

Description

This invention relates to a novel stabilized oxymethylene copolymer composition and more particularly it relates to an oxymethylene copolymer composition which is superior to conventional oxymethylene copolymer compositions in long-term stability, in particular, long-term hot water resistance and long-term heat ageing characteristics and which forms only a very small amount of deposit on a mold at the time of molding.

Oxymethylene copolymers are plastics which are widely utilized as engineering resins in various fields because they have excellent mechanical characteristics, moldability, etc.

However, the oxymethylene copolymers themselves are insufficient in stability and hence are disadvantageous, for example, in that they undergo depolymerization from the terminals or severance of the main chain under a high temperature atmosphere or in hot water. Therefore, they should usually be stabilized by various terminal treatments followed by addition of additives such as antioxidants, thermostabilizers, etc.

Particularly when the oxymethylene copolymer is used as an engineering resin, blending therewith a thermal oxidation inhibitor is indispensable for maintaining and improving the quality of the copolymer. Various stabilizers have heretofore been proposed.

For example, there have been proposed a stabilizer comprising a metal salt of an organic acid having 2 to 30 carbon atoms and containing at least one carboxyl group and no nitrogen, and at least one metal salt of an alcohol having 2 to 30 carbon atoms and containing no nitrogen (US-A-3484399); and a stabilizer comprising at least one compound selected from the group consisting of hydroxides, inorganic acid salts and alkoxides of alkali metals or alkaline earth metals, nitrogen-containing polymeric compounds, and a hindered phenol (Japanese Patent Publication No. 56-10939).

It is already known that an ester of boric acid of a glycerol monoester of a fatty acid is useful as an antistatic agent for oxymethylene copolymer (Japanese Patent Publication No. 57-15616), but this publication does not suggest that the boric acid ester is effective as a stabilizer.

As a method for suppressing the formation of a deposit on the surface of a mold (hereinafter referred to as MD) at the time of fabrication, there have been proposed, for example, a method using a polyamide (US-A-2993025 and Japanese Patent Appln. Kokai (Laid-Open) No. 50-145458) and a method using a nitrogen compound such as an amide compound or a hydrazine compound (Japanese Patent Appln. Kokai (Laid-Open) Nos. 57-111346, 57-102943 and 59-33353, and Japanese Patent Publication No. 54-32658).

However, an oxymethylene copolymer containing as additives the metal salt of a fatty acid and the metal salt of an aliphatic alcohol possesses improved physical properties by virtue of the additives when evaluated in terms of long-term heat ageing characteristics and long-term hot water resistance, but is disadvantageous in that a test piece thereof undergoes marked browning. An oxymethylene copolymer containing as additives the hydroxide, inorganic acid salt or alkoxide of a metal, the nitrogen-containing polymeric compound and the hindered phenol possesses improved long-term heat ageing characteristics to some degree by virtue of the additives, but is disadvantageous not only in that spots were formed on a test piece thereof in evaluation of the long-term hot water resistance but also in that the copolymer has a lowered mechanical strength. A polyacetal containing as additive the ester of boric acid of a glycerol monoester of a fatty acid which is an antistatic agent is excellent in antistatic properties but has neither improved long-term heat ageing characteristics nor improved long-term hot water resistance.

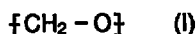
The polyamide reported to be effective against MD is undoubtedly effective as an agent for capturing formaldehyde and suppresses the formation of a deposit caused by formaldehyde. But since the polyamide itself tends to adhere to a mold, MD is formed owing to the adherence. The nitrogen compound such as an amide compound or a hydrazine compound adheres to a mold less firmly than the polyamide, but cannot suppress the formation of MD because it is poor in ability to capture formaldehyde.

Accordingly, the object of this invention is to provide an oxymethylene copolymer which is free from the defects of conventional oxymethylene copolymers, is excellent in long-term heat ageing characteristics and long-term hot water resistance as an engineering resin, and causes formation of only a very small amount of MD.

In order to develop a stabilizer which improves the long-term heat ageing characteristics and long-term hot water resistance of an oxymethylene copolymer and prevents the formation of MD without impairing desirable physical properties of the copolymer, the present inventors have devoted themselves to research and have consequently found that the object can be achieved by use of an alkaline earth metal salt of an ester, this ester being derivable from the reaction of a tribasic inorganic acid with an organic carboxylic acid monoester of an alcohol having two or more hydroxyl groups. On the basis of this finding, the present invention has been accomplished.

That is to say, the present invention provides a stabilized oxymethylene copolymer composition comprising a blend of an oxymethylene copolymer and at least one compound, as stabilizer, selected from the group consisting of alkaline earth metal salts of esters, these esters being derivable from the reaction of a tribasic inorganic acid with an organic carboxylic acid monoester of alcohols having two or more hydroxyl groups.

The oxymethylene copolymer used in the composition of this invention is a copolymer having a structure in which oxymethylene units represented by the general formula:



are bonded at random to oxyalkylene units represented by the general formula:



wherein R^1 and R^2 , which may be the same or different, are hydrogen atoms, alkyl groups or aryl groups, and m is an integer of 2 to 6. Although the proportion of the oxyalkylene units is not critical so long as it is more than zero, it ranges preferably from 0.05 to 50 moles, more preferably from 0.1 to 20 moles per 100 moles of the oxymethylene units. The oxyalkylene unit includes, for example, oxyethylene unit, oxypentylene unit, oxytetramethylene unit and oxyphenylethylene unit. Of these oxyalkylene units, oxypentylene unit $\{(\text{CH}_2)_5\text{O}\}$ and oxytetramethylene unit $\{(\text{CH}_2)_4\text{O}\}$ are particularly preferred from the viewpoint of improvement of physical properties of the oxymethylene copolymer.

The oxymethylene copolymer can be obtained by copolymerizing or reacting a formaldehyde, trioxane or oxymethylene homopolymer with a cyclic formal. The oxymethylene copolymer thus obtained is preferably subjected to a treatment for stabilizing the molecular terminals. As a method for the stabilizing treatment, there is usually employed, for example, a method of esterifying $-\text{OH}$ at the terminal of the copolymer, or a method of hydrolyzing the copolymer until a relatively stable carbon-carbon bond is located at each terminal.

In the composition of this invention, an alkaline earth metal salt of an ester is used as a stabilizer; this ester is derivable from the reaction of a tribasic inorganic acid with an organic carboxylic acid monoester of an alcohol having two or more hydroxyl groups (hereinafter referred to as "stabilizer G").

The alcohol having two or more hydroxyl groups in stabilizer G includes, for example, dihydric alcohols such as ethylene glycol, propylene glycol, 1, 3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,6-hexanediol, 1,5-pentanediol, and the like; trihydric alcohols such as glycerol, trimethylolpropane, trimethylolpropane, and the like; polyhydric alcohols such as pentaerythritol, sorbitan, sorbitol, mannitol, sucrose, and the like; phenyl- or phenoxy-substituted derivatives such as styrene glycol, phenylglycerol ether, and the like; and bisphenols such as bisphenol A and the like. Among them, polyhydric alcohols having three or more hydroxyl groups such as glycerol, trimethylolpropane, pentaerythritol, sorbitan, sorbitol, mannitol, sucrose, and the like are preferred, and glycerol and sorbitan are particularly preferred.

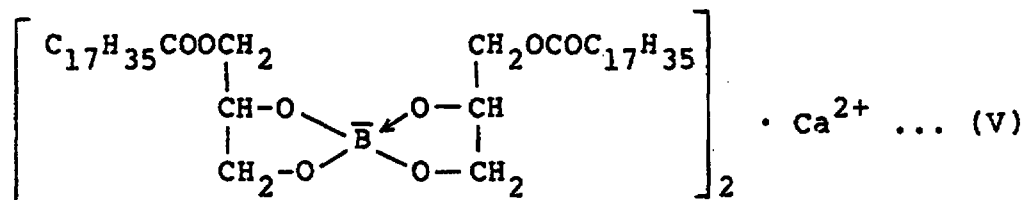
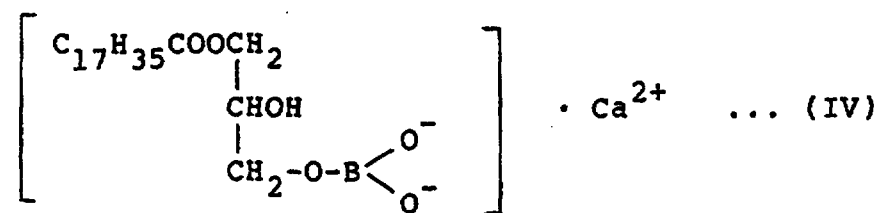
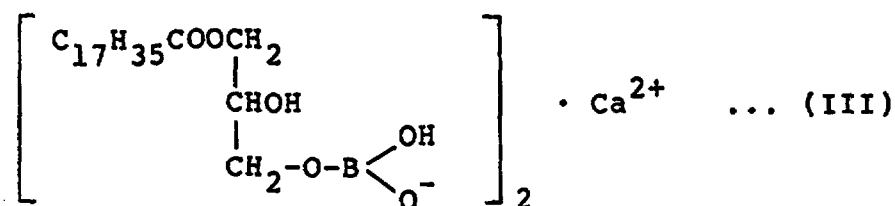
The organic carboxylic acid used in stabilizer G includes acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, behenic acid, etc. Among them, fatty acids having 8 to 22 carbon atoms such as capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, behenic acid, and the like are preferable, and lauric acid and stearic acid are more preferable.

Preferable examples of the tribasic inorganic acid in stabilizer G include phosphoric acid and boric acid. The alkaline earth metal in stabilizer G includes, for example, magnesium, calcium, barium, strontium, etc. Among them, magnesium, calcium and barium are preferred.

That is to say, stabilizer G includes magnesium salt of monoester of boric acid and ethylene glycol monolaurate, calcium salt of monoester of boric acid and 1,6-hexanediol monostearate, calcium salt of monoester of boric acid and glycerol monopropionate, calcium salt of monoester of boric acid and glycerol monostearate, magnesium salt of monoester of boric acid and glycerol monostearate, barium salt of monoester of boric acid and glycerol monostearate, calcium salt of monoester of boric acid and glycerol

monolaurate, magnesium salt of monoester of boric acid and glycerol monolaurate, calcium salt of monoester of phosphoric acid and glycerol monostearate, magnesium salt of monoester of phosphoric acid and glycerol monostearate, calcium salt of monoester of phosphoric acid and glycerol monolaurate, magnesium salt of monoester of phosphoric acid and glycerol monolaurate, calcium salt of monoester of boric acid and glycerol monobehenate, calcium salt of monoester of boric acid and sorbitan monostearate, magnesium salt of monoester of boric acid and sorbitan monostearate, barium salt of monoester of boric acid and sorbitan monostearate, calcium salt of monoester of boric acid and sorbitan monolaurate, magnesium salt of monoester of boric acid and sorbitan monolaurate, barium salt of monoester of boric acid and sorbitan monolaurate, calcium salt of monoester of phosphoric acid and sorbitan monolaurate, barium salt of monoester of phosphoric acid and sorbitan monolaurate, etc.

The chemical structure of the stabilizer G has not been identified yet, however, a possible structure thereof could be shown as follows if calcium salt of monoester of boric acid of glycerol monostearate is taken as an illustrative example:



Although not critical, a method for producing stabilizer G includes, for example, a method comprising mixing an organic carboxylic acid monoester of an alcohol having two or more hydroxyl groups with a tribasic inorganic acid, heating the resulting mixture to remove condensation water, dissolving the compound thus obtained in a suitable solvent, and neutralizing the resulting solution with hydroxide of an alkaline earth metal to obtain the desired compound, and a method comprising mixing an organic carboxylic acid monoester of an alcohol having two or more hydroxyl groups with an alkaline earth metal salt of a tribasic inorganic acid, and heating the resulting mixture to carry out condensation (Japanese Patent Publication Nos. 43-14322 and 48-43371).

Either a single stabilizer G or a combination of two or more stabilizers G may be used.

The blending amount of stabilizer G in the composition of this invention is selected usually in the range of 0.01 to 5% by weight, preferably 0.03 to 1% by weight, more preferably 0.05 to 0.5% by weight. When the blending amount is less than 0.01% by weight, there is brought about neither sufficient improving effect on the long-term heat ageing characteristics and the long-term hot water resistance nor sufficient suppressing effect on the formation of MD. When the blending amount exceeds 5% by weight, the formation of silver streaks or coloring as result of residing in a cylinder of a molding machine tends to occur at the time of injection molding. Therefore, it is not desirable.

Antioxidants which are conventionally used in oxymethylene copolymer compositions can be further included in the composition of this invention. As the antioxidants, hindered phenols, hindered amines, etc. can be used. Specifically, there can be used phenols such as 2,2'-methylene-bis(4-methyl-6-*t*-butylphenol), triethylene glycol-bis[3-(3-*t*-butyl-5-methyl-4-hydroxyphenyl)propionate], pentaerythrityl-tetrakis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate], 1,6-hexanediol-bis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate], distearyl-3,5-dibutyl-4-hydroxybenzyl phosphonate, and the like; and amines such as 3,5-di-*t*-butyl-4-hydroxyphenyl-3,5-distearyl-thiotriazylamine, *N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine, *N,N'*-diphenyl-*p*-phenylenediamine, 4,4'-bis(4- α , α -dimethylbenzyl)diphenylamine, *N,N'*-di- β -naphthyl-*p*-phenylenediamine, and the like. Of these antioxidants, 2,2'-methylene-bis(4-methyl-6-*t*-butylphenol), triethylene glycol-bis[3-(3-*t*-butyl-5-methyl-4-hydroxyphenyl)propionate], and pentaerythrityl-tetrakis [3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate] are particularly effective.

Furthermore, the composition of this invention can be incorporated with at least one nitrogen-containing compound selected from the group consisting of polyamides, triazine derivatives and dicyan-diamide.

As the polyamides, there can be used high molecular weight compounds having in the molecular chain a linkage represented by the formula:



wherein R is a hydrogen atom or an alkyl group. Specifically, there can be used, for example, polymers formed from lactams such as caprolactam, laurolactam and the like; polymers obtained by the reaction of dicarboxylic acids such as adipic acid, sebacic acid, dodecanoic diacid, linolic acid dimer and the like with diamines such as ethylenediamine, tetramethylenediamine, hexamethylenediamine, metaxylylenediamine and the like; poly- β -alanine (Japanese Patent Appln. Kokai (Laid-Open) Nos. 59-213722 and 59-213752); and copolymers of these polymers. More specifically, there can be used nylons 6, 12, 46, 66, 610 and 612, poly(xylyleneadipamide), etc. These polyamides may be used alone or in combination of two or more thereof.

As the triazine derivatives, there can be used melamine, acetoguanamine, acryloguanamine, etc. These triazine derivatives may be used alone or in combination of two or more thereof.

Of these nitrogen-containing compounds, the polyamides are preferred.

The blending amount of the nitrogen-containing compounds is selected usually in the range of 0.01 to 5% by weight, preferably 0.01 to 1% by weight, more preferably 0.05 to 0.5% by weight.

In producing the composition of this invention, the order in which stabilizer G, the antioxidant and the nitrogen-containing compound are added, is not critical. The forms of these components are also not critical and may be any of powder, liquid or solution forms.

If desired, the composition of this invention can be incorporated with other additives which are conventionally included in oxymethylene compositions, for example, antistatic agents, lubricants, inorganic fillers and reinforcing materials such as glass fiber, glass beads, carbon fiber, etc., and pigments.

By virtue of the addition of stabilizer G to an oxymethylene copolymer, the oxymethylene copolymer composition of this invention not only shows markedly improved tensile strength retention; tensile elongation retention, and weight retention both in a 140°C long-term heat ageing characteristics test and a 120°C long-term hot water resistance test, but also undergoes a much slighter change of the appearance of test molded products in said two tests, as compared with conventional oxymethylene copolymer compositions. Furthermore, when subjected to continuous molding, it forms much less MD and is excellent in the appearance of the molded product, as compared with conventional oxymethylene copolymer compositions.

It is conjectured that the reason for the improvement in the retention of physical properties in such long-term characteristics tests is that the alkaline earth metal salt contained in stabilizer G acts effectively as an acceptor for formic acid generated by thermal decomposition of the oxymethylene copolymer. Furthermore, it is conjectured that the improvement in retention of physical properties and coloring as a result of residing in the molding apparatus is attributable also to the fact that stabilizer G hardly catalyzes formose formation, unlike hydroxides and oxides of alkali metals and alkaline earth metals which are catalysts for formose formation. It is conjectured that the reason why only a small amount of MD is formed in continuous molding as described above is that stabilizer G inhibits adherence of formaldehyde gas to the

surface of a mold. Moreover, the formation of MD is suppressed synergistically by the inclusion of the nitrogen - containing compound.

Because of these advantages, the oxymethylene copolymer composition of this invention can withstand employment in a severe environment, for example, employment at high temperatures or in hot water for a long period of time, forms only a small amount of MD even in continuous molding for a long period of time, and can contribute greatly to improvement of the productivity.

Examples

This invention is further illustrated in more detail with reference to the following examples. Characteristics of compositions in Examples and Comparative Examples were evaluated as follows:

(1) Long-term hot water resistance test

A 120°C long-term hot water resistance test was carried out by means of an autoclave having a pressure regulating valve. Deionized water was used as test water. A temperature control unit and a flowmeter were set, and the test was carried out by a 120°C flowing water method.

The individual retention ratios of tensile strength (according to ASTM D-638), tensile elongation (according to ASTM D-638) and weight of molded products (measured in 10 mg unit) are calculated based on the following equations:

$$\text{Tensile strength retention ratio} = \frac{TS}{TS_0} \times 100$$

$$\text{Tensile elongation retention ratio} = \frac{TE}{TE_0} \times 100$$

$$\text{Weight retention ratio} = \frac{W}{W_0} \times 100$$

TS: Tensile strength after testing

TS₀: Tensile strength before testing

TE: Tensile strength after testing

TE₀: Tensile strength before testing

W: Weight of molded product after testing

W₀: Weight of molded product before testing

The appearance change of molded products was evaluated as shown in the following (2).

(2) Appearance change of molded product

The change of the appearance of an early molded product and a molded product after testing was observed with the naked eye and rated as follows:

o : A slight color change was observed with the naked eye.

Δ : Yellowing was clearly observed with the naked eye, or spots were observed at places on the surface of a molded product.

x : Browning was observed, or spots were observed all over the surface of a molded product.

(3) Long-term hot ageing characteristic test

A 140°C long-term hot ageing characteristic test was carried out in a Gear oven (Model GPS-222, mfd. by TABAI ESPEC, Co., Ltd.; exhaust duct: 20° opened). The evaluation items and method were the same as in the long-term hot water resistance test.

(4) Evaluation by a continuous molding test

Injection molding machine: JSW N70A (mfd. by THE JAPAN STEEL WORKS, Ltd.)

Cylinder temperature: 200°C

5 Injection pressure: 40 kg/cm²G

Injection time: 5 sec, cooling 5 sec.

Mold temperature: 90°C and 30°C

Continuous molding into JIS No. 3 tensile specimens was conducted 5,000 shots under the above molding conditions, after which the state of a deposit on a mold was observed with the naked eye and rated as follows:

- 10 0 : No mold deposit was observed.
 1 : Substantially no mold deposit was observed.
 2 : A thin mold deposit was observed.
 3 : An obvious mold deposit was observed.
 15 4 : A thick mold deposit adhered to the whole surface of a mold.

(5) Appearance change of a molded product after residence in an injection molding machine

After residence in an injection molding machine (Type Allrounder 221-55-250, mfd. by ARBURG) for 20 1 hour at a material temperature of 230°C, molding into test pieces having about 3 x 12 x 120 mm size was conducted, and the degree of the formation of silver streaks on the surface of the molded product was observed and rated as follows:

- o : Neither silver streaks nor yellowing was observed on the surface of the molded product.
 Δ : Silver streaks are observed at places on the surface of the molded product, or yellowing of the 25 molded article was observed.
 x : Silver streaks were observed all over the surface of the molded product, or obvious and strong yellowing of the molded product was observed.

Production of an oxymethylene copolymer

30 Using boron trifluoride-butyl ether complex as a catalyst, 98% by weight of trioxane and 2% by weight of ethylene oxide were polymerized to obtain a crude oxymethylene copolymer. The reaction was stopped by addition of triethylamine, and the polymer was separated. Then, a mixture of triethylamine and water was added to the polymer, and the terminal unstable portions of the polymer were removed in a vented extruder 35 of 65 φ. MI of the polymer after the stabilization of the terminals was 9.5 (g/10 min.) This polymer is named B-1.

In the same manner as described above, 97% by weight of trioxane and 3% by weight of 1,3-dioxepane were polymerized and a terminally stabilized oxymethylene copolymer [MI 9.0 (g/10 min.)] was prepared.

40 This polymer is named B-2.

Examples 1 to 36 and Comparative Examples 1 to 11

45 According to each recipe shown in Tables 1 to 4, the ingredients listed therein were homogeneously mixed in a Henschel mixer. The resulting mixture was passed through an extruder of 50 φ to be melted and stabilized, and a resin was taken out through a die head in the form of a strand. The strand was immediately pelletized, dried, and then subjected to various evaluation checks. The results obtained are shown in Tables 1 to 4.

The symbols in the tables show the following compounds:

50

Stabilizers G:

- G-1: calcium salt of monoester of boric acid and glycerol monostearate
 G-2: magnesium salt of monoester of boric acid and glycerol monostearate
 55 G-3: calcium salt of monoester of boric acid and glycerol monolaurate
 G-4: calcium salt of monoester of phosphoric acid and glycerol monostearate
 G-5: magnesium salt of monoester of phosphoric acid and glycerol monolaurate
 G-6: barium salt of monoester of boric acid and glycerol monostearate

- G-7: calcium salt of monoester of boric acid and sorbitan monostearate
- G-8: calcium salt of monoester of phosphoric acid and sorbitan monostearate
- G-9: barium salt of monoester of boric acid and sorbitan monolaurate
- G-10: calcium salt of monoester of boric acid and glycerol monopropionate
- G-11: magnesium salt of monoester of boric acid and ethylene glycol monolaurate
- G-12: calcium salt of monoester of boric acid and 1,6-hexanediol monostearate
- G-13: calcium salt of monoester of boric acid and glycerol monobehenate

Antioxidants:

- A-1: triethylene glycol-bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate] (trade name: Inganox 245, mfd. by Ciba-Geigy Co.)
- A-2: pentaerythryl-tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (trade name: Inganox 1010, mfd. by Ciba Geigy Co.)
- A-3: 2,2'-methylene-bis(4-methyl-6-t-butylphenol) (trade name: Yoshinox 2246, mfd. by Yoshitomi Pharmaceutical Industries)

Nitrogen-containing compounds:

- C-1: nylon 66
- C-2: nylon 6/66/610 (40%/30%/30%)
- C-3: poly-β-alanine
- C-4: melamine
- C-5: dicyandiamide

Other additives:

- D-1: monoester of boric acid and glycerol monostearate
- D-2: calcium stearate
- D-3: calcium ricinolate
- D-4: calcium hydroxide
- D-5: sodium salt of monoester of boric acid and glycerol monostearate

Table 1

Example	Composition (wt %)						water resistance		
	stabilizer G		Antioxidant		Nitrogen-containing compound		Oxymethylene copolymer		
		Blending amount		Blending amount		Blending amount	500 hrs.		
							Tensile strength retention (%)	Tensile elongation retention (%)	
1	G-1	0.2	A-1	0.5	-	-	B-1	100	100
2	G-1	0.05	A-1	0.5	-	-	B-1	100	100
3	G-1	0.01	A-1	0.5	-	-	B-1	100	100
4	G-1	0.1	A-1	0.5	-	-	B-1	100	100
5	G-1	5.0	A-1	0.5	-	-	B-1	100	100
6	G-1	0.2	A-2	0.5	-	-	B-1	100	100
7	G-1	0.2	A-3	0.5	-	-	B-1	100	100
8	G-2	0.2	A-1	0.5	-	-	B-1	100	100
9	G-3	0.2	A-1	0.5	-	-	B-1	100	100
10	G-4	0.1	A-1	0.5	-	-	B-1	100	100
11	G-5	0.1	A-1	0.5	-	-	B-1	100	100

- cont'd -

Table 1 (cont'd)

12	G-6	0.2	A-1	0.5	-	-	B-1	100	100
13	G-7	0.3	A-1	0.5	-	-	B-1	100	100
14	G-8	0.2	A-1	0.5	-	-	B-1	100	100
15	G-9	0.2	A-1	0.5	-	-	B-1	100	100
16	G-10	0.2	A-1	0.5	-	-	B-1	100	100

Table 1 (cont'd)

120°C long-term hot water resistance										
500 hrs		1500 hrs.				3000 hrs.				Appearance
Weight retention (%)	Appearance	Tensile strength retention (%)	Tensile elongation (%)	Weight retention (%)	Appearance	Tensile strength retention (%)	Tensile elongation (%)	Weight retention (%)	Appearance	
100	o	100	100	100	o	98	82	99	o	
100	o	100	100	99	o	90	37	97	o	
100	o	100	80	99	o	75	17	94	Δ	
100	o	100	100	99	o	98	80	99	o	
100	o	100	100	99	o	97	75	98	Δ	
100	o	100	100	100	o	98	78	99	o	
100	o	100	100	99	o	88	33	95	o	
100	o	100	100	100	o	98	80	99	o	
100	o	100	100	100	o	95	74	98	o	
100	o	100	100	99	Δ	86	34	94	Δ	
100	o	100	100	99	Δ	88	35	96	Δ	

- cont'd -

Table 1 (cont'd)

100	0	100	100	99	0	96	61	97	0
100	0	100	100	99	0	85	33	97	0
100	0	100	90	99	Δ	72	15	93	Δ
100	0	100	100	99	0	86	40	97	0
100	0	100	100	99	0	90	41	95	0

- cont'd -

Table 1 (cont'd)

140°C long-term heat ageing characteristic test							
500 hrs.				1000 hrs.			
Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance	Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance
100	100	100	o	100	100	99	o
100	100	100	o	100	98	99	o
100	100	100	o	100	60	98	o
100	100	100	o	100	100	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	98	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	98	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	98	99	o

-- cont'd --

Table 1 (cont'd)

100	100	100	100	0	100	99	99	0
100	100	100	100	0	100	98	99	0
100	100	100	100	0	100	97	99	0
100	100	100	100	0	100	97	99	0
100	100	100	100	0	100	95	99	0

- cont'd -

Table 1 (cont'd)

heat ageing characteristic test				Continuous molding test		Appearance of a molded product after residence in a molding machine 230°C x 1 hr.
2000 hrs.				High tem-perature mold (90°C)	Low tem-perature mold (30°C)	
Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance			
98	63	98	0	0	2	0
84	31	95	0	0	2	0
75	19	95	Δ	0	2	Δ
99	68	99	Δ	0	2	0
93	42	98	Δ	0	2	Δ
99	80	99	0	0	2	0
83	27	95	0	0	2	0
98	68	98	0	0	2	0
98	53	97	0	0	2	0
88	30	96	Δ	0	2	Δ
85	26	96	Δ	0	2	Δ

- cont'd -

Table 1 (cont'd)

95	53	97	0	0	2	0
83	35	95	0	0	2	0
70	12	93	Δ	0	2	Δ
86	32	95	0	0	2	0
81	30	96	0	0	2	0

Table 2

Example	Composition (wt %)						water resistance	
	stabilizer G	Antioxidant		Nitrogen-containing compound		Oxymethylene copolymer	500 hrs.	
		Blending amount	Blending amount	Blending amount	Blending amount		Tensile strength retention (%)	Tensile elongation retention (%)
17	G-11	0.1	A-1 0.5	-	-	B-1	100	100
18	G-12	0.2	A-1 0.5	-	-	B-1	100	100
19	G-13	0.2	A-1 0.5	-	-	B-1	100	100
20	G-1	0.2	A-1 0.5	-	-	B-2	100	100
21	G-1	0.2	A-1 0.5	C-1	0.1	B-1	100	100
22	G-1	0.2	A-1 0.5	C-2	0.1	B-1	100	100
23	G-1	0.2	A-1 0.5	C-3	0.1	B-1	100	100
24	G-1	0.2	A-1 0.5	C-4	0.1	B-1	100	100
25	G-1	0.2	A-1 0.5	C-5	0.1	B-1	100	100
26	G-1	0.01	A-1 0.5	C-1	0.1	B-1	100	100
27	G-1	5.0	A-1 0.5	C-1	0.1	B-1	100	100

- cont'd -

Table 2 (cont'd)

28	G-1	0.2	A-1	0.5	C-1	0.01	B-1	100	100
29	G-1	0.2	A-1	0.5	C-1	3.0	B-1	100	100
30	G-1	0.2	A-2	0.5	C-1	0.1	B-1	100	100
31	G-1	0.2	A-3	0.5	C-1	0.1	B-1	100	100
32	G-2	0.2	A-1	0.5	C-1	0.1	B-1	100	100

- cont'd -

Table 2 (cont'd)

120°C long-term hot water resistance									
500 hrs.			1500 hrs.			3000 hrs.			
Weight retention (%)	Appearance	Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance	Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance
100	0	100	88	99	0	71	16	93	0
100	0	100	85	99	0	74	15	93	0
100	0	100	100	99	0	94	55	96	0
100	0	100	100	99	0	96	75	98	0
100	0	100	100	99	0	96	75	98	0
100	0	100	100	99	0	97	78	98	0
100	0	100	100	99	0	95	55	98	0
100	0	100	100	99	0	94	49	97	0
100	0	100	100	99	0	94	40	96	0
100	0	100	83	99	0	88	32	97	0
100	0	100	100	99	0	96	79	98	Δ

- cont'd -

Table 2 (cont'd)

100	0	100	100	99	0	97	77	99	0
100	0	100	100	99	Δ	95	59	97	Δ
100	0	100	100	99	0	95	80	98	0
100	0	100	100	99	0	93	62	98	0
100	0	100	100	99	0	97	80	97	0

- cont'd -

Table 2 (cont'd)

140°C long-term heat ageing characteristic test							
500 hrs.				1000 hrs.			
Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance	Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance
100	100	100	o	100	90	99	o
100	100	100	o	100	89	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	96	99	o
100	100	100	o	100	98	99	o
100	100	100	o	100	64	99	o
100	100	100	o	100	100	99	o

- cont'd -

Table 2 (cont'd)

100	100	100	100	100	100	100	100	99	0
100	100	100	100	100	100	100	100	99	Δ
100	100	100	100	100	100	100	100	99	0
100	100	100	100	100	100	100	100	99	0
100	100	100	100	100	100	100	100	99	0

- cont'd -

Table 2 (cont'd)

heat ageing characteristic test					Continuous molding test		Appearance of a molded product after residence in a molding machine 230°C x 1 hr.
2000 hrs.					High temperature mold (90°C)	Low temperature mold (30°C)	
Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance				
73	72	93	0		0	2	0
75	74	93	0		0	2	0
87	31	96	0		0	2	0
96	43	98	0		0	2	0
97	60	98	0		0	0	0
95	62	98	0		1	0	0
95	58	98	0		0	0	0
92	43	97	0		0	1	0
91	39	96	0		0	1	0
80	33	94	0		1	1	Δ
92	40	98	Δ		0	0	Δ

- cont'd -

Table 2 (cont'd)

95	70	98	0	0	1	0
93	51	96	Δ	2	0	Δ
94	66	98	0	0	0	0
95	57	98	0	0	0	0
96	70	97	0	0	0	0

Table 3

Example	Composition (wt %)						water resistance		
	stabilizer G		Antioxidant		Nitrogen- containing compound		Oxymeth- ylene copoly- mer	500 hrs.	
	Blending amount		Blending amount		Blending amount		Tensile strength retention (%)	Tensile elongation retention (%)	
33	G-3	0.2	A-1	0.5	C-1	0.1	B-1	100	100
34	G-4	0.2	A-1	0.5	C-1	0.1	B-1	100	100
35	G-1	0.2	A-1	0.5	C-1	0.1	B-1	100	100
36	G-1	0.2	A-1	0.5	C-1	0.1	B-2	100	100

- cont'd -

Table 3 (cont'd)

120°C long-term hot water resistance									
500 hrs.		1500 hrs.				3000 hrs.			
Weight retention (%)	Appearance	Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance	Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance
100	o	100	100	99	o	96	66	97	o
100	o	100	100	99	Δ	82	31	94	Δ
100	o	100	100	99	o	82	29	94	o
100	o	100	100	99	o	95	77	98	o

- cont'd -

Table 3 (cont'd)

140°C long-term heat ageing characteristic test							
500 hrs.				1000 hrs.			
Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance	Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance
100	100	100	o	100	99	99	o
100	100	100	o	100	100	99	o
100	100	100	o	100	99	99	o
100	100	100	o	100	99	99	o

- cont'd -

Table 3 (cont'd)

heat ageing characteristic test					Continuous molding test		Appearance of a molded product after residence in a molding machine
2000 hrs.					High temperature mold (90°C)	Low temperature mold (30°C)	
Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance				
95	64	97	0		0	0	0
87	28	96	Δ		1	1	Δ
80	33	95	0		0	0	0
95	48	98	0		0	0	0

Table 4

Comparative Example	Composition (wt %)						water resistance	
	stabilizer G	Antioxidant		Nitrogen- containing compound	Oxymeth- ylene copoly- mer	500 hrs.	Tensile strength retention (%)	Tensile elongation retention (%)
		Blending amount	Blending amount					
1	-	-	A-1 0.5	C-1 0.5	B-1	100	100	52
2	-	-	A-1 0.5	C-2 0.5	B-1	100	100	44
3	-	-	A-1 0.5	C-4 0.2	B-1	100	100	85
4	-	-	A-1 0.5	C-5 0.1	B-1	100	100	81
5	-	-	A-3 0.3	C-2 0.6	B-1	100	100	40
6	D-1	0.2	A-1 0.5	-	B-1	75	75	17
7	D-2	0.1	A-3 0.5	-	B-1	100	100	100
8	D-3	0.1	A-3 0.5	-	B-1	100	100	100
9	D-4	0.1	A-1 0.5	C-1 0.1	B-1	62	62	15
10	D-1	0.2	A-1 0.5	C-1 0.1	B-1	100	100	69
11	D-5	0.2	A-1 0.5	C-2 0.6	B-1			

- cont'd -

Table 4 (cont'd)

120°C long-term hot water resistance

500 hrs.		1500 hrs.				3000 hrs.			
Weight retention (%)	Appearance	Tensile strength retention (%)	Tensile elongation (%)	Weight retention (%)	Appearance	Tensile strength retention (%)	Tensile elongation (%)	Weight retention (%)	Appearance
99	o	30	11	78	Δ	*	*	8	x
99	o	25	10	82	Δ	*	*	10	x
100	o	85	29	96	o	20	10	80	Δ
99	o	89	37	94	o	18	7	73	Δ
99	o	13	8	80	Δ	*	*	4	x
87	o	8	8	75	x	*	*	4	x
100	Δ	100	100	99	x	92	63	97	x
100	Δ	100	100	98	x	90	46	97	x
84	Δ	35	10	80	x	*	*	0	*
99	o	12	10	78	Δ	*	*	5	x
Extrusion was impossible because of foaming and no pellet could be obtained.									

Remarks *: unmeasurable

- cont'd -

Table 4 (cont'd)

140°C long-term heat ageing characteristic test									
500 hrs.					1000 hrs.				
Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance		Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance	
100	55	99	o		94	38	95	Δ	
100	50	99	o		91	39	95	Δ	
100	92	100	o		100	40	99	o	
100	53	99	o		88	30	93	Δ	
100	35	99	o		86	32	96	Δ	
93	29	97	o		78	16	88	Δ	
100	100	100	Δ		100	99	99	Δ	
100	100	100	Δ		100	92	99	Δ	
100	100	99	Δ		98	34	98	x	
100	44	99	o		92	30	96	Δ	

- cont'd -

Table 4 (cont'd)

heat ageing characteristic test					Continuous molding test		Appearance of a molded product after residing in a molding machine
2000 hrs.					High temperature mold (90°C)	Low temperature mold (30°C)	
Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance				
83	25	93	Δ		3	2	Δ
80	25	93	Δ		4	2	Δ
85	31	89	Δ		3	3	x
70	18	88	Δ		3	3	x
74	22	88	Δ		4	2	x
38	8	79	x		3	3	x
98	75	98	x		2	3	x
91	49	98	x		2	3	x
70	12	86	x		3	2	x
71	15	86	Δ		2	1	o

Claims

1. A stabilized oxymethylene copolymer composition, comprising a blend of an oxymethylene copolymer and, as a stabilizer, an alkaline earth metal salt of an ester, this ester being derivable from the reaction

Table 4 (cont'd)

heat ageing characteristic test					Continuous molding test		Appearance of a molded product after residing in a molding machine 230°C x 1 hr.
2000 hrs.					High temperature mold (90°C)	Low temperature mold (30°C)	
Tensile strength retention (%)	Tensile elongation retention (%)	Weight retention (%)	Appearance				
83	25	93	Δ		3	2	Δ
80	25	93	Δ		4	2	Δ
85	31	89	Δ		3	3	x
70	18	88	Δ		3	3	x
74	22	88	Δ		4	2	x
38	8	79	x		3	3	x
98	75	98	x		2	3	x
91	49	98	x		2	3	x
70	12	86	x		3	2	x
71	15	86	Δ		2	1	o

Claims

1. A stabilized oxymethylene copolymer composition, comprising a blend of an oxymethylene copolymer and, as a stabilizer, an alkaline earth metal salt of an ester, this ester being derivable from the reaction



of a tribasic inorganic acid with an organic carboxylic acid monoester of an alcohol having two or more hydroxyl groups .

2. A composition according to Claim 1, wherein the alcohol is a polyhydric alcohol having three or more hydroxyl groups.
3. A composition according to Claim 2, wherein the alcohol is glycerol or sorbitan.
4. A composition according to any of the claims 1 to 3 wherein the organic carboxylic acid of the organic carboxylic acid monoester is a fatty acid having 8 to 22 carbon atoms.
5. A composition according to claim 4, wherein the organic carboxylic acid of the organic carboxylic acid monoester is lauric acid or stearic acid.
6. A composition according to any of the claims 1 to 5, wherein the inorganic acid of the ester of tribasic inorganic acid is boric acid or phosphoric acid.
7. A composition according to any of the claims 1 to 6, wherein the alkaline earth metal salt is a magnesium, calcium or barium salt.
8. A composition according to any of the claims 1 to 7, wherein the content of the stabilizer is 0.01 to 5% by weight.
9. A composition according to any of the claims 1 to 8, which additionally comprises at least one nitrogen - containing compound selected from the group consisting of polyamides, triazine derivatives and dicyanamide being blended to the stabilized oxymethylene copolymer.
10. A composition according to claim 9, wherein the nitrogen - containing compound is a polyamide.
11. A composition according to claim 9 or 10, wherein the content of the nitrogen - containing compound is 0.1 to 5 % by weight.

Patentansprüche

1. Stabilisierte Oxymethylen - Copolymerzusammensetzung, die eine Mischung aus einem Oxymethylen - Copolymer und, als Stabilisator, einem Erdalkalimetallsalz eines Esters umfaßt, wobei der Ester durch Umsetzung einer tribasischen anorganischen Säure mit einem Monoester einer organischen Carbonsäure eines Alkohols mit zwei oder mehr Hydroxylgruppen erhältlich ist.
2. Zusammensetzung gemäß Anspruch 1, wobei der Alkohol ein Polyhydroxyalkohol mit drei oder mehr Hydroxylgruppen ist.
3. Zusammensetzung gemäß Anspruch 2, wobei der Alkohol Glycerin oder Sorbit ist.
4. Zusammensetzung gemäß einem der Ansprüche 1 bis 3, wobei die organische Carbonsäure in dem Monoester der organischen Carbonsäure eine Fettsäure mit 8 bis 22 Kohlenstoffatomen ist.
5. Zusammensetzung gemäß Anspruch 4, worin die organische Carbonsäure in dem Monoester der organischen Carbonsäure Laurin - oder Stearinsäure ist.
6. Zusammensetzung gemäß einem der Ansprüche 1 bis 5, worin die anorganische Säure in dem Ester der tribasischen anorganischen Säure Borsäure oder Phosphorsäure ist.
7. Zusammensetzung gemäß einem der Ansprüche 1 bis 6, worin das Erdalkalimetallsalz ein Magnesium -, Calcium -, oder Bariumsalz ist.
8. Zusammensetzung gemäß einem der Ansprüche 1 bis 7, worin der Gehalt an dem Stabilisator 0,01 bis 5 Gew. - % beträgt.



9. Zusammensetzung gemäß einem der Ansprüche 1 bis 8, die zusätzlich mindestens eine Stickstoffverbindung, ausgewählt aus der Gruppe der Polyamide, Triazinderivate und Dicyanamid, enthält, die dem stabilisierten Oxymethylen-Copolymer zugemischt ist.
10. Zusammensetzung gemäß Anspruch 9, worin die Stickstoffverbindung ein Polyamid ist.
11. Zusammensetzung gemäß Anspruch 9 oder 10, worin der Gehalt an der Stickstoffverbindung 0,1 bis 5 Gew.-% beträgt.

10 Revendications

1. Composition de copolymère d'oxyméthylène stabilisé, ladite composition comprenant un mélange d'un copolymère d'oxyméthylène et, en tant que stabilisant, d'un sel de métal alcalino-terreux d'un ester, ledit ester étant capable de provenir de la réaction d'un triacide minéral sur un monoester d'un acide carboxylique aromatique avec un alcool ayant deux groupes hydroxyle ou plus.
2. Composition suivant la revendication 1, dans laquelle ledit alcool est un alcool polyhydrique ayant trois groupes hydroxyle ou plus.
3. Composition suivant la revendication 2, dans laquelle ledit alcool est le glycérol ou le sorbitan.
4. Composition suivant l'une quelconque des revendications 1 à 3, dans laquelle l'acide carboxylique aromatique du monoester d'acide carboxylique aromatique est un acide gras ayant de 8 à 22 atomes de carbone.
5. Composition suivant la revendication 4, dans laquelle l'acide carboxylique aromatique du monoester d'acide carboxylique aromatique est l'acide laurique ou l'acide stéarique.
6. Composition suivant l'une quelconque des revendications 1 à 5, dans laquelle l'acide minéral du monoester du triacide minéral est l'acide borique ou l'acide phosphorique.
7. Composition suivant l'une quelconque des revendications 1 à 6, dans laquelle ledit sel de métal alcalinoterreux est un sel de magnésium, calcium ou baryum.
8. Composition suivant l'une quelconque des revendications 1 à 7, dans laquelle la teneur en stabilisant est de 0,01 à 5 % en poids.
9. Composition suivant l'une quelconque des revendications 1 à 8, comprenant en plus au moins un composé d'azote choisi dans le groupe comprenant les polyamides, les dérivatives de triazine et le dicyanamide qui est mélangé au copolymère d'oxyméthylène stabilisé.
10. Composition suivant la revendication 9, dans laquelle le composé d'azote est un polyamide.
11. Composition suivant la revendication 9 ou 10, dans laquelle la teneur du composé d'azote est 0,1 à 5 % en poids.

