

Description

The present invention relates to a process for producing an oxymethylene copolymer excellent in heat resistance and mechanical properties. It also relates to an oxymethylene copolymer composition.

5 It has been known from, for example, Japanese Patent Publication No. 14640/61 that oxymethylene copolymer is obtained by polymerizing trioxane and cyclic ether in the presence of a catalyst. Since the polymer thus obtained is thermally unstable, terminal sealing through esterification, or degradation and removal of unstable chain ends, is carried out for stabilization, before which, however, deactivation of the catalyst in order to inhibit further reaction is required. That is, polyoxymethylene derived from cationoid
10 polymerization of trioxane or the like will slowly generate depolymerization, resulting in remarkably lowered molecular weight and/or extreme thermal instability, unless the catalyst remaining therein is deactivated.

As to deactivation of a boron trifluoride polymerization catalyst, U.S. Patent No. 2989509 discloses the use of aliphatic amine or heterocyclic amine. By deactivating the catalyst with such amine followed by washing to remove them, the polymer is stabilized enough to avoid lowering the molecular weight when preserved
15 as it is for a long period.

However, unless the catalyst is removed from the polymer by washing after it is deactivated by a general amine compound, depolymerization will still occur and the molecular weight will be lowered when the polymer is melted or dissolved.

Accordingly, it has been essential to remove the catalyst from the polymer by a thorough washing operation
20 after the catalyst is deactivated by normal amine. Japanese Patent Publication Nos. 8071/64 and 1875/68, for example, propose methods of stabilizing copolymer chain ends, in which cases also prior to starting the chain ends stabilizing process, a polymerization catalyst is deactivated by amine and then removed by washing. In order to produce an oxymethylene copolymer with higher thermal stability, however, it is essential to blend a stabilizer as well as to degrade the unstable chain ends after deactivation of the
25 catalyst. For this purpose, a variety of stabilizers have conventionally been known such as polyamide and hindered phenol to be milled for stabilization according to Japanese Patent Publication No. 5440/59.

By milling such stabilizers as mentioned above, the thermal stability is surely increased, but not satisfactorily, because when the polymer is kept in the melted state for a long time in a molding process or the like, decomposition with foaming occurs and mold-deposits are generated. In addition, if washing to remove the
30 catalyst is omitted in the process of catalyst deactivation by normal amine, thermal stability of the polymer will remain too low to withstand molding or the like, whichever stabilizer is milled.

An objective of this invention is to propose a very simple but effective method of halting the polymerization.

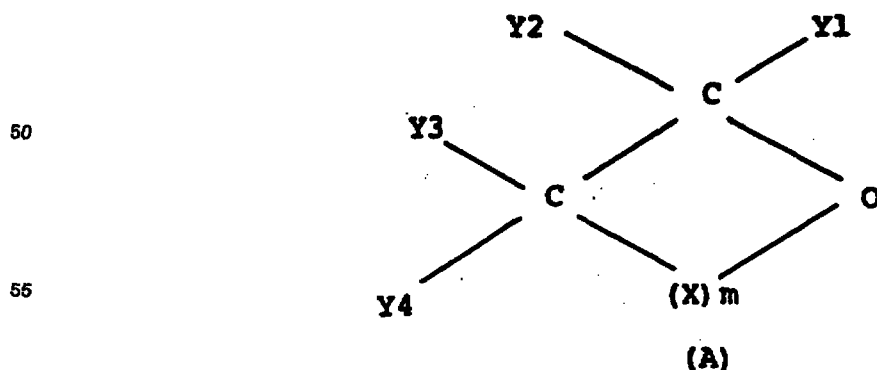
Another objective of this invention is to propose a process for producing an oxymethylene copolymer
35 excellent in heat resistance. A further objective of this invention is to propose a process for producing an oxymethylene copolymer excellent in mechanical properties.

A still further objective of this invention is to provide a resinous composition of oxymethylene copolymer excellent in both heat resistance and mechanical properties.

These objectives of this invention are achieved by polymerizing trioxane and cyclic ether in the presence of
40 a boron trifluoride catalyst to produce a copolymer to which is added a hindered amine compound containing at least one (2,2,6,6-tetramethyl)-piperidino moiety for deactivation of the catalyst, which is followed by stabilization of the unstable chain ends of the copolymer.

A cyclic ether employed in this invention may be represented by a compound expressed by the following general formula (A):

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wherein "Y1" to "Y4" denote a hydrogen atom or an alkyl group with one to six carbons, and may or may not be the same; "X" denotes $-\text{CH}_2-$ or $-\text{OCH}_2-$ in which hydrogens may be substituted by an alkyl group; and "m" denotes an integer in the range from 0 to 3. In addition, as far as "m" = 1, "X" may be either $-(\text{CH}_2)_p-\text{O}-\text{CH}_2-$ or $-\text{OCH}_2-(\text{CH}_2)_p-\text{OCH}_2-$ wherein "p" is an integer in the range from 1 to 3.

- 5 The compounds particularly preferable as the cyclic ether as specified by the above general formula (A) include ethylene oxide, propylene oxide, 1,3-dioxolane, 1,3-dioxane, 1,3-dioxepane, 1,3,5-trioxepane, 1,3,6-trioxocane, and epichlorohydrin.

It is desirable that the amount of copolymerized cyclic ether be 3×10^{-5} to 3×10^{-1} moles, preferably in the range of 6×10^{-5} to 2×10^{-1} moles with respect to one mole of trioxane; with less than 3×10^{-5} moles, 10 the resulting polymer provides lower thermal stability, while with more than 3×10^{-1} moles, the resulting polymer has a lower melting point and poor crystallinity which decreases the mechanical strength and moldability.

As the polymerization catalyst in this invention, one or more compounds selected from the group consisting of boron trifluoride, boron trifluoride hydrate, and coordination compounds of an organic compound having 15 an oxygen or sulphur atom with boron trifluoride are used. They may be employed in the form of gas, liquid or solution dissolved in a suitable organic solvent. The organic compound having an oxygen or sulphur atom used to form the coordination compound with boron trifluoride includes alcohol, ether, phenol, and sulfide. Among these catalysts, the coordination compound of boron trifluoride with an organic compound having an oxygen atom is especially desirable; in particular, boron trifluoride diethyletherate and boron 20 trifluoride dibutyletherate are preferably used.

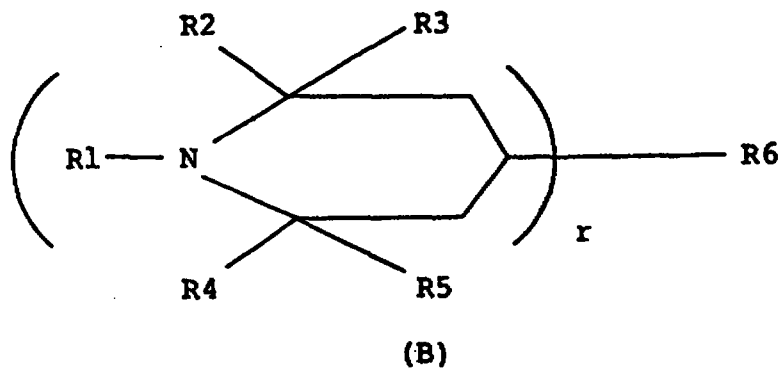
The solvent for use with the polymerization catalyst in this invention includes aromatic hydrocarbons such as benzene, toluene, and xylene; aliphatic hydrocarbons such as n-hexane, n-heptane, and cyclohexane; alcohols such as methanol and ethanol; halogenated hydrocarbons such as chloroform, dichloromethane, and 1,2-dichloroethane; and ketones such as acetone and methylethyl ketone. The boiling point of the 25 organic solvent used is preferably in the range of 20° to 200°C under atmospheric pressure. The added amount of the polymerization catalyst is preferably 5×10^{-6} to 1×10^{-1} moles, preferably 1×10^{-5} to 1×10^{-2} moles with respect to one mole of trioxane. The cyclic ether and catalyst may be mixed in advance, and then contacted with the trioxane. The polymerization of trioxane and cyclic ether may be in either a solution mode or substantially solventless mode, although the solventless bulk polymerization is advantageous in terms of cost because the post-treatment is easy. 30

Since radical hardening and heat generation occur in the bulk polymerization, it is desirable to use equipment capable of providing powerful agitation and of controlling the reaction temperature.

The polymerization equipment with such capabilities includes a kneader having Sigmate agitation blades; a mixer using a cylindrical barrel as the reaction zone in which a screw with a number of intermittent threads 35 is coaxially located in such a way that teeth projected from the internal surface of the barrel are engaged with the intermittent parts of the Screw threads during operation; and a general screw extruder with a pair of parallel screws which are located so as to be engaged with each other in a long case having a heat or cooling jacket. Polymerization equipment also needs a self-cleaning type mixer provided with a number of paddles on two horizontal agitating axes so that these axes are rotated simultaneously in the same direction 40 with a slight clearance kept between the corresponding paddles and also between the paddles and internal surface of the case. In the bulk polymerization, sudden hardening occurs and, therefore, the powerful agitating capability is required only in the early stage of the polymerization reaction. Once the hardened product is broken into fragments, strong agitation is no longer necessary. Accordingly, the bulk polymerization process may be divided into two steps.

- 45 The polymerization reaction temperature is preferably in the range from 30 to 140°C , particularly in the range from 60 to 90°C .

Since in the early stage of the polymerization the temperature in the reaction equipment tends to increase due to reaction heat generation, it is desirable to control the reaction temperature by passing the cooling water through the jacket or the like. The typical hindered amine compound for use in this invention in order 50 to deactivate the boron trifluoride catalyst to inhibit the polymerization reaction is represented by the following general formula (B):



15 wherein R1 denotes a hydrogen atom or hydrocarbon group with 1 to 30 carbons; R2 to R5 represents methyl; r denotes an integer in the range from 1 to 30; and R6 denotes an r-valent hydrocarbon group. Thus the following compounds may be included:

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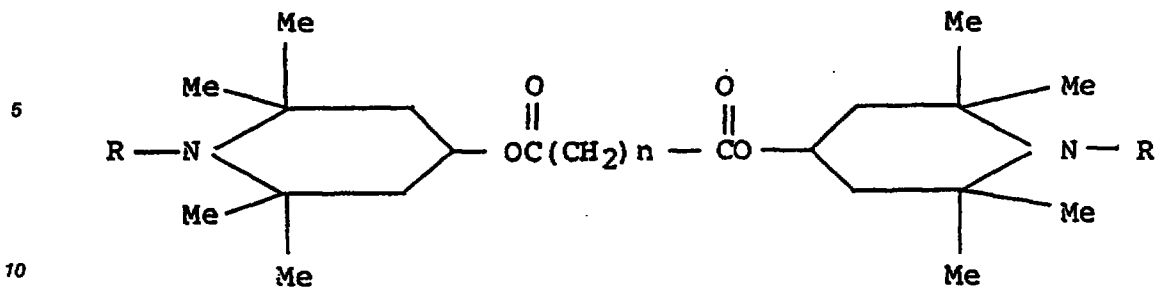
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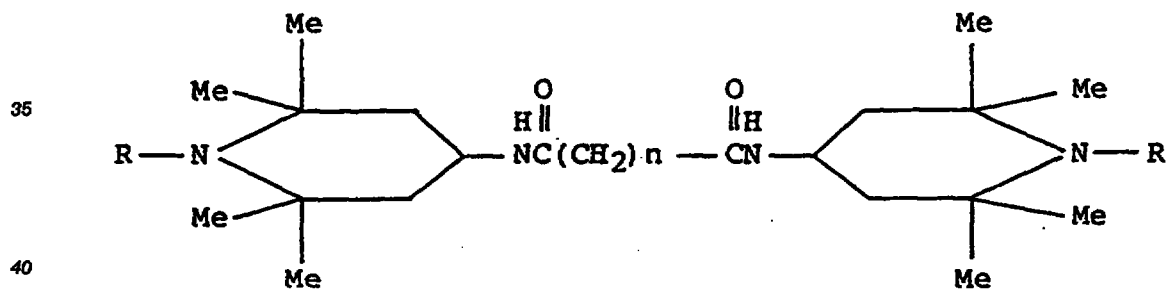
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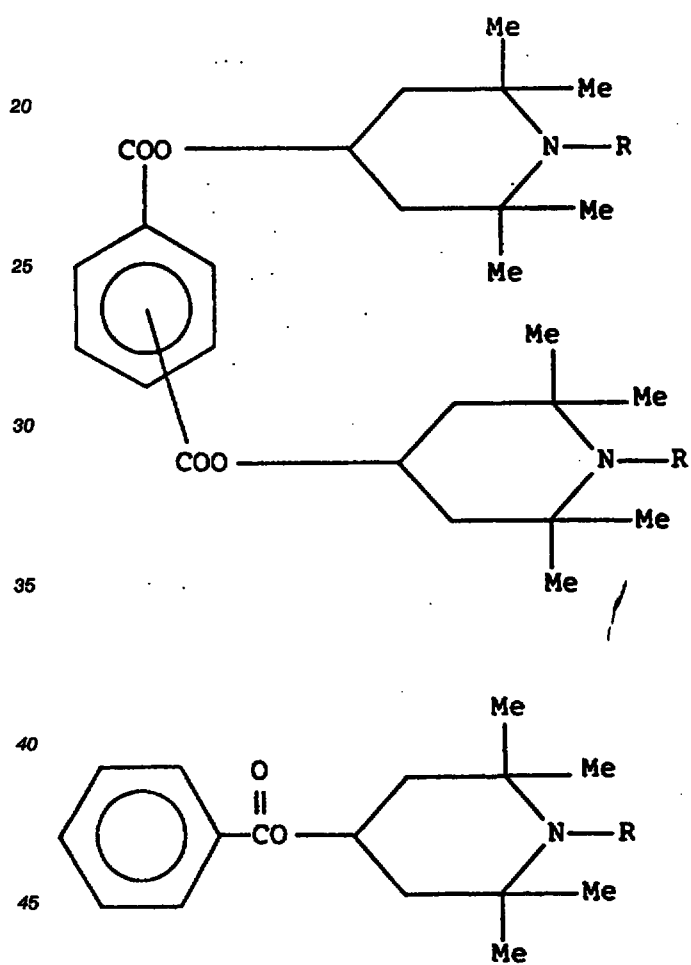
No	n	R
A-1	0	H
A-2	0	Me
B-1	1	H
B-2	1	Me
C-1	2	H
C-2	2	Me
D-1	3	H
D-2	3	Me

No	n	R
E-1	4	H
E-2	4	Me
F-1	6	H
F-2	6	Me
G-1	8	H
G-2	8	Me
H-1	10	H
H-2	10	Me



No	n	R
I-1	0	H
I-2	0	Me
J-1	1	H
J-2	1	Me
K-1	4	H
K-2	4	Me

No	n	R
L-1	6	H
L-2	6	Me
M-1	8	H
M-2	8	Me
N-1	10	H
N-2	10	Me



No	Orientation	R
P-1	o-orientation	H
P-2	o-orientation	Me
Q-1	m-orientation	H
Q-2	m-orientation	Me
R-1	p-orientation	H
R-2	p-orientation	Me

No	R
S-1	H
S-2	Me

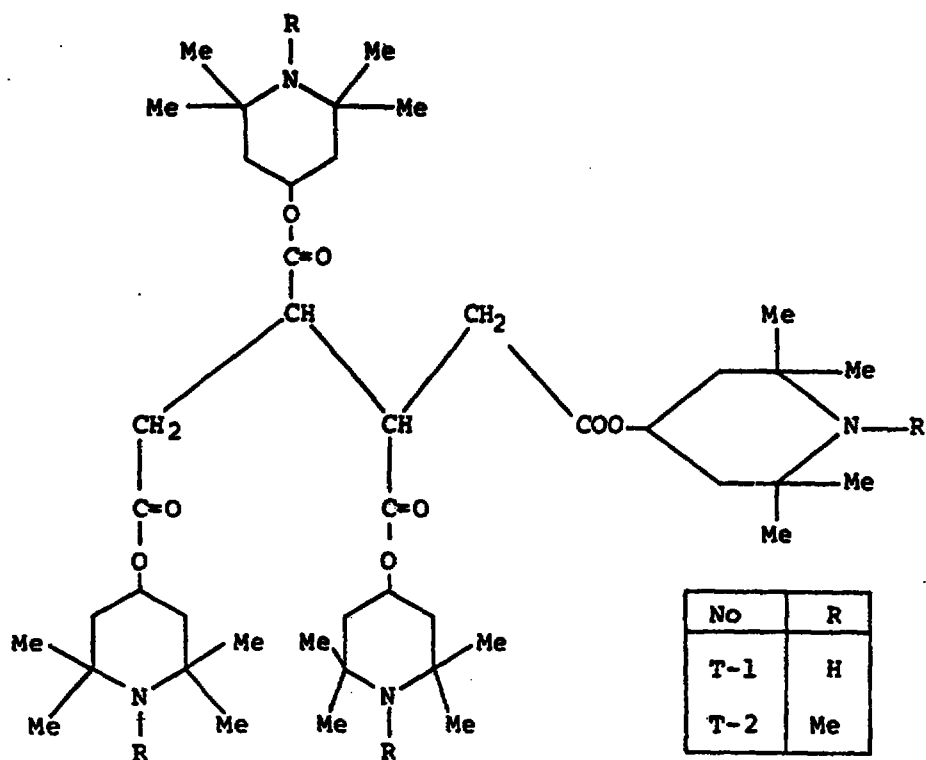
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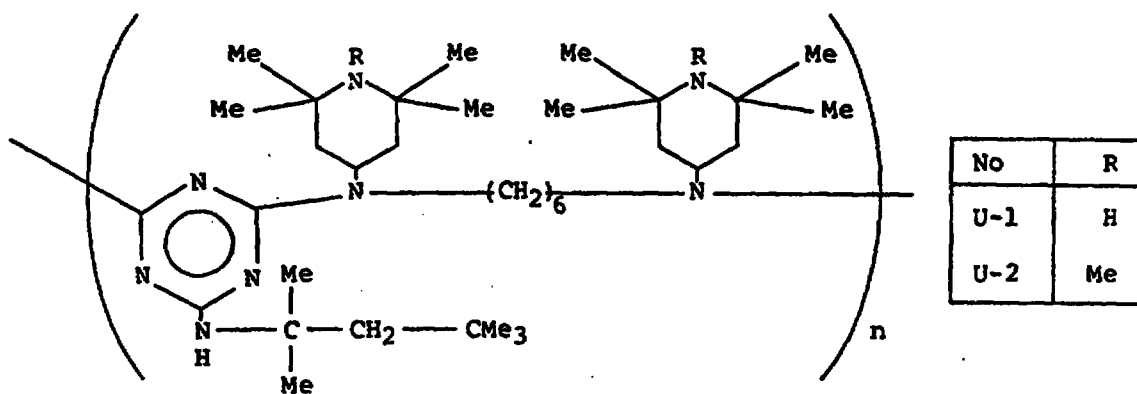
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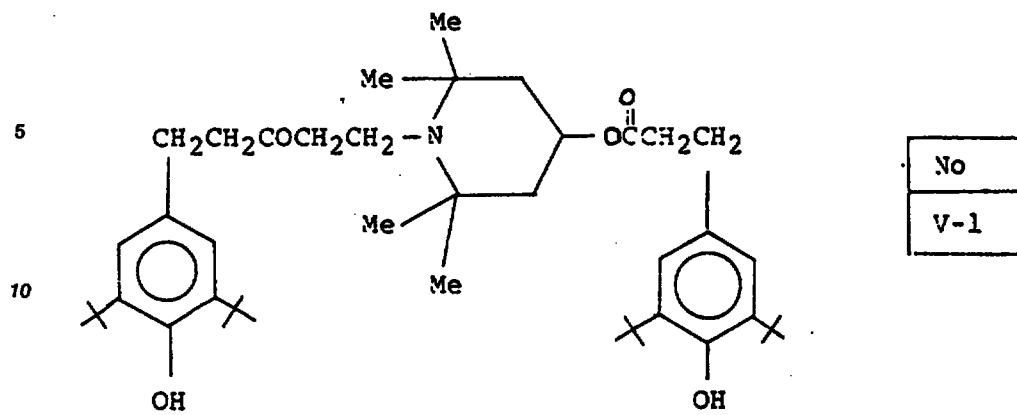
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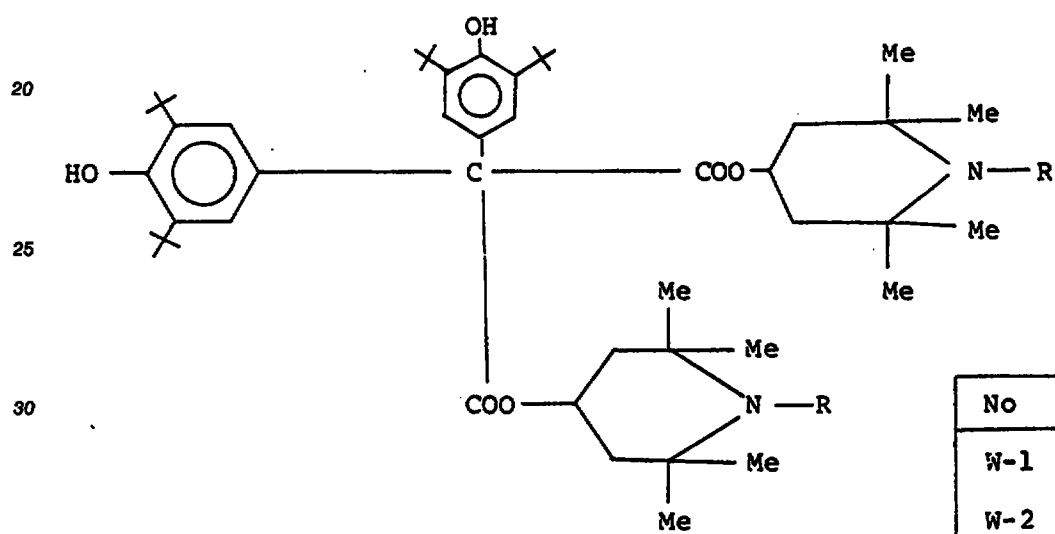
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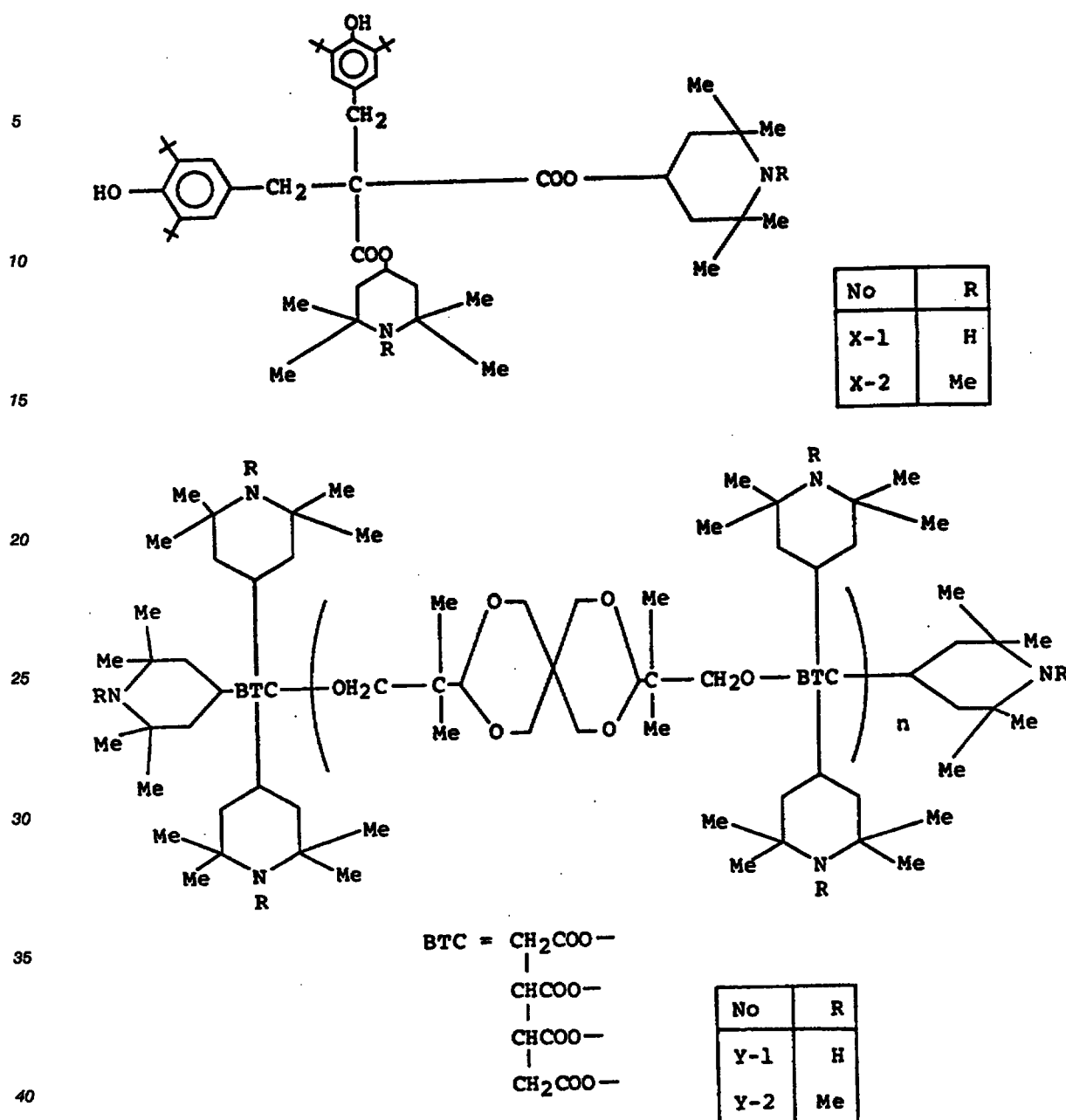




No
V-1



No	R
W-1	H
W-2	Me



Of these hindered amine compounds, the tertiary amine type is especially desirable because the
45 resulting polymer provides excellent color tone.

The added amount of the hindered amine compound may be 0.001 to 5.0 parts by weight with respect to 100 parts by weight of the polymer. The amount should desirably be such as to provide the hindered amine structure of moles equivalent to or more than that of the boron trifluoride catalyst used for the polymerization.

Even if the mole number of the hindered amine structure is less than that of the catalyst, deactivation effect on the catalyst is observed, but the heat resistance of the derived polymer is slightly lowered. Thus, it is necessary to control the added amount depending on the aimed degree of heat resistance. After deactivation of the catalyst, unstable chain ends of the polymer are degraded for stabilization. For this purpose the polymer may be heated to a temperature between 100° and 270°C. At that time, it is desirable to add a degradation accelerator such as one or more of the following, viz: hydroxides, inorganic acid salts, organic acid salts, and alkoxides of alkaline metals and alkali earth metals. Specifically there may be mentioned degradation accelerators consisting of at least one type of compound selected from hydroxides, carbonates, phosphates, borates, sulfites, hydrogen-sulfates, silicates, oxalates, acetates, ben-

zoates, isophthalates, terephthalates, phthalates, methoxide, ethoxides, isopropoxides and phenoxides of lithium, sodium, potassium, magnesium, calcium and barium.

Thus, the following compounds may be included:

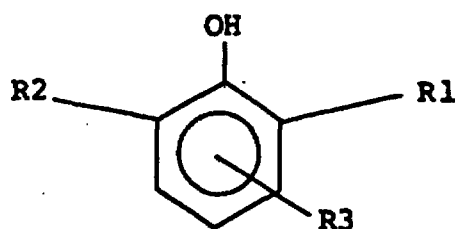
Lithium hydroxide, sodium hydroxide, potassium hydroxide, magnesium hydroxide, calcium hydroxide, barium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, sodium phosphate, sodium borate, sodium sulfite, sodium thiosulfate, sodium hydrogensulfate, sodium silicate, sodium oxalate, sodium acetate, magnesium acetate, sodium benzoate, sodium terephthalate, sodium methoxide, potassium methoxide, sodium ethoxide, potassium ethoxide, magnesium ethoxide, sodium isopropoxide, sodium phenoxide, or n-butyl lithium.

The added amount of the degradation accelerator employed in this invention may be 0.001 to 5 parts, preferably 0.05 to 3 parts, with respect to 100 parts of the copolymer, taking the parts by weight. If it is less than 0.001 parts, the resulting copolymer provides poor thermal stability. On the other hand, if it is more than 5 parts, the mechanical properties and antihydrolysis resistance will be lowered.

The stabilization may be carried out either in a solution or without a solvent, although the solventless process is advantageous in terms of cost because the recovery of solvent is not necessary.

In the stabilization process, it is preferable to add an antioxidant in order to suppress the decomposition of the polymer main chains; use of a hindered phenolic antioxidant is particularly desirable.

The hindered phenolic antioxidant used in this invention may include a compound which is represented by the following general formula (C):



(C)

wherein R1 and R2 denote an alkyl group with 1 to 6 carbons, triazolyl group, or substituted triazolyl group, which may or may not be the same; and R3 denotes a hydrogen atom or an amino group, or monovalent organic group such as an alkyl group, substituted alkyl group, aryl group, substituted aryl group, alkoxy group, aryloxy group, and substituted amino group each with 1 to 99 carbons.

Thus the following compounds may be included: 2,2-methylene-bis (4-methyl-6-tert-butyl phenol), triethylene glycol-bis [3-(3-tert-butyl-5-methyl-4-hydroxyphenyl) propionate], 2,2-thio-diethylene bis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], pentaerythrityl-tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], 1,6-hexanediol-bis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], 2,4-bis-(n-octylthio) -6-(4-hydroxy-3,5-di-tert-butylanilino)-1,3,5-triazine, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate; 1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxybenzyl) benzene; 2,2-thiobis (4-methyl-6-tert-butyl-phenol); 1,3,5-tris (4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanuric acid; 3,5-di-tert-butyl-4-hydroxybenzylphosphonate diethylester; N,N'-hexamethylene bis (3,5-di-tert-butyl-4-hydroxy-hydrocinnamamide)-bis (3, 5-di- tert-butyl-4-hydroxybenzyl phosphonic acid ethylester) calcium; N,N'-bis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionyl] hydrazine; 2-[2-hydroxy-3,5-bis (α,α -dimethylbenzyl) phenyl]-2H-benzotriazole; 2-(3,5-di-tert-amyl-2-hydroxyphenyl) benzotriazole; 2-(3-tert-butyl-5-methyl-2-hydroxyphenyl)- 5-chlorobenzotriazole; 2-(3,5-di-tert-butyl-2-hydroxyphenyl)- 5-chlorobenzotriazole; 2-(3,5-di-tert-butyl-2-hydroxyphenyl) benzotriazole; stearyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate; and 2,2-bis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propanoyloxy] methyl-1,3-propanediol-bis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate].

The added amount of the hindered phenolic antioxidant used in this invention may be in the range from 0.001 to 5 parts, preferably in the range from 0.05 to 3 parts, with respect to 100 parts of the copolymer, taking the parts by weight.

With less than 0.001 parts by weight, the resulting products provide lower thermal stability, while with more than 5 parts by weight, the antioxidant will be precipitated in a powdery form on the surface of the oxymethylene copolymer.

Although the oxymethylene copolymer as it is derived in accordance with the present invention is sufficiently excellent in heat resistance, it is further enhanced by mixing a formaldehyde capturing agent

including N,N-dimethylformamide, N,N-dimethylacetamide, N,N-diphenylformamide, N,N-diphenylacetamide, N,N-diphenylbenzamide, N,N,N,N-tetramethyladipamide, oxaloyl dianilide, adipoyl dianilide, N-phenylacetanilide; homopolymers or copolymers of lactams such as Nylon 6, Nylon 11, Nylon 12; polyamide homopolymers or copolymers which are derived from dicarboxylic acid such as adipic acid, 5 Sebacic acid, decane dicarboxylic acid, and dimer acid, and diamine such as ethylene diamine, tetramethylene diamine, hexamethylene diamine, and m-xylylene diamine; polyamide copolymers derived from lactams, dicarboxylic acid and diamine; amide compounds such as polyacrylamide, polymethacrylamide, N,N-bis (hydroxymethyl) suberamide, poly (γ -methylglutamate), poly (γ -ethylglutamate), poly (N-vinylactam), and poly (N-vinylpyrrolidone); polyurethane derived from diisocyanate such as toluene 10 diisocyanate and diphenylmethane diisocyanate, and glycol such as 1,4-butanediol or high molecular glycol such as poly tetramethyleneoxide) glycol, polybutyleneadipate, and polycaprolactone; triazine derivatives such as: melamine, benzoguanamine, acetoguanamine, N-butylmelamine, N-phenylmelamine, N,N-diphenylmelamine, N,N,N-triphenylmelamine, N-methylolmelamine, N,N-dimethylolmelamine, N,N,N-trimethylolmelamine, 2,4-diamino-6-benzoyloxytriazine, 2,4-diamino-6-cyclohexyltriazine, melem, melam, and 15 melon; urea derivatives such as N-phenylurea, N,N-diphenylurea, thiourea, N-phenylthiourea, N,N-diphenylthiourea, and nonamethylene polyurea; hydrazine derivatives such as phenylhydrazine, diphenyl hydrazine, benzaldehyde hydrazone, benzaldehyde semicarbazone, benzaldehyde-1-methyl-1-phenylhydrazine, benzaldehyde thiosemicarbazone; amidine compounds such as dicycandiamide, guanidine, guanidine, aminoguanidine, guanine, guanacine, guanochlor, guanoxane, guanosine, amiloride, and N-amidino-3-amino-6-chloro- 20 pyrazine carboxamide; and pyridine derivatives such as poly (2-vinylpyridine), poly (2-methyl-5-vinylpyridine), poly (2-ethyl-5-vinylpyridine), and 2-vinylpyridine/styrene copolymer.

In particular, polyamides derived from dimer acid, melamine, guanamine, benzoguanamine, N-methylolmelamine, N-methylolbenzoguanamine, thermoplastic polyurethane, dicyandiamide, guanidine, poly (vinylpyrrolidone), poly (2-vinylpyridine), polyurea, melem, melam are especially preferable for higher thermal 25 stability of the resulting oxymethylene copolymer.

The added amount of the formaldehyde capturing agent may be 0.001 to 5 parts by weight, preferably 0.05 to 3 parts by weight, with respect to 100 parts by weight of the oxymethylene copolymer.

With less than 0.001 parts by weight, the resulting polymer provides insufficient thermal stability. With more than 5 parts by weight, the formaldehyde capturing agent is precipitated on the surface of the composition 30 and/or the polymer is colored.

The process of this invention in its preferred form comprises polymerizing trioxane and cyclic ether in the presence of a boron trifluoride catalyst, inhibiting polymerization reaction by adding a hindered amine compound as the agent for deactivating the catalyst, and stabilizing the unstable chain ends of the polymer by a method comprising melting and milling the polymer at a temperature between the melting point of the 35 polymer and 270°C. Preferably the method includes adding and milling a degradation accelerator and a hindered phenolic antioxidant. During melting and milling the polymer the pressure in the system is preferably kept lower than the atmospheric pressure. These additives may be added sequentially one by one, or all at the same time. In addition, the additives may be added as they are, or in the form of solution in organic solvent, which may include: aromatic hydrocarbon such as toluene and xylene; aliphatic 40 hydrocarbons such as n-hexane, n-heptane, and cyclohexane; alcohols such as methanol and ethanol; halogenated hydrocarbons such as chloroform, dichloromethane, and 1,2-dichloroethane; and ketones such as acetone and methylethyl ketone.

In addition, as far as the effect of this invention is not affected, the following additives may be optionally added to the polymer of this invention: filler such as calcium carbonate, barium sulfate, clay, titanium 45 dioxide, silicon oxide, and mica powder; reinforcements such as carbon fiber, fiberglass, ceramic fiber, and aramide fiber; colorant (pigment and/or dye); nucleating agent; plasticizer; mold release agent; flame retardant; antistatic agent; electrical conductor; tackifier; lubricant; hydrolytic stabilizer, and adherent additives.

As shown in the examples given below, the oxymethylene copolymer with excellent heat resistance can be 50 produced by a very simple process according to this invention without removing the catalyst by washing.

In addition, the oxymethylene copolymer obtained in accordance with this invention is excellent in moldability, mechanical properties, and melting stability as well as the heat resistive aging capability, so that it can be used in a variety of applications including the parts in mechanical mechanisms, automobiles, and electric and electronic equipment.

55 The following examples and comparisons further illustrate this invention. Meanwhile, the surface condition of the molded products, mechanical properties, relative viscosity (η_r), heating decomposition rate (K), polymer melting point (T_m) and crystallization temperature (T_c) as mentioned in the examples and comparisons are measured in the following manner.

Surface condition of the molded products:

Using an injection molder capable of injecting 5 oz. at a time, ASTM No. 1 dumbbell test pieces and Izod impact test pieces were injection-molded with the cylinder temperature set to 230 °C, molding temperature to 80 °, and molding cycle to 50 sec. Visual inspection was then carried out on the surface of the ASTM No. 1 dumbbell test pieces.

Mechanical properties:

Using ASTM No. 1 dumbbell test pieces obtained by the above-mentioned injection-molding, tensile characteristics was measured in accordance with ASTM D-638. In addition, using Izod impact test pieces, the impact strength was measured in accordance with ASTM D-256.

Relative viscosity (η_r):

0.5 g of the polymer was dissolved in 100 ml of p-chlorophenol containing 2% of α -pinene, and then the viscosity was measured at 60 °C.

Heating decomposition rate (Kx):

"Kx" means the decomposition rate of the material which is allowed to stand for a predetermined period of time at X °C. Using a thermobalancer, about 10 mg of the sample was allowed to stand in the atmosphere of air at X °C, and then the rate was determined by the following equation:

$$Kx = (W_0 - W_1) \times 100/W_0 (\%)$$

wherein W_0 means the weight of the sample before heating, and W_1 means the weight of the sample after heating. DuPont's Thermal Analyzer 1090/1091 was used as the thermal balancer.

Polymer melting point (T_m) and crystallization temperature (T_c):

Using a differential scanning calorimeter, the polymer melting point (T_m) was measured in the atmosphere of nitrogen while increasing the temperature at 10 °C/min. Then, the crystallization temperature (T_c) was measured while decreasing the temperature at 10 °C/min.

Reference Example 1

A kneader of 3 liters in capacity equipped with two sigrnate agitating blades was heated to 80 °C. Then, 3.0 kg of trioxane, 112 g of 1,3-dioxolane, and as the catalyst, boron trifluoride diethyletherate in concentration of 100 ppm with respect to the weight of trioxane in the form of 10% benzene solution were introduced into the kneader and then stirred at 30 rpm. The contents were immediately hardened, and the temperature in the system rose up to 100 °C in 3 min. due to the reaction heat and frictional heat.

The agitation continued as it was for 10 min. further and then the polymer was taken out of the kneader. The polymer thus obtained was in the form of white powder showing the viscosity $\eta_r = 2.37$. This polymer is referred to as oxymethylene copolymer "A" in the following description.

Reference Example 2

The bulk polymerization was carried out in the same way as Reference Example 1, except that 66 g of ethylene oxide was used in place of 1,3-dioxolane.

The polymer thus obtained was in the form of white powder showing the viscosity $\eta_r = 2.40$.

This polymer is referred to as oxymethylene copolymer "B" in the following description.

Examples 1 to 5; Comparisons 1 and 2

To 3.0 kg of oxymethylene copolymer "A" as obtained in Reference Example 1 above, various hindered amine compounds having the structural formulae previously illustrated were added in proportions as shown in Table 1 in the form of about 20% benzene solution. They were milled for 5 min. at 35 °C. Then, calcium hydroxide of 3 parts by weight and pentaerythrityl-tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] ("Irganox" 1010 by Ciba-Geigy) of 15 parts by weight were added, and after the temperature was increased to 210 °C in 10 min., they were milled for 20 min. at that temperature.

For comparison, the oxymethylene copolymer was produced using tri (n-butyl) amine in place of a hindered amine compound.

The copolymers thus produced provide the measurements on various physical properties as shown in Table 1. From this table, it is clearly observed that the copolymers according to this invention provide excellent properties independently of the types of hindered amine compounds employed.

Example 6

To oxymethylene copolymer "A" as obtained in Reference Example 1, a hindered amine compound, calcium hydroxide, and "Irganox" 1010 were added simultaneously in the same proportions as Example 2, and they were milled for 5 min. at 35°C. Then, the temperature was increased to 210°C in 10 min., and then the milling was again carried out for 20 min. at that temperature. The copolymer thus obtained provided the measurements on various physical properties as shown in Table 1.

Example 7

To 3.0 kg of oxymethylene copolymer "A" as obtained in Reference Example 1 above, a hindered amine compound, calcium hydroxide, and "Irganox" 1010 were added simultaneously in the same proportions as Example 2, and they were milled for 5 min. at 35°C. Then, the temperature was increased to 210°C in 10 min. and the milling was again carried out for 20 min. at that temperature. Then, dicyandiamide of 3 parts by weight was added, which was followed by milling for another 10 min. at the same temperature. The polymer thus obtained provided the measurements on various physical properties as shown in Table 1. From Example 2 (sequential addition mode) and Example 6 (simultaneous addition mode), it is clearly shown that the copolymers according to this invention has excellent physical properties regardless of milling mode.

It is also noticed from Example 7 that the heat resistance is further improved by adding the formaldehyde capturing agent.

Table 1

	Kindered Amine		Antioxidant Ir1010 (in parts by weight)	Degradation Accelerator Ca(OH) ₂ (in parts by weight)	Polymer Melting Point (°C)	Crystallization Temperature (°C)	n _r	Mechanical Properties				Surface Condition of Molded Product	K222 60min. (%)	K240 60min. (%)		
	Type	Added Amount (in parts by weight)						Tensile Strength (MPa)	Rupture Elongation (%)	Isod Impact Value						
Example																
1	G-2	3	15	3	167	141	1.99	61	49	5.3	Normal	2.0	6.6			
2	"	12	15	3	168	145	2.05	63	53	6.2	Good	0.6	3.8			
3	J-2	12	15	3	168	145	2.10	62	51	6.2	Good	0.4	3.6			
4	B-1	12	15	3	168	145	2.03	62	51	6.1	Good	0.8	3.9			
5	U-2	12	15	3	168	145	2.04	63	52	6.0	Good	0.6	3.9			
6	G-2	12	15	3	168	145	2.03	62	52	6.0	Good	0.8	4.0			
7	"	12	15	3	168	145	2.04	61	52	6.0	Good	0.4	3.0			
Com- parison																
1	TNB	3	15	3	159	134	1.35	Impossible to mold because of decomposition and foaming							90.1	98.4
2	"	12	15	3	158	133	1.40								89.2	97.3

TNB: Tri (n-butyl) amine

Ir1010: Irganox 1010 (produced by Ciba-Geigy)

Isod Impact Value: with 1/2 notches; (units: kg . cm/cm)

In Example 7 only, dicyandiamide of 3 parts by weight was added as the formaldehyde capturing agent.

55 Examples 8 to 13

The polymers were produced in the same way as Examples 2, 6, and 7 except that magnesium hydroxide and potassium carbonate are used in place of calcium hydroxide.

The polymers thus obtained provided the measurements on the various physical properties as shown in Table 2. It is clearly noticed from this table that the polymers according to this invention provide excellent properties regardless of type of degradation accelerator used and of milling mode.

Table 2

	Degradation Accelerator		Antioxidant Ir1010 (in parts by weight)	Polymer Melting Point (°C)	Crystallization Temperature (°C)	n _r	Mechanical Properties				Surface Condition of Molded Product	K222 60min. (%)	K240 60min. (%)
	Type	Added Amount (in parts by weight)					Tensile Strength (MPa)	Rupture Elongation (%)	Isod Impact Value				
Example 8	Mg(OH)2	3	15	168	145	2.06	59	50	5.9	Good	0.8	3.7	
" 9	"	3	15	168	145	2.05	63	53	6.2	Good	0.6	3.8	
" 10	"	3	15	168	145	2.01	59	50	5.6	Good	0.4	3.0	
" 11	K2CO3	3	15	168	145	2.03	62	51	6.0	Good	0.7	3.6	
" 12	"	3	15	168	145	2.02	62	51	6.0	Good	0.6	3.8	
" 13	"	3	15	168	145	2.05	61	51	6.0	Good	0.3	3.0	

Ir1010: Irganox 1010 (produced by Ciba-Geigy)

Isod Impact Value: with 1/2 notches; (unit: kg . cm/cm)

Sequential addition mode is used in Examples 8 and 11;

simultaneous addition mode is used in Examples 9 and 12.

In examples 10 and 13, Dicyandiamide of 3 parts by weight is added as the formaldehyde capturing agent.

Examples 14 to 19

The polymers were produced in the same way as Examples 2, 6 and 7 except that triethyleneglycol-bis [3-(3-tert-butyl-5-methyl-4-hydroxyphenyl) propionate] ("Irganox" 245 by Ciba-Geigy) and N,N-hexamethylene-bis (3,5-di-tert-butyl-4-hydroxy-hydrocinnamamide) ("Irganox" 1098 by Ciba-Geigy) were used in place of pentaerythrityl-tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate].

The polymers thus obtained provided the measurements on the various physical properties as shown in Table 3. It is clearly noticed from this table that the polymers according to this invention have excellent physical properties regardless of type of antioxidant used and of milling mode.

Table 3

	Antioxidant		Degradation Accelerator Ca(OH) ₂ (in parts by weight)	Polymer Melting Point (°C)	Crystallization Temperature (°C)	η_{sp}	Mechanical Properties			Surface Condition of Molded Product	K222 60min. (t)	K240 60min. (t)
	Type	Added Amount (in parts by weight)					Tensile Strength (MPa)	Rupture Elongation (t)	Isod Impact Value			
Example 14	Ir 245	15	3	168	145	2.03	60	50	5.9	Good	0.8	3.9
" 15	"	15	3	168	145	2.05	63	53	6.2	Good	0.6	3.7
" 16	"	15	3	168	145	2.09	63	53	6.1	Good	0.3	2.7
" 17	Ir1098	15	3	168	145	2.02	62	51	6.0	Good	0.7	3.8
" 18	"	15	3	168	145	2.02	61	51	6.0	Good	0.8	3.8
" 19	"	15	3	168	145	2.01	60	50	5.8	Good	0.4	3.2

Ir 245: Irganox 245 (produced by Ciba-Geigy)

Ir1098: Irganox 1098 (produced by Ciba-Geigy)

Isod Impact Value: with 1/2 notches; (unit: kg · cm/cm)

Sequential addition mode is used in Examples 14 and 17;

simultaneous addition mode is used in Examples 15 and 18.

In examples 16 and 19, dicyandiamide of 3 parts by weight is added as the formaldehyde capturing agent.

55 Examples 20 and 21

The polymers were produced in the same way as Example 7 except that melamine and polyamide derived from dimer acid were used in place of dicyandiamide.

The polymers thus obtained provided the measurements on various physical properties as shown in Table 4. It is clearly noticed from this table that the polymers according to this invention have excellent physical properties regardless of type of formaldehyde capturing agent used.

Table 4

	Formaldehyde Capturing Agent		Polymer Melting Point (°C)	Crystallization Temperature (°C)	η_{sp}	Mechanical Properties			Surface Condition of Molded Product	K222 60min. (%)	K240 60min. (%)
	Type	Added Amount (in parts by weight)				Tensile Strength (MPa)	Rupture Elongation (%)	Isod Impact Value			
Example 20	Melamine	3	168	145	2.05	60	50	5.9	Good	0.4	3.1
" 21	Milbex	3	168	145	2.04	61	51	6.0	Good	0.3	3.0

Isod Impact Value: with 1/2 notches; (unit: kg . cm/cm)

Milbex: Milbex 1000 (polysulfide derived from dimer acid produced by Nihon General Mills)

As the antioxidant used was Irganox 1010 (by Ciba-Geigy) of 15 parts by weight.

As the degradation accelerator used was calcium hydronide of 3 parts by weight.

Examples 22 to 24

The polymers were produced in the same way as Examples 2, 6, and 7 except that oxymethylene copolymer "B" as obtained in Reference Example 2 was used.

- 5 The polymers thus obtained provided the measurements on the various physical properties as shown in Table 5. It is clearly noticed from this table that polymers excellent in physical properties can be produced even if the co-monomer is changed.

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Table 5

	Polymer Melting Point (°C)	Crystallization Temperature (°C)	η_{sp}	Mechanical Properties			Surface Condition of Molded Product	K222 60min. (%)	K240 60min. (%)
				Tensile Strength (MPa)	Rupture Elongation (%)	Izod Impact Value			
Example 22	168	145	2.05	63	53	6.2	Good	0.6	3.6
" 23	168	145	2.04	61	51	5.9	Good	0.7	3.8
" 24	168	145	2.03	61	50	5.8	Good	0.3	3.0

Izod Impact Value: with 1/2 notches; (unit: kg . cm/cm)
the antioxidant used was Irganox 1010 (by Ciba-Geigy)
of 15 parts by weight.

the degradation accelerator used was calcium hydroxide of 3
parts by weight.

Sequential addition mode is used in Example 22; simultaneous addition
mode in Example 23. In Example 24, dicyandiamide of 3 parts by weight is
added as the formaldehyde capturing agent.

Claims

1. A process for producing an oxymethylene copolymer, comprising polymerizing trioxane and cyclic ether in the presence of at least one type of polymerization catalyst selected from the group consisting of (a) boron trifluoride, (b) boron trifluoride hydrate, and (c) coordination compounds formed from boron

**Table 5**

	Polymer Melting Point (°C)	Crystallization Temperature (°C)	n _r	Mechanical Properties			Surface Condition of Molded Product	K222 60min. (%)	K240 60min. (%)
				Tensile Strength (MPa)	Rupture Elongation (%)	Izod Impact Value			
Example 22	168	145	2.05	63	53	6.2	Good	0.6	3.6
" 23	168	145	2.04	61	51	5.9	Good	0.7	3.8
" 24	168	145	2.03	61	50	5.8	Good	0.3	3.0

Izod Impact Value: with 1/2 notches; (unit: kg . cm/cm)
the antioxidant used was Irganox 1010 (by Ciba-Geigy)
of 15 parts by weight.

the degradation accelerator used was calcium hydroxide of 3
parts by weight.

Sequential addition mode is used in Example 22; simultaneous addition
mode in Example 23. In Example 24, dicyandiamide of 3 parts by weight is
added as the formaldehyde capturing agent.

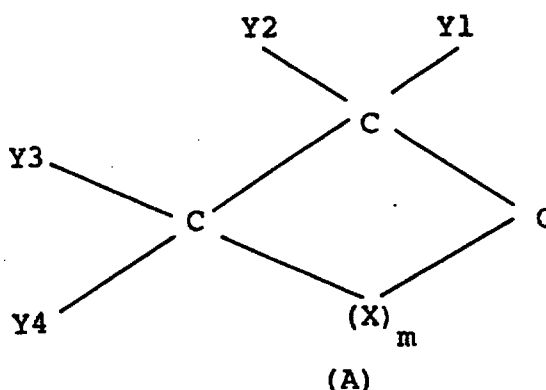
Claims

1. A process for producing an oxymethylene copolymer, comprising polymerizing trioxane and cyclic ether in the presence of at least one type of polymerization catalyst selected from the group consisting of (a) boron trifluoride, (b) boron trifluoride hydrate, and (c) coordination compounds formed from boron



trifluoride and an organic compound containing an oxygen and/or sulphur atom; adding a hindered amine compound to the polymer obtained by said polymerization; and then stabilizing unstable chain ends of the polymer, the hindered amine containing at least one (2,2,6,6-tetramethyl)-piperidino moiety.

- 5 2. A process for producing an oxymethylene copolymer according to Claim 1, wherein the added amount of the hindered amine compound is 0.001 to 5.0 parts by weight with respect to 100 parts by weight of the polymer.
3. A process for producing an oxymethylene copolymer according to either preceding claim, wherein the cyclic ether is expressed by the following formula (A):



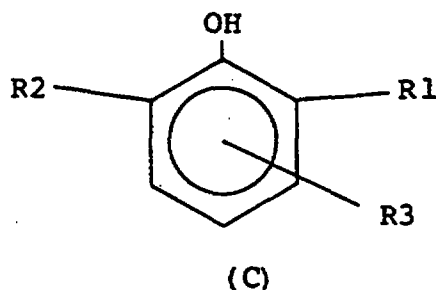
wherein Y1 to Y4 represent hydrogen atoms or alkyl groups of 1 to 6 carbons, and may or may not be the same; X represents either a direct bond (if m is 0) or either -CH₂- or -OCH₂- in which hydrogens may be substituted by an alkyl group; m represents zero or an integer in the range from 1 to 3, and if m = 1, X may be either -(CH₂)_p-OCH₂- or -OCH₂-(CH₂)_p-OCH₂- in which case p is an integer in the range from 1 to 3.

4. A process for producing an oxymethylene copolymer according to any preceding claim, wherein the added amount of cyclic ether is 3×10^{-5} to 3×10^{-1} moles with respect to one mole of trioxane.
5. A process for producing an oxymethylene copolymer according to any preceding claim, wherein the polymerization catalyst is a coordination compound formed of boron trifluoride and a compound containing an oxygen atom.
6. A process for producing an oxymethylene copolymer according to any preceding claim, wherein the added amount of the polymerization catalyst is 5×10^{-6} to 1×10^{-1} moles with respect to one mole of trioxane.
7. A process for producing an oxymethylene copolymer according to any preceding claim, wherein the polymerization temperature is 30 to 140 °C.
8. A process for producing an oxymethylene copolymer according to any preceding claim, wherein the polymerization is carried out substantially in the solventless state.
9. A process for producing an oxymethylene copolymer according to any preceding claim, wherein the polymerization catalyst is added in a form dissolved in an organic solvent having its boiling point in the range from 20 to 200 °C under atmospheric pressure.
10. A process for producing an oxymethylene copolymer according to any preceding claim, wherein cyclic ether and catalyst are mixed in advance and then put into contact with trioxane.
11. A process for producing an oxymethylene copolymer according to any preceding claim, wherein the stabilizing process comprises heating the polymer at 100 to 270 °C.



12. A process for producing an oxymethylene copolymer according to any preceding claim, wherein at least one type of antioxidant and at least one type of degradation accelerator selected from hydroxides, inorganic acid salts, organic acid salts, and alkoxides of alkaline metals and alkali earth metals are added in the stabilizing process.

13. A process for producing an oxymethylene copolymer according to Claim 12 wherein the antioxidant is expressed by the following formula (C):



wherein R1 and R2 are alkyl groups of 1 to 6 carbons, triazolyl groups, or substituted triazolyl groups, and may or may not be the same; and R3 represents a hydrogen atom, an amino group, or a monovalent organic group such as an alkyl group, substituted alkyl group, aryl group, substituted aryl group, alkoxy group, aryloxy group, and substituted amino group of 1 to 99 carbons.

14. A process for producing an oxymethylene copolymer according to Claim 12 or Claim 13, wherein the degradation accelerator is at least one type of compound selected from hydroxides, carbonates, phosphates, borates, sulfites, hydrogen-sulfates, silicates, oxalates, acetates, benzoates, isophthalates, terephthalates, phthalates, methoxide, ethoxides, isopropoxides, and phenoxides of lithium, sodium, potassium, magnesium, calcium, and barium.

15. A process for producing an oxymethylene copolymer according to any of Claims 12 to 14, wherein the added amount of the antioxidant is 0.001 to 5.0 parts by weight with respect to 100 parts by weight of the polymer.

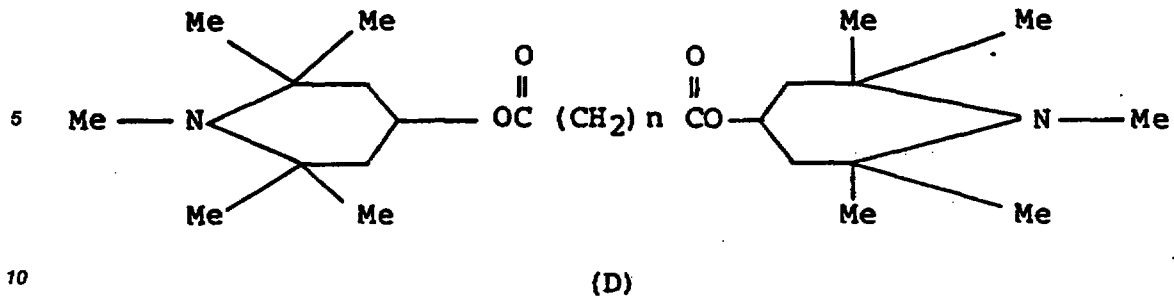
16. A process for producing an oxymethylene copolymer according to any of Claims 12 to 15, wherein the added amount of the degradation accelerator is 0.001 to 5.0 parts by weight with respect to 100 parts by weight of the polymer.

17. A process for producing an oxymethylene copolymer according to any preceding claim, wherein the stabilizing process comprises melting and milling the polymer at a temperature in the range from the melting point of the polymer to 270 °C.

18. A process for producing an oxymethylene copolymer according to Claim 17, wherein the pressure in the system is kept lower than the atmospheric pressure in melting and milling the polymer.

19. A resinous composition produced by adding a hindered amine compound containing at least one (2,2,6,6-tetramethyl)-piperidino moiety, an antioxidant, and at least one type of degradation accelerator into a copolymer produced from trioxane and cyclic ether in the presence of a polymerization catalyst.

20. A resinous composition according to Claim 19, wherein the hindered amine compound is expressed by the following formula (D), and the molecular weight of the antioxidant is not less than 400:

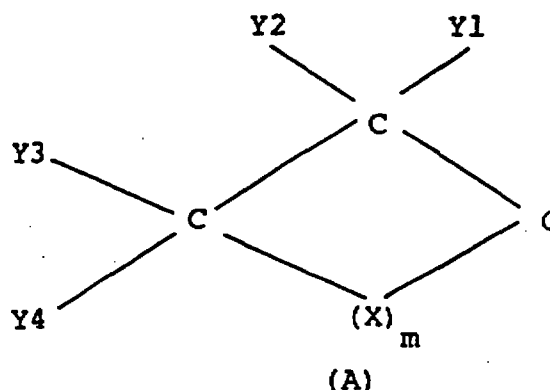


wherein n represents an integer in the range from 0 to 20.

- 15 21. A resinous composition according to Claim 20, wherein at least one of dicyandiamide, melamine, and polyamide is further mixed into the composition.

Patentansprüche

- 20 1. Verfahren zur Herstellung eines Oxymethylen-Copolymers, das umfaßt: das Polymerisieren von Trioxan und einem zyklischen Äther in Gegenwart von zumindest eines Typs eines Polymerisationskatalysators, ausgewählt aus der Gruppe bestehend aus (a) Bortrifluorid, (b) Bortrifluoridhydrat und (c) Koordinationsverbindungen, die aus Bortrifluorid und einer organischen Verbindung, die ein Sauerstoff-und/oder Schwefelatom enthält, gebildet werden; Zufügen einer sterisch gehinderten Aminverbindung zu dem
- 25 durch diese Polymerisation erhaltenen Polymer; und anschließend Stabilisieren von instabilen Kettenenden des Polymers, wobei das sterisch gehinderte Amin zumindest eine (2,2,6,6-Tetramethyl)piperidino-Gruppe enthält.
- 30 2. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach Anspruch 1, worin die zugegebene Menge an sterisch gehinderter Aminverbindung 0,001 bis 5,0 Gewichtsteile bezogen auf 100 Gewichtsteile Polymer beträgt.
- 35 3. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der beiden vorangegangenen Ansprüche, worin der zyklische Äther durch folgende Formel (A) dargestellt ist:



50 worin Y1 bis Y4 Wasserstoffatome oder gleiche oder voneinander verschiedene Alkylgruppen mit 1 - 6 Kohlenstoffatomen darstellen; X entweder eine direkte Bindung (wenn m = 0) oder entweder -CH₂- oder -OCH₂- darstellt, in denen Wasserstoffe durch Alkylgruppen substituiert sein können; m = 0 oder eine ganze Zahl im Bereich von 1 bis 3 ist, und für m = 1 X entweder -(CH₂)_p-OCH₂- oder -OCH₂-(CH₂)_p-OCH₂- ist, wobei p eine ganze Zahl im Bereich von 1 bis 3 ist.

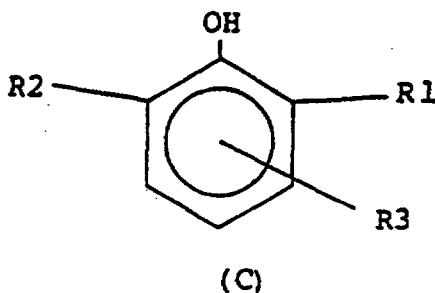
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4. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der vorangegangenen Ansprüche, worin die zugegebene Menge an zyklischem Äther 3×10^{-5} bis 3×10^{-1} Mol bezogen auf 1 Mol



Trioxan ist.

5. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der vorangegangenen Ansprüche, worin der Polymerisationskatalysator eine Koordinationsverbindung, die aus Bortrifluorid und einer Verbindung, die ein Sauerstoffatom enthält, gebildet ist.
6. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der vorangegangenen Ansprüche, worin die zugegebene Menge des Polymerisationskatalysators 5×10^{-6} bis 1×10^{-1} Mol bezogen auf 1 Mol Trioxan ist.
7. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der vorangegangenen Ansprüche, worin die Polymerisationstemperatur 30 bis 140°C beträgt.
8. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der vorangegangenen Ansprüche, worin die Polymerisation im wesentlichen lösungsmittelfrei durchgeführt wird.
9. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der vorangegangenen Ansprüche, worin der Polymerisationskatalysator in gelöster Form, in einem organischen Lösungsmittel mit einem Siedepunkt im Bereich von 20 bis 200°C unter Normaldruck, zugegeben wird.
10. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der vorangegangenen Ansprüche, worin zyklischer Äther und Katalysator vorher vermischt und danach mit Trioxan in Kontakt gebracht werden.
11. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der vorangegangenen Ansprüche, worin der stabilisierende Vorgang Erhitzen des Polymers auf $100 - 270^\circ\text{C}$ umfaßt.
12. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der vorangegangenen Ansprüche, worin zumindest ein Typ von Antioxidantien und zumindest ein Typ von Abbaubeschleunigern, ausgewählt aus Hydroxiden, Salzen von anorganischen Säuren, Salzen von organischen Säuren und Alkoxiden von Alkali- und Erdalkalimetallen, beim stabilisierenden Vorgang zugegeben werden.
13. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach Anspruch 12, worin das Antioxidans durch die folgende Formel (C) dargestellt wird:

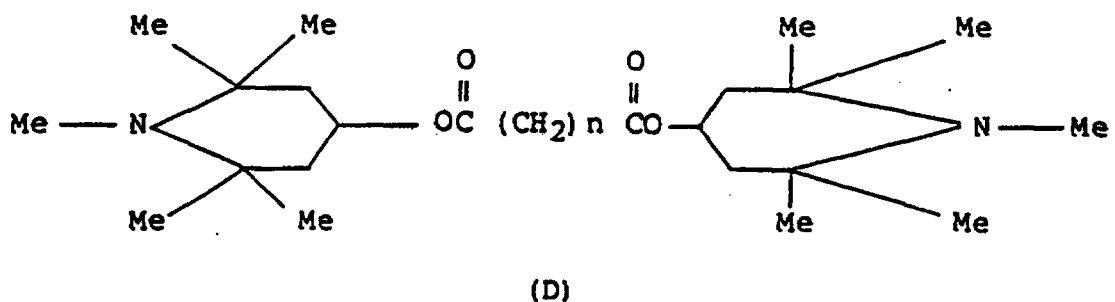


worin R1 und R2 gleiche oder voneinander verschiedene Alkylgruppen mit 1-6 Kohlenstoffatomen, Triazolygruppen oder substituierte Triazolygruppen sind, und R3 ein Wasserstoffatom, eine Aminogruppe oder eine einwertige organische Gruppe, wie z.B. eine Alkylgruppe, substituierte Alkylgruppe, Arylgruppe, substituierte Arylgruppe, Alkoxygruppe, Aryloxygruppe und eine substituierte Aminogruppe mit 1 - 99 Kohlenstoffatomen, darstellt.

14. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach Anspruch 12 oder 13, worin der Abbaubeschleuniger zumindest ein Typ einer Verbindung, ausgewählt aus Hydroxiden, Carbonaten, Phosphaten, Boraten, Sulfiten, Hydrogensulfaten, Silikaten, Oxalaten, Acetaten, Benzoaten, Isophthalaten, Terephthalaten, Phthalaten, Methoxid, Äthoxiden, Isopropoxiden und Phenoxiden von Lithium, Natrium, Kalium, Magnesium, Kalzium und Barium, ist.



15. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der Ansprüche 12 bis 14, worin die zugegebene Menge an Antioxidans 0,001 bis 5,0 Gewichtsteile bezogen auf 100 Gewichtsteile Polymer beträgt.
- 5 16. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der Ansprüche 12 bis 15, worin die zugegebene Menge an Abbaubeschleuniger 0,001 bis 5,0 Gewichtsteile bezogen auf 100 Gewichtsteile Polymer beträgt.
- 10 17. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach einem der vorangegangenen Ansprüche, worin der stabilisierende Vorgang Schmelzen und Quirlen bzw. Rühren des Polymers bei einer Temperatur im Bereich vom Schmelzpunkt des Polymers bis 270 °C umfaßt.
- 15 18. Verfahren zur Herstellung eines Oxymethylen-Copolymers nach Anspruch 17, worin der Systemdruck beim Schmelzen und Rühren des Polymers unterhalb des Normaldrucks gehalten wird.
- 20 19. Harzartige Zusammensetzung, hergestellt durch Zugabe einer sterisch gehinderten Aminverbindung, die zumindest eine (2,2,6,6-Tetramethyl)piperidino-Gruppe enthält, eines Antioxidans und zumindest eines Typs eines Abbaubeschleunigers zu einem aus Trioxan und einem zyklischen Äther in Gegenwart eines Polymerisationskatalysators hergestellten Copolymer.
- 25 20. Harzartige Zusammensetzung nach Anspruch 19, worin die sterisch gehinderte Aminverbindung durch die folgende Formel (D) dargestellt ist und das Molekulargewicht des Antioxidans nicht unter 400 liegt:

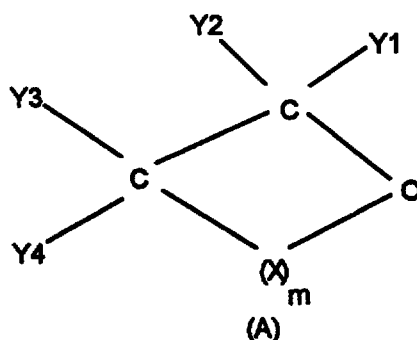


35 worin n eine ganze Zahl im Bereich von 0 bis 20 ist.

- 40 21. Harzartige Zusammensetzung nach Anspruch 20, worin weiters zumindest eines von Dicyandiamid, Melamin oder Polyamid in die Zusammensetzung gemischt wird.

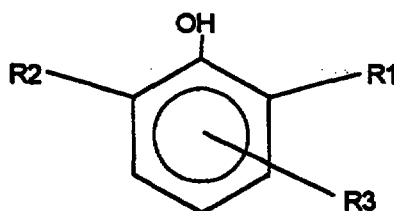
Revendications

- 45 1. Procédé de préparation d'un copolyoxyméthylène, consistant à polymériser du trioxane et d'un éther cyclique en présence d'au moins un type de catalyseur de polymérisation sélectionné dans le groupe consistant en (a) trifluorure de bore, (b) trifluorure de bore hydraté, et (c) composés de coordination formés à partir de trifluorure de bore et d'un composé organique contenant un atome d'oxygène et/ou de soufre; à ajouter un composé d'amine empêchée au polymère obtenu par ladite polymérisation; puis à stabiliser les bouts de chaîne instables du polymère, l'amine empêchée contenant au moins un fragment (2,2,6,6-tétraméthyl)-pipéridino.
- 50 2. Procédé de préparation d'un copolyoxyméthylène selon la revendication 1, où la quantité ajoutée du composé d'amine empêchée est de 0,001 à 5,0 parties en poids pour 100 parties en poids du polymère.
- 55 3. Procédé de préparation d'un copolyoxyméthylène selon l'une des revendications précédentes, où l'éther cyclique peut s'exprimer par la formule suivante (A) :



où Y1 à Y4 représentent des atomes d'hydrogène ou des groupes alkyles de 1 à 6 carbones, et peuvent être identiques ou non; X représente soit une liaison directe (si m est 0) ou soit -CH₂- ou -OCH₂- où les hydrogènes peuvent être substitués par un groupe alkyle; m représente 0 ou un nombre entier compris entre 1 et 3, et si m = 1, X peut être soit -(CH₂)_p-OCH₂- ou -OCH₂-(CH₂)_p-OCH₂-, auquel cas p est un nombre entier compris entre 1 et 3.

4. Procédé de préparation d'un copolyoxyméthylène selon toute revendication précédente, où la quantité ajoutée de l'éther cyclique est de 3×10^{-5} à 3×10^{-1} mole pour une mole de trioxane.
5. Procédé de préparation d'un copolyoxyméthylène selon toute revendication précédente, où le catalyseur de polymérisation est un composé de coordination formé de trifluorure de bore et d'un composé contenant un atome d'oxygène.
6. Procédé de préparation d'un copolyoxyméthylène selon toute revendication précédente, où la quantité ajoutée du catalyseur de polymérisation est de 5×10^{-6} à 1×10^{-1} mole pour une mole de trioxane.
7. Procédé de préparation d'un copolyoxyméthylène selon toute revendication précédente, où la température de polymérisation est de 30 à 140 °C.
8. Procédé de préparation d'un copolyoxyméthylène selon toute revendication précédente, où la polymérisation est effectuée sensiblement à l'état sans solvant.
9. Procédé de préparation d'un copolyoxyméthylène selon toute revendication précédente, où le catalyseur de polymérisation est ajouté sous une forme dissoute dans un solvant organique dont le point d'ébullition est compris entre 20 et 200 °C à la pression atmosphérique.
10. Procédé de préparation d'un copolyoxyméthylène selon toute revendication précédente, où on mélange de l'éther cyclique à un catalyseur à l'avance puis on les met en contact avec du trioxane.
11. Procédé de préparation d'un copolyoxyméthylène selon toute revendication précédente, où le procédé de stabilisation consiste à chauffer le polymère entre 100 et 270 °C.
12. Procédé de préparation d'un copolyoxyméthylène selon toute revendication précédente, où on ajoute, dans le procédé de stabilisation, au moins un type d'un antioxydant et au moins un type d'un accélérateur de dégradation choisi parmi des hydroxydes, sels d'acides inorganiques, sels d'acides organiques et alcoolates de métaux alcalins et des métaux alcalino-terreux.
13. Procédé de préparation d'un copolyoxyméthylène selon la revendication 12 où l'antioxydant peut s'exprimer par la formule (C) qui suit :



(C)

où R1 et R2 sont des groupes alkyles de 1 à 6 carbones, des groupes triazolyles, ou des groupes triazolyles substitués et peuvent être les mêmes ou non; et R3 représente un atome d'hydrogène, un groupe amino ou un groupe organique monovalent tel qu'un groupe alkyle, un groupe alkyle substitué, un groupe aryle, un groupe aryle substitué, un groupe alcoxy, un groupe aryloxy, et un groupe amino substitué de 1 à 99 carbones.

14. Procédé de préparation d'un copolyoxyméthylène selon la revendication 12 ou la revendication 13, où l'accélérateur de dégradation est au moins un type de composé choisi parmi des hydroxydes, carbonates, phosphates, borates, sulfites, hydrogène-sulfates, silicates, oxalates, acétates, benzoates, isophthalates, téréphthalates, phthalates, méthoxyde, éthyoxides, isopropoxydes, et phénoxydes de lithium, sodium, potassium, magnésium, calcium et baryum.

15. Procédé de préparation d'un copolyoxyméthylène selon l'une quelconque des revendications 12 à 14, où la quantité ajoutée de l'antioxydant est de 0,001 à 5,0 parties en poids pour 100 parties en poids du polymère.

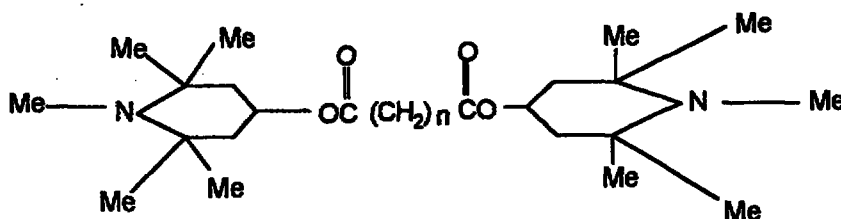
16. Procédé de préparation d'un copolyoxyméthylène selon l'une quelconque des revendications 12 à 15 où la quantité ajoutée de l'accélérateur de dégradation est comprise entre 0,001 et 5,0 parties en poids pour 100 parties en poids du polymère.

17. Procédé de préparation d'un copolyoxyméthylène selon toute revendication précédente, où le procédé de stabilisation consiste à faire fondre et à broyer le polymère à une température comprise entre le point de fusion du polymère et 270 °C.

18. Procédé de préparation d'un copolyoxyméthylène selon la revendication 17 où la pression dans le système est maintenue plus faible que la pression atmosphérique lors de la fusion et du broyage et du polymère.

19. Composition de résine produite par addition d'un composé d'amine empêchée contenant au moins un fragment de (2,2,6,6-tétraméthyl)-pipéridino, d'un antioxydant et d'au moins un type d'accélérateur de dégradation dans un copolymère produit à partir de trioxane et d'éther cyclique en présence d'un catalyseur de polymérisation.

20. Composition de résine selon la revendication 19, où le composé d'amine empêchée peut s'exprimer par la formule (D) qui suit et le poids moléculaire de l'antioxydant n'est pas inférieur à 400 :



(D)

où n représente un nombre entier compris entre 0 et 20.



21. Composition de résine selon la revendication 20, où on mélange de plus, dans la composition, au moins l'un du dicyandiamide, de mélamine, et de polyamide.

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