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DESCRIPTION

PROCESS FOR PRODUCTION OF STABILIZED
OXYMETHYLENE COPOLYMER

Technical Field

The present invention relates to a process for producing a stable oxymethylene copolymer by efficiently mixing a stabilizer and/or an additive into an oxymethylene copolymer. More particularly, the present invention relates to a process for producing a stabilized oxymethylene copolymer, which comprises subjecting a crude oxymethylene copolymer to terminal stabilization in an extruder (A) having a terminal-stabilizing zone and a vacuum zone for volatile components removal and mixing the terminal-stabilized oxymethylene copolymer with a stabilizer and/or an additive, wherein the total or part of a melt-kneading mixture obtained by melt-kneading a polyoxymethylene and a stabilizer and/or an additive in other extruder (B) is fed in a molten state into a section of the extruder (A) following the vacuum zone for volatile components removal, to knead the terminal-stabilized oxymethylene copolymer, the polyoxymethylene and the stabilizer and/or the additive.

Background Art

Mixing of a stabilizer and/or an additive

into a synthetic resin for improvement of properties of the resin has heretofore been conducted by uniformly mixing a synthetic resin powder with a stabilizer and/or an additive in a Henschel mixer and then heat-
5 melting the resulting mixture in a single or double screw extruder.

In the case of an oxymethylene copolymer, the copolymer right after polymerization has thermally unstable terminals $[-(\text{OCH}_2)_n\text{-OH}]$ and therefore is
10 generally subjected to terminal stabilization in a molten state by the use of a vent type screw extruder. With respect to the mixing of a stabilizer and/or an additive into a crude oxymethylene copolymer, JP-A-63-196615 discloses completely melting a crude copolymer
15 in an extruder, then mixing therewith a terminal stabilizer and an auxiliary in a pressurized region in the extruder and continuously removing unstable components from the crude copolymer. This publication also discloses in examples a method for removing
20 unstable components wherein a melt-kneading mixture composed of a stabilizer and/or an additive and polyoxymethylene is introduced into the pressurized region in the extruder.

The position at which and the amount in which
25 the melt-kneading mixture is introduced into the extruder, being disclosed in the above publication, however, results in problems of reduced thermal stability, coloring, etc. of the resulting oxymethylene

copolymer, when there is used such a stabilizer and/or an additive as to have reactivity with the terminal stabilizer used or with a formaldehyde gas generated during terminal stabilization. Further, since it is often conducted in the vacuum zone of extruder for volatile components removal to intensify the vacuum removal of volatile components for higher terminal stabilization, the stabilizer and/or the additive is diffused into the gas to be vented; thus, the above mixing is disadvantageous also in economy.

It is also known to subject a crude oxymethylene copolymer to terminal stabilization and then feeding a stabilizer and/or an additive to a section of an extruder following the vacuum zone for volatile components removal. In this case, however, direct feeding of the stabilizer and/or the additive per se to the copolymer tends to invite poor dispersion of the stabilizer and/or the additive; in order to improve the dispersibility, a means such as making larger L/D of the extruder, wherein L is the length of the extruder in the direction of the rotation axis and D is the inner diameter of the extruder, is necessary. This approach is disadvantageous in economy as well and tends to invite the thermal deterioration of resin.

Hence, there has been strongly desired a process for producing a stable oxymethylene copolymer excellent in quality and economy, which is free from the above-mentioned problems of the prior art.

Disclosure of the Invention

The present invention has been made in view of the above-mentioned situation. According to the present invention there is provided a process for
5 producing a stabilized oxymethylene copolymer, which comprises subjecting a crude oxymethylene copolymer to terminal stabilization in an extruder (A) having a terminal-stabilizing zone and a vacuum zone for volatile components removal to obtain a terminal-
10 stabilized oxymethylene copolymer, separately melt-kneading a polyoxymethylene and a stabilizer and/or an additive in other extruder (B), feeding the resulting melt-kneading mixture in a molten state into a section of the extruder (A) following the vacuum zone for
15 volatile components removal so that the proportions of the polyoxymethylene to be fed from the extruder (B) and the crude oxymethylene copolymer to be subjected to terminal stabilization in the extruder (A) become 1:3 to 1:45 by weight ratio, and kneading the polyoxy-
20 methylene, the stabilizer and/or the additive and the terminal-stabilized oxymethylene copolymer.

Best Mode for Carrying Out the Invention

The present invention is described in detail below.

25 In the present invention, the polyoxymethylene to be melt-kneaded with a stabilizer and/or an additive in the extruder (B) may be any of a

homopolymer and a copolymer, or a mixture thereof.

The extruder (A) can be any of a single screw extruder and a multiple screw extruder as long as it has a terminal-stabilizing zone and a vacuum zone for volatile components removal. A vent type double screw extruder is used preferably. The extruder (B) may have or may not have a vent hole, and may be a single screw type.

The crude oxymethylene copolymer in the present invention is a copolymer of formaldehyde or trioxane with a cyclic ether and/or a cyclic formal and has a thermally unstable group $-(OCH_2)_n-OH$ at part of the molecular terminals. The word "crude" preceding the term "oxymethylene copolymer" means the said copolymer having the above-mentioned thermally unstable group at part of the molecular terminals. Therefore, the stabilization of the molecular terminals in the extruder (A) is necessary.

In the present specification, the terminal-stabilizing zone refers to a section of the extruder (A) wherein the unstable molecular terminals are decomposed under pressure by the use of a terminal stabilizer (e.g. a basic substance) and an auxiliary, i.e. water and/or an organic solvent to stabilize the oxymethylene copolymer. Since the sufficient kneading of the crude oxymethylene copolymer, the terminal stabilizer and the auxiliary is important, a screw preferably used in the extruder is preferably

constituted by kneading elements in a part or the whole region of the terminal-stabilizing zone. Each kneading element may be a disc type, but a block type composed of a plurality of kneading elements may also be used.

5 The temperature for terminal stabilization is in a range of the melting point of the oxymethylene copolymer to 265°C and a particularly preferable temperature range is 190-230°C.

 The vacuum zone for volatile components
10 removal refers to a section of the extruder (A) which has a vent and wherein the unreacted monomers contained in the crude oxymethylene copolymer, the formaldehyde generated during terminal stabilization, the terminal stabilizer, the auxiliary, etc. are removed under
15 reduced pressure.

 The extruder (A) and the extruder (B) may be connected by the use of, for example, a double tube, or may be connected directly.

 The basic substance used as terminal
20 stabilizer is particularly preferably ammonia or an aliphatic amine compound such as triethylamine, tributylamine, etc. As other basic substances, there are mentioned hydroxides, inorganic weak acid salts, organic acid salts, etc. of alkali metals or alkaline
25 earth metals. Specific examples thereof are hydroxides, carbonates, phosphates, silicates, borates, formates, acetates, stearates, palmitates, propionates,

succinates, etc. of sodium, potassium, magnesium, calcium or barium.

The amount of these basic substances added is 0.01-5 parts by weight based on the oxymethylene copolymer in the case of ammonia or the amine compounds and, in the case of hydroxides, inorganic weak acid salts, organic acid salts, etc. of alkali metals or alkaline earth metals, the amount added is limited to 2 to 5,000 ppm because of the problems of coloring, etc.

In the extruder (B) were melt-kneaded polyoxymethylene and a stabilizer and/or an additive.

Preferably 50-100%, more preferably 70-100% of the resulting melt-kneaded mixture is fed into a section of the extruder (A) following the vacuum zone for volatile components removal, with the molten state being kept. When the amount fed into the said section of the extruder (A) is less than 50%, the resulting oxymethylene copolymer has problems in quality, coloring, etc.

In the present invention, the extruder (A) is preferably a double screw extruder, and the section of the extruder (A) following the inlet for the polyoxymethylene containing a stabilizer and/or an additive has an L/D of preferably 0.5-25, more preferably 1-20. When the L/D is less than 0.5, the uniform mixing of the oxymethylene copolymer, the polyoxymethylene and the stabilizer and/or the additive is difficult. When the L/D is more than 25, the resulting oxymethylene

copolymer has a problem in thermal stability.

The proportions of the polyoxymethylene to be fed from the extruder (B) and the crude oxymethylene copolymer to be subjected to terminal stabilization in the extruder (A) are 1:3 to 1:45, preferably 1:5 to 1:40, more preferably 1:5 to 1:30, all by weight ratio. A proportion of the crude oxymethylene copolymer smaller than the above results in poor economy. With a proportion of the crude oxymethylene copolymer larger than the above, the concentration of the stabilizer and/or the additive in the polyoxymethylene in the extruder (B) has to be very high in order to feed a required amount of the stabilizer and/or the additive to the extruder (A), which makes difficult the dispersion of the stabilizer and/or the additive in the polyoxymethylene in the extruder (B) and invites the thermal deterioration, discoloration, etc. of the stabilizer and/or the additive. Further, screw slippage, etc. occurs depending upon the kind of stabilizer and/or additive used, reducing the operability of the system. Furthermore, the uniform dispersion of the polyoxymethylene and the stabilizer and/or the additive in the oxymethylene copolymer in the extruder (A) is difficult and the resulting oxymethylene copolymer has reduced thermal stability.

With respect to the resin properties of the oxymethylene copolymer and the polyoxymethylene both used in the present invention, the ratio of the MI of

the polyoxymethylene to be fed from the extruder (B) and the MI of the crude oxymethylene copolymer to be subjected to terminal stabilization in the extruder (A) is preferably 1/50 to 50, more preferably 1/30 to 30.

- 5 When the ratio deviates from the range, the uniform mixing of the polyoxymethylene and the oxymethylene copolymer is difficult.

In the extruder (A), it is preferable that the amount of formaldehyde in the oxymethylene
10 copolymer after terminal stabilization and volatile components removal under reduced pressure, which is formed by the decomposition of unstable terminals or which is present as residual formaldehyde, is controlled at 1,000 ppm or less. When the amount of
15 formaldehyde is more than 1,000 ppm, there arise problems such as coloring of oxymethylene copolymer and the like.

According to the present invention, an stabilizer and/or an additive can be stably and
20 uniformly mixed into the crude oxymethylene copolymer, and an oxymethylene copolymer excellent in quality and economy can be obtained.

In the present invention, there can be used, as the stabilizer and the additive, known stabilizers
25 and additives added to oxymethylene copolymers, that is, an antioxidant, a formaldehyde catcher, a light stabilizer, an ultraviolet absorber, a lubricant, a nucleating agent, an antistatic agent, a filler, talc,

etc.

As the antioxidant, there can be mentioned, for example, n-octadecyl 3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate, n-octadecyl 3-(3'-methyl-5'-t-butyl-4'-hydroxyphenyl)propionate, n-tetradecyl 3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate, 1,6-hexanediol bis-(3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate, 1,4-butanediol bis-(3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, triethylene glycol bis-(3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate, tetrakis-(methylene 3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate methane, N,N'-bis(3-(3,5-di-t-butyl-4-hydroxyphenol)propionyl)hydrazine, N,N'-tetramethylenebis-3-(3'-methyl-5'-t-butyl-4-hydroxyphenol)-propionyldiamine, N,N'-bis-3-(3',5'-di-t-butyl-4-hydroxyphenol)propionylhexamethylenediamine, 3-(N-salicyloyl)amino-1,2,4-triazole, N,N'-bis(2-(3-(3,5-dibutyl-4-hydroxyphenyl)propionyloxy)ethyl)oxyamide, etc. These antioxidants may be used singly or as admixture of two or more. The amount of the antioxidant used is preferably 0.01-3 parts by weight, more preferably 0.03-1 part by weight per 100 parts by weight of the oxymethylene copolymer.

The formaldehyde catcher is typically a nitrogen-containing compound reactive with formaldehyde and includes, for example, polyamide resins, amide compounds, urea derivatives, triazine derivatives, urethane compounds, etc. The formaldehyde catcher

specifically includes nylon 6, nylon 11, nylon 12, nylon 66, nylon 6•10, nylon 6/6•10, nylon 6/6•6, nylon 6•6/6•10 and nylon 6/6•6/6•10, which are obtained by condensation of a diamine and a dicarboxylic acid, condensation of amino acids, ring-opening polymerization of a lactam, etc; polyamide resins such as poly(β -alanine) and the like; amide compounds such as stearyl-stearamide, stearyl-oleamide, stearyl-erucamide, ethylenediamine-distearic acid amide, ethylenediamine-dibehenic acid amide, hexamethylenediamine-distearic acid amide, ethylenediamine-dierucic acid amide, xylylenediamine-dierucic acid amide, di(xylylene-diamine-stearic acid amide), sebacamide and the like, which are formed by an aliphatic monocarboxylic acid, an aliphatic dicarboxylic acid, an aromatic monocarboxylic acid or an aromatic dicarboxylic acid and an aliphatic monoamine, an aliphatic diamine, an aromatic monoamine or an aromatic diamine; urea derivatives such as N-phenylurea, N,N'-diphenylurea, N-phenylthiourea, N,N'-diphenylthiourea and the like; triazine derivatives such as melamine, benzoguanamine, N-phenylmelamine, melem, N,N'-diphenylmelamine, N-methylolmelamine, N,N'-trimethylolmelamine, 2,4-diamino-6-cyclohexyltriazine, melam and the like; and so forth.

These nitrogen-containing compounds may be used singly or as admixture of two or more. The amount of the nitrogen-containing compound added is preferably

0.01-2 parts by weight, more preferably 0.03-1 part by weight per 100 parts by weight of the oxymethylene copolymer.

As other stabilizer, there is mentioned a
5 basic compound capable of neutralizing formic acid. It includes, for example, hydroxides, inorganic weak acid salts, organic acid salts, etc. of alkali metals or alkaline earth metals. Specific examples thereof are hydroxides, carbonates, phosphates, silicates, borates,
10 formates, acetates, stearates, palmitates, propionates, succinates, etc. of sodium, potassium, magnesium, calcium, or barium.

These basic compounds may be used singly or as admixture of two or more. The amount of the basic
15 compound used is preferably 0.01-3 parts by weight, more preferably 0.03-1 part by weight per 100 parts by weight of the oxymethylene copolymer.

Some of the stabilizers and additives are not reacted with the terminal stabilizer or the formal-
20 dehyde generated during terminal stabilization and are thermally stable. Such a stabilizer and/or an additive, when used, may be directly and by itself added to the extruder (A) separately from the extruder (B) before terminal stabilization, if economy is
25 ignored.

Next, the present invention is described more specifically by way of Examples. However, the present invention is not restricted to these Examples unless it

deviates from the scope of the claims. The substances and methods used in the Examples are as follows.

(1) Production of crude oxymethylene copolymer

Trioxane (3 kg/hr), 1,3-dioxolane (4.5 mole %
5 per mole of trioxane) and boron trifluoride dibutyl etherate as polymerization catalyst (0.15×10^{-4} mole) were continuously fed into a continuous mixer and reactor constituted by two rotary shafts each provided with a plurality of paddles, the paddles of one shaft
10 being engaged with the paddles of the other shaft. The polymer discharged from the reactor was introduced into a 1% aqueous triethylamine solution in a nitrogen atmosphere to conduct a deactivation treatment for 1 hour. The resulting polymer was collected by filtration and
15 dried to obtain a crude oxymethylene copolymer. The polymer had an MI of 9.8.

(2) Extruder (A)

A 30 mm anisotropic double screw extruder having a terminal-stabilizing zone constituted by
20 kneading elements and a vacuum zone for volatile components removal. The extrusion temperature was 200°C and the L/D of the section following the inlet for feed from an extruder (B) was 5.

(3) Extruder (B)

25 A 30 mm anisotropic double screw extruder

having no vent was used. The extrusion temperature was 200°C.

(4) Amount of formaldehyde generated

Expressed as the amount of formaldehyde
5 generated when heated at 230°C. The formaldehyde gas generated at 230°C for 40 minutes in nitrogen was allowed to be absorbed by water and then titration was conducted to measure the amount (ppm) of formaldehyde.

(5) TGA

10 A time (min) up to when 5% reduction in weight takes place at 230°C in air.

(6) Color (bl: yellowness)

Measured by the use of a color difference
meter (MODEL 1000 DP, a product of Nippon Denshoku
15 Kogyo Co., Ltd.).

(7) MI (ASTM D1238)

Flowability was measured by the use of MELT
INDEXER, a product of Toyo Seiki, under the conditions
of 190°C and 2,160 g load (g/10 min).

20 Example 1 (present invention)

Ninety parts by weight of a crude oxy-
methylenecopolymer was fed into an extruder (A). In
the extruder (A), the fed crude oxymethylenecopolymer

was sent under pressure to the terminal-stabilizing zone while being heat-melted. In the terminal-stabilizing zone, 3 parts by weight of a terminal stabilizer (aqueous triethylamine solution) was added
5 to the crude oxymethylene copolymer to conduct the terminal stabilization of the copolymer, and the stabilized copolymer was sent under pressure to the next vacuum zone for volatile components removal. In the vacuum zone for volatile components removal, the
10 formaldehyde generated associated with the terminal stabilization and the like were removed out of the system by pressure reduction. Separately, into an extruder (B) were fed 10 parts by weight of a poly-oxymethylene (a copolymer of MI=9.2), 0.3 part by
15 weight of an antioxidant [N,N-bis(3-(3,5-di-t-butyl-4-hydroxyphenol)propionyl)hydrazine] and 0.2 part by weight of a heat stabilizer (St-Ca), and they were melt-kneaded. The whole of the melt-kneading mixture was fed in a molten state into a section of the
20 extruder (A) following the vacuum zone for volatile components removal and was kneaded with the terminal-stabilized oxymethylene copolymer, after which the kneading mixture was pelletized.

Separately from the above operation, there
25 was measured the amount of formaldehyde in the oxymethylene copolymer after terminal stabilization and volatile components removal under reduced pressure, which was generated by the decomposition of unstable

terminals and which was present as residual formaldehyde. Added to the oxymethylene copolymer was, for prevention of decomposition of the main chain, only an antioxidant (triethylene glycol bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate]), and the copolymer
5 was subjected to terminal stabilization in the extruder (A). The amount of formaldehyde measured was 510 ppm.

Example 2 (present invention)

10 Terminal stabilization and volatile components removal were conducted in the same manner as in Example 1 except that the amount of the polyoxymethylene containing an antioxidant and a heat stabilizer, fed into a section of the extruder (A)
15 following the vacuum zone for volatile components removal was changed to 9 parts by weight and remaining 1 part by weight was fed into the terminal-stabilizing zone of the extruder (A). The resulting oxymethylene copolymer was pelletized.

20 The amount of formaldehyde in the oxymethylene copolymer after terminal stabilization and volatile components removal under reduced pressure, which was generated by the decomposition of unstable terminals and which was present as residual formaldehyde, was 520
25 ppm.

Example 3 (present invention)

Terminal stabilization and volatile compo-

nents removal were conducted in the same manner as in Example 1 except that the antioxidant fed into the extruder (B) was changed to 0.2 part by weight of 2,2'-methylenebis(4-methyl-6-t-butylphenol). The resulting
5 oxymethylene copolymer was pelletized.

The amount of formaldehyde in the oxymethylene copolymer after terminal stabilization and volatile components removal under reduced pressure, which was generated by the decomposition of unstable terminals
10 and which was present as residual formaldehyde, was 500 ppm.

Example 4 (present invention)

Terminal stabilization and volatile components removal were conducted in the same manner as in
15 Example 1 except that the antioxidant and stabilizer fed into the extruder (B) were changed to 0.2 part by weight of triethylene glycol bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate] and 0.2 part by weight of nylon 66, respectively. The resulting oxymethylene
20 copolymer was pelletized.

The amount of formaldehyde in the oxymethylene copolymer after terminal stabilization and volatile components removal under reduced pressure, which was generated by the decomposition of unstable terminals
25 and which was present as residual formaldehyde, was 530 ppm.

Example 5 (present invention)

Terminal stabilization and volatile components removal were conducted in the same manner as in Example 1 except that the antioxidant and heat
5 stabilizer fed into the extruder (B) were changed to pentaerythrityl tetrakis(3-(3,5-t-butyl-4-hydroxy-phenyl)propionate) and 0.2 part by weight of melamine, respectively. The resulting oxymethylene copolymer was pelletized.

10 The amount of formaldehyde in the oxymethylene copolymer after terminal stabilization and volatile components removal under reduced pressure, which was generated by the decomposition of unstable terminals and which was present as residual formaldehyde, was 520
15 ppm.

Example 6 (present invention)

Terminal stabilization and volatile components removal were conducted in the same manner as in Example 4 except that 0.2 part by weight of melamine
20 was further added as another heat stabilizer fed into the extruder (B). The resulting oxymethylene copolymer was pelletized.

The amount of formaldehyde in the oxymethylene copolymer after terminal stabilization and volatile
25 components removal under reduced pressure, which was generated by the decomposition of unstable terminals and which was present as residual formaldehyde, was 530

ppm.

Example 7 (present invention)

Terminal stabilization and volatile components removal were conducted in the same manner as in Example 1 except that the amount of the crude oxymethylene copolymer fed into the extruder (A) was changed to 95 parts by weight and, in the extruder (B), the amount of the polyoxymethylene fed was changed to 5 parts by weight and there were added 0.3 part by weight of an antioxidant (N,N'-bis-(3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyl)hydrazine) and 0.2 part by weight of a heat stabilizer (melamine). The resulting oxymethylene copolymer was pelletized.

The amount of formaldehyde in the oxymethylene copolymer after terminal stabilization and volatile components removal under reduced pressure, which was generated by the decomposition of unstable terminals and which was present as residual formaldehyde, was 540 ppm.

20. Example 8 (present invention)

Terminal stabilization and volatile components removal were conducted in the same manner as in Example 1 except that in the extruder (A), the L/D of the section following an inlet for a polyoxymethylene containing a stabilizer and/or an additive was changed to 3 and, in the extruder (B), the antioxidant and heat

stabilizer both to be fed together with a polyoxy-
methylenes were changed to 0.2 part by weight of 2,2'-
methylenebis-(4-methyl-6-*t*-butylphenol) and 0.3 part by
weight of nylon 66, respectively. The resulting oxy-
5 methylene copolymer was pelletized.

The amount of formaldehyde in the oxymethyl-
ene copolymer after terminal stabilization and volatile
components removal under reduced pressure, which was
generated by the decomposition of unstable terminals
10 and which was present as residual formaldehyde, was 540
ppm.

Example 9 (present invention)

Terminal stabilization and volatile compo-
nents removal were conducted in the same manner as in
15 Example 1 except that in the extruder (A), the L/D of
the section following an inlet for a polyoxymethylene
containing a stabilizer and/or an additive was changed
to 10 and, in the extruder (B), the antioxidant and
heat stabilizer both to be fed together with a
20 polyoxymethylene were changed to 0.2 part by weight of
triethylene glycol bis[3-(3-*t*-butyl-5-methyl-4-hydroxy-
phenyl)propionate] and 0.3 part by weight of St-Ca,
respectively. The resulting oxymethylene copolymer was
pelletized.

25 The amount of formaldehyde in the oxymethyl-
ene copolymer after terminal stabilization and volatile
components removal under reduced pressure, which was

generated by the decomposition of unstable terminals and which was present as residual formaldehyde, was 530 ppm.

Example 10 (present invention)

5 Terminal stabilization and volatile components removal were conducted in the same manner as in Example 4 except that the polyoxymethylene fed into the extruder (B) was changed to a copolymer of MI=3.2. The resulting oxymethylene copolymer was pelletized.

10 The amount of formaldehyde in the oxymethylene copolymer after terminal stabilization and volatile components removal under reduced pressure, which was generated by the decomposition of unstable terminals and which was present as residual formaldehyde, was 520
15 ppm.

Example 11 (comparison)

 Added to 100 parts by weight of a crude oxymethylene copolymer were 0.3 part by weight of an antioxidant (N,N'-bis(3-(3,5-di-t-butyl-4-hydroxy-
20 phenol)propionyl)hydrazine) and 0.2 part by weight of a heat stabilizer (melamine). They were stirred and mixed in a Henschel mixer for 10 minutes and fed into an extruder (A). In the extruder (A), the crude oxymethylene copolymer and stabilizer fed were sent
25 under pressure to the terminal-stabilizing zone while being heat-melted. In the terminal-stabilizing zone, 3

parts by weight of a terminal stabilizer (aqueous triethylamine solution) was added to the crude oxymethylene copolymer to conduct the terminal stabilization of the copolymer, and the stabilized copolymer was
5 sent to the next vacuum zone for volatile components removal. In the vacuum zone for volatile components removal, the formaldehyde generated associated with the terminal stabilization and the like were removed out of the system by pressure reduction. The oxymethylene
10 copolymer, the stabilizer and the additive were discharged with further kneading and pelletized.

Example 12 (comparison)

Terminal stabilization and volatile components removal were conducted in the same manner as
15 in Example 11 except that the antioxidant was changed to 0.3 part by weight of 2,2'-methylenebis(4-methyl-6-t-butylphenol) and the heat stabilizer was changed to 0.2 part by weight of calcium stearate. The resulting oxymethylene copolymer was pelletized.

20 Example 13 (comparison)

Terminal stabilization and volatile components removal were conducted in the same manner as in Example 11 except that the antioxidant was changed to 0.3 part by weight of triethylene glycol bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate] and the heat
25 stabilizer was changed to 0.2 part by weight of nylon

66. The resulting oxymethylene copolymer was pelletized.

Example 14 (comparison)

Terminal stabilization and volatile components removal were conducted in the same manner as in Example 11 except that the antioxidant was changed to 0.3 part by weight of pentaerythrityl tetrakis(3-(3,5-t-butyl-4-hydroxyphenyl)propionate) and the heat stabilizer was changed to 0.2 part by weight of melamine. The resulting oxymethylene copolymer was pelletized.

Example 15 (comparison)

One hundred parts by weight of a crude oxymethylene copolymer was fed into an extruder (A). In the extruder (A), the fed crude oxymethylene copolymer was sent under pressure to the terminal-stabilizing zone while being heat-melted. In the terminal-stabilizing zone, 3 parts by weight of a terminal stabilizer (aqueous triethylamine solution) was added to the crude oxymethylene copolymer to conduct the terminal stabilization of the copolymer, and the stabilized copolymer was sent under pressure to the next vacuum zone for volatile components removal. In the vacuum zone for volatile components removal, the formaldehyde generated associated with the terminal stabilization and the like were removed out of the

system by pressure reduction. Into the section of the extruder (A) following the vacuum zone for volatile components removal were fed, directly in powdery forms, 0.3 part by weight of an antioxidant (triethylene glycol bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)-propionate]) and 0.2 part by weight of a heat stabilizer (nylon 66), and they were kneaded with the terminal-stabilized oxymethylene copolymer. The kneading mixture was discharged and pelletized.

10 The oxymethylene copolymers obtained in Examples 1-10 (present invention) and Examples 11-15 (comparison) were measured for heat stability and coloring, and the results are shown in Tables 1 and 2. In Examples 1-10 (present invention), as compared with
15 Examples 11-15 (comparison), uniform dispersion of antioxidant and heat stabilizer was possible and polymers excellent in heat stability and coloring could be obtained.

Table 1

Example No. (present invention)	Extruder (A)			Extruder (B)			Evaluation	
	Crude oxy-methylene copolymer (parts by wt.)	Stabilizer and additive (part by wt.)	L/D of section following inlet for feed from extruder (B)	Polyoxy-methylene (parts by wt.)	Stabilizer and additive (part by wt.)		Upper: amount of formaldehyde generated (ppm) Lower: TGA (min)	Color bl
Example 1	90	0	5	10	Antioxidant A* ¹ 0.3 St-Ca 0.2		401 51	-1.8
5 Example 2	90	0	5	10	Antioxidant A ¹ 0.3 St-Ca 0.2		433 50	-1.3
Example 3	90	0	5	10	Antioxidant B* ² 0.3 St-Ca 0.2		427 50	-1.7
Example 4	90	0	5	10	Antioxidant C* ³ 0.3 Nylon 66 0.2		6 45	-1.7
Example 5	90	0	5	10	Antioxidant D* ⁴ 0.3 Melamine 0.2		109 52	-1.6
Example 6	90	0	5	10	Antioxidant C* ³ 0.3 Nylon 66 0.2 Melamine 0.2		3 59	-1.8
Example 7	95	0	5	5	Antioxidant A* ¹ 0.3 Melamine 0.2		95 48	-1.8
Example 8	90	0	3	10	Antioxidant B* ² 0.3 Nylon 66 0.2		14 42	-1.6
Example 9	90	0	10	10	Antioxidant C* ³ 0.3 St-Ca 0.2		364 53	-1.8
Example 10	90	0	5	10	Antioxidant D* ⁴ 0.3 Melamine 0.2		122 45	-1.7

Table 2

Example No. (comparison)	Extruder (A)			Extruder, (B)		Evaluation	
	Crude oxy-methylene copolymer (parts by wt.)	Stabilizer and additive (part by wt.)	L/D of section following inlet for feed from extruder (B)	Polyoxy-methylene (parts by wt.)	Stabilizer and additive (part by wt.)	Upper: amount of formaldehyde generated (ppm) Lower: TGA (min)	Color b _l
Example 11	100	Antioxidant A* ¹ 0.3 Melamine 0.2	5	0	0	447 30	+0.4
Example 12	100	Antioxidant B* ² 0.3 St-Ca 0.2	5	0	0	586 34	+2.1
Example 13	100	Antioxidant C* ³ 0.3 Nylon 66 0.2	5	0	0	229 22	+1.4
Example 14	100	Antioxidant D* ⁴ 0.3 Melamine 0.2	5	0	0	395 33	+0.5
6 Example 15	100	0	5	0	Antioxidant C ³ 0.3 Nylon 66 0.2	127 20	-1.4

*1 Antioxidant A: N,N'-bis(3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyl)hydrazine

*2 Antioxidant B: 2,2'-methylenebis(4-methyl-6-t-butylphenol)

*3 Antioxidant C: triethylene glycol bis(3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate)

*4 Antioxidant D: pentaerythrityl tetrakis(3-(3,5-t-butyl-4-hydroxyphenyl)propionate)

*5 In Example 2, the feeding of the oxymethylene copolymer containing an antioxidant and a heat stabilizer was conducted by, as mentioned above, feeding said copolymer of molten state in two portions, that is, 9 parts by weight into a section of the extruder (A) following the vacuum zone for volatile components removal and 1 part by weight into the terminal-stabilizing zone of the extruder (A).

*6 In Example 15, the addition of the antioxidant and the heat stabilizer was conducted by, as mentioned above, feeding them directly in respective powder forms through an inlet of the extruder (A) for feed from the extruder (B), located downstream of the vacuum zone for volatile components removal.

Example 16 (comparison)

Ninety parts by weight of a crude oxymethylene copolymer was fed into an extruder (A). In the extruder (A), the fed crude oxymethylene copolymer was
5 sent under pressure to the terminal-stabilizing zone while being heat-melted. In the terminal-stabilizing zone, 3 parts by weight of a terminal stabilizer (aqueous triethylamine solution) was added to the crude oxymethylene copolymer to conduct the terminal stabili-
10 zation of the copolymer, and the stabilized copolymer was sent under pressure to the next vacuum zone for volatile components removal. In the vacuum zone for volatile components removal, the formaldehyde generated associated with the terminal stabilization and the like
15 were removed out of the system by pressure reduction. Separately, into an extruder (B) were fed 10 parts by weight of a polyoxymethylene (a copolymer of MI=9.2), 0.3 part by weight of an antioxidant (2,2'-methylene-bis(4-methyl-6-t-butylphenol) and 0.2 part by weight of
20 a heat stabilizer (St-Ca), and they were melt-kneaded. The melt-kneading mixture was fed in a molten state into the terminal-stabilizing zone of the extruder (A). The resulting oxymethylene copolymer was pelletized. The results are shown in Table 3.

Example 17 (comparison)

A crude oxymethylene copolymer (98.5 parts by weight) was fed into an extruder (A). In the extruder (A), the fed crude oxymethylene copolymer was sent
5 under pressure to the terminal-stabilizing zone while being heat-melted. In the terminal-stabilizing zone, 3 parts by weight of a terminal stabilizer (aqueous triethylamine solution) was added to the crude oxymethylene copolymer to conduct the terminal stabili-
10 zation of the copolymer, and the stabilized copolymer was sent under pressure to the next vacuum zone for volatile components removal. In the vacuum zone for volatile components removal, the formaldehyde generated associated with the terminal stabilization and the like
15 were removed out of the system by pressure reduction. Separately, into an extruder (B) were fed 1.5 parts by weight of a polyoxymethylene (a copolymer of MI=9.2), 0.3 part by weight of an antioxidant (N,N'-bis(3-(3,5-di-t-butyl-4-hydroxyphenol)propionyl)hydrazine) and 0.2
20 part by weight of a heat stabilizer (melamine), and they were melt-kneaded. The melt-kneading mixture was fed in a molten state into the terminal-stabilizing zone of the extruder (A) and kneaded with the terminally stabilized oxymethylene copolymer. The
25 resulting oxymethylene copolymer was pelletized. The results are shown in Table 3.

Table 3

Example No. (present invention)	Extruder (A)			Extruder (B)		Evaluation	
	Crude oxy-methylene copolymer (parts by wt.)	Stabilizer and additive (part by wt.)	L/D of section following inlet for feed from extruder (B)	Polyoxy-methylene (parts by wt.)	Stabilizer and additive (part by wt.)	Upper: amount of formaldehyde generated (ppm) Lower: TGA (min)	Color bl
*7 Example 16	90	0	15	10	Antioxidant B*2 0.3 St-Ca 0.2	598 30	+2.3
Example 17	98.5	0	5	1.5	Antioxidant A*1 0.3 Melamine 0.2	331 31	-0.5

*1) Same as in Table 2

*2) Same as in Table 2

*7 The addition of the stabilizer and the additive was conducted by, as mentioned above, melt-kneading, in the extruder (B), the polyoxymethylene, the stabilizer and the additive and then feeding the melt-kneading mixture into the terminal-stabilizing zone of the extruder (A).

Industrial Applicability

According to the present invention, a stabilizer and/or an additive can be stably and uniformly mixed into a crude oxymethylene copolymer, and an oxymethylene copolymer excellent in quality and economy can be obtained.

5



CLAIMS

1. A process for producing a stabilized
oxymethylene copolymer, which comprises subjecting a
crude oxymethylene copolymer to terminal stabilization
5 in an extruder (A) having a terminal-stabilizing zone
and a vacuum zone for volatile components removal to
obtain a terminal-stabilized oxymethylene copolymer,
separately melt-kneading a polyoxymethylene and a
stabilizer and/or an additive in other extruder (B),
10 feeding the resulting melt-kneading mixture in a molten
state into a section of the extruder (A) following the
vacuum zone for volatile components removal so that the
proportions of the polyoxymethylene to be fed from the
extruder (B) and the crude oxymethylene copolymer to be
15 subjected to terminal stabilization in the extruder (A)
become 1:3 to 1:45 by weight ratio, and kneading the
polyoxymethylene, the stabilizer and/or the additive
and the terminal-stabilized oxymethylene copolymer.
2. A process for producing a stabilized
20 oxymethylene copolymer according to Claim 1, wherein
50-100% of the melt-kneading mixture of the polyoxy-
methylen containing a stabilizer and/or an additive is
fed from the extruder (B) into a section of the
extruder (A) following the vacuum zone for volatile
25 components removal.
3. A process for producing a stabilized
oxymethylene copolymer according to Claim 1, wherein
the extruder (A) is a double screw extruder and has,



after the position at which the polyoxymethylene containing a stabilizer and/or an additive is fed, a kneading zone of L/D of 0.5-25.

4. A process for producing a stabilized oxy-
- 5 methylene copolymer according to Claim 1, wherein the ratio of the MI of the polyoxymethylene to be fed from the extruder (B) and the MI of the crude oxymethylene copolymer to be subjected to terminal stabilization in the extruder (A) is 1/50 to 50.
- 10 5. A process for producing a stabilized oxy-
- methylene copolymer according to Claim 1, wherein in the extruder (A), the amount of formaldehyde in the oxymethylene copolymer after terminal stabilization and volatile components removal under reduced pressure,
- 15 which is generated by the decomposition of unstable terminals and which is present as residual formaldehyde, is less than or equal to 1,000 ppm.