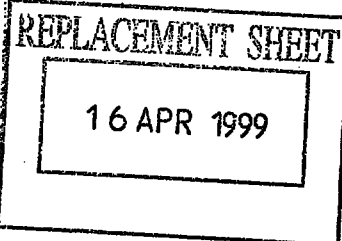
~~(4) 0 to 30% by weight of the particles have
a diameter of shorter than 0.18 mm~~

~~(the total being 100% by weight).~~

4. ~~5.~~ The process for deactivating a catalyst
contained in an oxymethylene copolymer according to
any of ~~claims 1 to 4~~ ^{claims 1 to 3}, wherein the oxymethylene
copolymer is one obtained by the polymerization
conducted in the presence of a proton acid as the
catalyst.

5. ~~6.~~ The process for deactivating a catalyst
contained in an oxymethylene copolymer according to
any of ~~claims 1 to 4~~ ^{claims 1 to 3}, wherein the oxymethylene
copolymer is one obtained by the polymerization
conducted in the presence of 15 to 25 ppm, based on
the starting monomer, of a Lewis acid as the
catalyst.

6. ~~7.~~ The process for deactivating a catalyst
contained in an oxymethylene copolymer according to



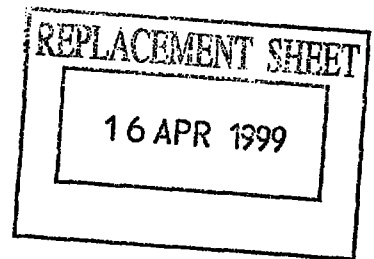
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any of ~~claims 1 to 6~~^{claims 1 to 5}, wherein the oxymethylene copolymer is one obtained by the polymerization conducted in the presence of a hindered phenolic compound.

7. ~~8~~ The process for deactivating a catalyst contained in an oxymethylene copolymer according to any of ~~claims 1 to 7~~^{claims 1 to 6}, wherein the oxymethylene copolymer is one obtained by the polymerization of a monomer having a water content of 10 ppm or below.

8. ~~9~~ The process for deactivating a catalyst contained in an oxymethylene copolymer according to any of ~~claims 1 to 8~~^{claims 1 to 7}, wherein the pulverization is conducted by the wet pulverization method and the deactivation treatment is conducted with an aqueous solution of a basic compound.

9. ~~10~~ The process for deactivating a catalyst contained in an oxymethylene copolymer according to any of ~~claims 1 to 9~~^{claims 1 to 8}, wherein the deactivation treatment is conducted by adding the aqueous solution of a basic compound between the point immediately before the outlet for the polymer of the



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polymerizer and the inlet of the pulverizer.

10. ~~11~~ A process for producing a stabilized oxymethylene copolymer, characterized by melt-kneading the oxymethylene copolymer, after the deactivation of the catalyst by the process according to any of claims 1 to 9 ~~claims 1 to 10~~, with a stabilizer substantially without any step of stabilizing the ends by removing an unstable end part by decomposition.

11. ~~12~~ The process for producing a stabilized oxymethylene copolymer according to claim 10 ~~claim 11~~, wherein the oxymethylene copolymer has 0.3 to 0.8% by weight (based on the copolymer) of the unstable ends after the deactivation of the catalyst.