

VERIFICATION OF TRANSLATION

National Stage in Singapore
Patent Application of
PCT/JP95/02209

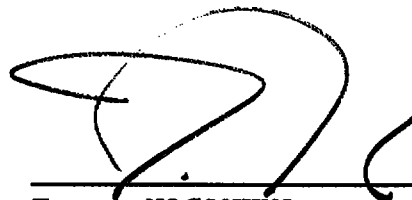
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DATED this 12th day of March, 1997.

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Teruo NAGANUMA
Registered Patent Attorney

DESCRIPTION

POLYACETAL RESIN COMPOSITION

TECHNICAL FIELD

The present invention relates to a polyacetal resin composition having excellent flowability and thermal stability in good balance.

BACKGROUND ART

5 Polyacetal resins find wide applications in the fields of automobiles, electrical appliances, construction materials, etc., for their excellency in mechanical properties, fatigue resistance and sliding property.

10 With the expansion of the applications of polyacetal resins, however, the quality requirements for said resins have become increasingly severe. The increased quality requirements include improved moldability. Polyacetal resins, as compared with
15 amorphous resins, tend to generate molding stress during injection molding because they have a relatively high crystallization rate and are crystallized at a high degree. Conventional polyacetal resins have no sufficient properties particularly when molded into a
20 molding of complex shape or a thin molding or when molded in a short cycle; thus, their improvement in moldability is required.

In order to improve the moldability of polyacetal resin, it was attempted to add other components to a polyacetal resin to improve the melt flowability of the polyacetal resin. JP-B-37-8816
5 proposed a polyacetal resin composition comprising a polyalkylene glycol; JP-B-52-3754 proposed a polyacetal resin composition comprising an aliphatic alcohol ester; JP-A-60-90248 proposed a polyacetal resin composition comprising a bisphenol derivative; and JP-
10 A-4-239566 proposed a polyacetal resin composition comprising a liquid ethylene- α -olefin random copolymer. In these compositions, the flowability of polyacetal resin is improved; however, the moldings produced from the compositions have not only reduced mechanical
15 properties but also deteriorated thermal stability, and have no practical applicability.

DISCLOSURE OF THE INVENTION

The object of the present invention is to provide a polyacetal resin composition which has
20 improved melt flowability without reducing the mechanical properties inherently possessed by polyacetal resins, which further has excellent thermal stability and which has balanced properties.

The present inventors made an extensive study
25 in order to solve the above-mentioned problems of the prior art and, as a result, found out that a polyacetal

resin composition aimed by the above object can be obtained by allowing a polyacetal resin to contain a polyacetal oligomer and fluorine in given proportions.

The present invention provides a polyacetal
5 resin composition comprising oxymethylene units as the main constitute, 2-10 mole % of comonomer units, 50-5,000 ppm of a polyacetal oligomer and 3-13 ppm of fluorine, which has excellent flowability and thermal stability.

10 BEST MODE FOR CARRYING OUT THE INVENTION

The polyacetal resin of the present invention is an oxymethylene copolymer containing 0.1-20% by weight of oxyalkylene units each having 2-8 carbon atoms, which is produced from a formaldehyde monomer,
15 its trimer (trioxane) or tetramer (tetraoxane) or the like and a cyclic ether such as ethylene oxide, propylene oxide, epichlorohydrin, 1,3-dioxolane, glycol formal or the like. A polyacetal resin produced from trioxane and 1,3-dioxolane is particularly preferred.

20 In the present invention, the polyacetal oligomer is a low-molecular polymer having a PMMA-reduced number-average molecular weight (M_n) of 5,000 or less as measured at 40°C by gel permeation chromatography (GPC) using two GPC HFIP80M columns,
25 hexafluoroisopropanol (a solvent) and SHODEX RI (a detector).

The polyacetal oligomer is preferably an acetal copolymer containing oxymethylene units as the main constitute and 2-10 mole %, based on the oxymethylene units, of comonomer units. The content of 5 the comonomer units is preferably 2-5 mole %. When the comonomer units content is less than 2 mole %, the polyacetal oligomer tends to be decomposed and generate a formaldehyde gas, and has inferior thermal stability. When the comonomer units content is more than 10 mole 10 %, the resulting polyacetal resin composition has inferior MD resistance and thermal property.

The comonomer is a cyclic ether having an oxyalkylene unit having 2-8 adjacent carbon atoms, and includes, for example, ethylene oxide, 1,3-dioxolane, 15 diethylene glycol formal, 1,4-butanediol formal. The most preferable comonomer is 1,3-dioxolane, which is highly active at a low catalyst amount.

The polyacetal oligomer is formed in producing the polyacetal resin and does not need to be 20 added to the resin separately. However, the oligomer prepared separately can be added to the resin in a determined amount, if necessary.

The amount of the polyacetal oligomer allowed to be present in the polyacetal resin composition is 25 50-5,000 ppm, preferably 100-1,000 ppm, more preferably 300-600 ppm. When the oligomer content is less than 50 ppm, the resulting polyacetal resin composition has no

improved flowability; when the oligomer content is more than 5,000 ppm, the polyacetal resin composition has deteriorated thermal stability.

In the present invention, fluorine may be
5 derived from a fluorine compound (e.g. boron trifluoride) used as a polymerization initiator, or from a fluorine-containing compound added after the production of polyacetal.

The fluorine content of the polyacetal resin
10 composition is determined, for example, by hydrolyzing 5 g of the resin composition sample in 15 g of 1 N hydrochloric acid and measuring the fluorine concentration by the use of a fluorine ion meter (HORIBA N-8F), and is expressed in terms of ppm by
15 weight.

The fluorine content of the polyacetal resin composition is 3-13 ppm, preferably 3-8 ppm. When the fluorine content is less than 3 ppm, the resulting polyacetal resin composition has no improved
20 flowability. When the fluorine content is more than 13 ppm, too large an amount of fluorine invites the decomposition of the polyacetal resin itself during its processing, causing reduction in thermal stability of the resin.

25 The polyacetal resin composition of the present invention can be prepared by any method as long as the acetal oligomer content and fluorine content of the composition are in given ranges.

A polyacetal resin composition having excellent flowability and thermal stability can also be provided by allowing the above-mentioned polyacetal resin composition to contain the following components:

5 (A) at least one member selected from the group consisting of an antioxidant, a polymer or compound containing formaldehyde-reactive nitrogen, a formic acid-capturing agent, a weathering (light-resistant) agent and a releasant (a lubricant),

10 (B) at least one member selected from the group consisting of a reinforcing agent, an electroconductive material, a thermoplastic resin and a thermoplastic elastomer, and/or

 (C) a pigment.

15 The at least one member selected from the group consisting of an antioxidant, a polymer or compound containing formaldehyde-reactive nitrogen, a formic acid-capturing agent, a weathering (light-resistant) agent and a releasant (a lubricant) is used
20 in an amount of 0.1-10 parts by weight per 100 parts by weight of the polyacetal resin. When the amount is less than 0.1 part by weight, no addition effect of the above additives is obtained. When the amount is more than 10 parts by weight, the resulting polyacetal resin
25 composition has remarkably reduced thermal stability.

 Specific examples of each of the additives are mentioned below.

The antioxidant is preferably a hindered phenol antioxidant and includes, for example, n-octadecyl-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)-propionate, n-octadecyl-3-(3'-methyl-5'-tert-butyl-4'-hydroxyphenyl)-propionate, n-tetradecyl-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)-propionate, 1,6-hexanediol-bis-(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, 1,4-butanediol-bis-(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, triethylene glycol-bis-(3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)-propionate), tetrakis-(methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate)methane, 3,9-bis(2-(3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy)-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane, N,N'-bis-3-(3',5'-di-tert-butyl-4-hydroxyphenol)-propionylhexamethylenediamine, N,N'-tetramethylenebis-3-(3'-methyl-5'-tert-butyl-4-hydroxyphenol)propionyl-diamine, N,N'-bis-(3-(3,5-di-tert-butyl-4-hydroxyphenol)propionyl)hydrazine, N-salicyloyl-N'-salicylidenehydrazine, 3-(N-salicyloyl)amino-1,2,4-triazole and N,N'-bis(2-(3-(3,5-dibutyl-4-hydroxyphenyl)propionyloxy)ethyl)oxyamide. These antioxidants can be used singly or in combination of two or more of them. Particularly preferable are triethylene glycol-bis-(3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)-propionate) and tetrakis-(methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate-methane.

The polymer or compound containing formaldehyde-reactive nitrogen includes, for example, (i) a polyamide resin, (ii) a β -alanine polymer containing 1.4-10 milli moles, per g of the polymer, of a primary amide unit, obtained by polymerizing acrylamide or its derivative in the presence of a metal alcoholate, or a β -alanine copolymer containing 1.4-10 milli moles, per g of the copolymer, of a primary amide unit, obtained by polymerizing acrylamide or its derivative with other vinyl monomer in the presence of a metal alcoholate, (iii) a polymer obtained by polymerizing acrylamide or its derivative, or acrylamide or its derivative and other vinyl monomer in the presence of a radical polymerization catalyst, and (iv) an amide compound.

Examples of the polyamide resin (i) are nylon 4-6, nylon 6, nylon 6-6, nylon 6-10, nylon 6-12 and nylon 12 and copolymers thereof, preferably nylon 6/nylon 6-6/nylon 6-10 copolymer and nylon 6/nylon 6-12 copolymer. The β -alanine polymer or β -alanine copolymer (ii) can be produced by the process described in JP-A-63-118328 or JP-A-3-234729. The polymer (iii) can be produced by the process described in JP-A-3-28260. Examples of the amide compound (iv) include those produced from an aliphatic monocarboxylic acid, an aliphatic dicarboxylic acid, an aromatic monocarboxylic acid or an aromatic dicarboxylic acid and an aliphatic monoamine, an aliphatic diamine, an

aromatic monoamine or an aromatic diamine. Preferable specific examples of the amide compound (iv) are stearyl stearic acid amide, stearyl oleic acid amide, ethylenediamine-distearic acid amide, hexamethylene-
5 diamine-distearic acid amide, ethylenediamine-dioleic acid amide, ethylenediamine-dierucic acid amide, xylylenediamine-dierucic acid amide, di(xylylene-diamine-stearic acid amide) and sebacic acid amide. Particularly preferable as the polymer or compound
10 containing formaldehyde-reactive nitrogen are nylon 6-6, a β -alanine copolymer having particle diameters of 10 μm or less, preferably 6 μm or less, ethylenediamine-distearic acid amide and ethylenediamine-dioleic acid amide.

15 The formic acid-capturing agent has a function of neutralizing and capturing the formic acid which accelerates the decomposition of polyacetal.

 The formic acid-capturing agent includes, for example, (i) an amino-substituted triazine, (ii) a
20 cocondensate of an amino-substituted triazine and formaldehyde and (iii) a hydroxide, inorganic acid salt, carboxylate or alkoxide of an alkali metal or an alkaline earth metal.

 Examples of the amino-substituted triazine
25 include guanamine (2,4-diamino-sym-triazine), melamine (2,4,6-triamino-sym-triazine), N-butylmelamine, N-phenylmelamine, N,N-diphenylmelamine, N,N-diallylmelamine, N,N',N''-triphenylmelamine, N-

methyloimelamine, N,N'-dimethyloimelamine, N,N',N''-
trimethyloimelamine, benzoguanamine (2,4-diamino-6-
phenyl-sym-triazine), 2,4-diamino-6-methyl-sym-
triazine, 2,4-diamino-6-butyl-sym-triazine, 2,4-
5 diamino-6-benzyloxy-sym-triazine, 2,4-diamino-6-butoxy-
sym-triazine, 2,4-diamino-6-cyclohexyl-sym-triazine,
2,4-diamino-6-chloro-sym-triazine, 2,4-diamino-6-
mercapto-sym-triazine, 2,4-dioxy-6-amino-sym-triazine,
2-oxy-4,6-diamino-sym-triazine and N,N,N',N'-
10 tetracyanoethylbenzoguanamine.

Examples of the cocondensate of an amino-
substituted triazine and formaldehyde include a
melamine-formaldehyde polycondensate.

Examples of the hydroxide, inorganic acid
15 salt, carboxylate or alkoxide of an alkali metal or an
alkaline earth metal include a hydroxide, carbonate,
phosphate, silicate, borate, carboxylate or alkoxide
of sodium, potassium, magnesium, calcium or barium.

The carboxylic acid of the carboxylate
20 includes a saturated or unsaturated aliphatic
carboxylic acid having 10-36 carbon atoms. The
carboxylic acid may be substituted with a hydroxyl
group(s). The saturated aliphatic carboxylic acid
includes capric acid, lauric acid, myristic acid,
25 palmitic acid, stearic acid, arachic acid, behenic
acid, lignoceric acid, cerotic acid, montanic acid,
melissic acid, ceroplastic acid, etc. The unsaturated
aliphatic carboxylic acid includes undecylenic acid,

oleic acid, elaidic acid, cetoleic acid, erucic acid, brassidic acid, sorbic acid, linolic acid, linoleic acid, linolenic acid, arachidonic acid, propiolic acid, stearolic acid, etc.

5 The alkoxide includes the methoxides, ethoxides, etc. of the above-mentioned metals.

 Preferable of these formic acid-capturing agents are melamine; a melamine-formaldehyde polycondensate, particularly a melamine-formaldehyde
10 polycondensate soluble in hot water; and a calcium carboxylate (e.g. calcium laurate, calcium stearate or calcium behenate), particularly a calcium carboxylate containing 1-50 ppm of calcium ion.

 The weathering (light-resistant) agent is
15 preferably a benzotriazole type substance, an oxalic anilide type substance or a hindered amine type substance. The benzotriazole type substance includes, for example, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-[2'-hydroxy-3,5-di-tert-butyl-phenyl)-
20 benzotriazole, 2-[2'-hydroxy-3,5-diisoamylphenyl)-benzotriazole, 2-[2'-hydroxy-3,5-bis-(α,α -dimethylbenzyl)phenyl]-2H-benzotriazole and 2-(2'-hydroxy-4'-octoxyphenyl)benzotriazole. The oxalic
25 2'-ethyloxalic bisanilide, 2-ethoxy-5-tert-butyl-2'-ethyloxalic bisanilide and 2-ethoxy-3'-dodecyloxalic bisanilide. These substances can be used singly or in combination of two or more of them. The hindered amine

type substance includes 4-acetoxy-2,2,6,6-tetramethylpiperidine, 4-stearoyloxy-2,2,6,6-tetramethylpiperidine, 4-acryloyloxy-2,2,6,6-tetramethylpiperidine, 4-(phenylacetoxy)-2,2,6,6-tetramethylpiperidine, 4-benzoyloxy-2,2,6,6-tetramethylpiperidine, 4-methoxy-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, 4-cyclohexyloxy-2,2,6,6-tetramethylpiperidine, 4-benzyloxy-2,2,6,6-tetramethylpiperidine, 4-phenoxy-2,2,6,6-tetramethylpiperidine, 4-(ethylcarbamoyloxy)-2,2,6,6-tetramethylpiperidine, 4-(cyclohexylcarbamoyloxy)-2,2,6,6-tetramethylpiperidine, 4-(phenylcarbamoyloxy)-2,2,6,6-tetramethylpiperidine, bis(2,2,6,6-tetramethyl-4-piperidyl)carbonate, bis(2,2,6,6-tetramethyl-4-piperidyl)oxalate, bis(2,2,6,6-tetramethyl-4-piperidyl)malonate, bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)adipate, bis(2,2,6,6-tetramethyl-4-piperidyl)terephthalate, 1,2-bis(2,2,6,6-tetramethyl-4-piperidyloxy)ethane, α,α' -bis(2,2,6,6-tetramethyl-4-piperidyloxy)-p-xylene, bis(2,2,6,6-tetramethyl-4-piperidyl)tolyene-2,4-dicarbamate, bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylene-1,6-dicarbamate, tris(2,2,6,6-tetramethyl-4-piperidyl)benzene-1,3,5-tricarboxylate, tris(2,2,6,6-tetramethyl-4-piperidyl)benzene-1,3,4-tricarboxylate, etc. These

hindered amine type substances can be used singly or in combination of two or more of them. The use of the benzotriazole type substance or the oxalic anilide type substance in combination with the hindered amine type
5 substance is preferable.

The releasant (lubricant) includes an alcohol, a fatty acid, a fatty acid ester, a polyoxyalkylene glycol, an olefin compound having an average polymerization degree of 10-500 and a silicone
10 oil.

As the alcohol, a monohydric alcohol or a polyhydric alcohol is used.

Examples of the monohydric alcohol include octyl alcohol, capryl alcohol, nonyl alcohol, decyl
15 alcohol, undecyl alcohol, lauryl alcohol, tridecyl alcohol, myristyl alcohol, pentadecyl alcohol, cetyl alcohol, heptadecyl alcohol, stearyl alcohol, oleyl alcohol, nonadecyl alcohol, eicosyl alcohol, behenyl alcohol, ceryl alcohol, melissyl alcohol, 2-hexyl-
20 decanol, 2-isoheptylisoundecanol, 2-octyldodecanol, 2-decyltetradecanol, and 2-latylstearinalcohol.

As the polyhydric alcohol, a polyhydric alcohol having 2-6 carbon atoms is used. Examples thereof are ethylene glycol, diethylene glycol,
25 triethylene glycol, propylene glycol, dipropylene glycol, butanediol, pentanediol, hexanediol, glycerine,

diglycerine, triglycerine, threitol, erythritol, pentaerythritol, arabitol, ribitol, xylitol, sorbitan, sorbitol and mannitol. At least one polyhydric alcohol selected from them is used.

5 The fatty acid includes capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, 12-hydroxystearic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, melissic acid, ceroplastic acid, etc. The fatty acid includes
10 unsaturated aliphatic carboxylic acids, and examples thereof are undecylenic acid, oleic acid, elaidic acid, cetoleic acid, erucic acid, brassidic acid, sorbic acid, linolic acid, linolenic acid, arachidonic acid, propiolic acid, stearolic acid and natural fatty acids
15 containing the above acids or mixtures thereof. These fatty acids may be substituted with a hydroxyl group(s).

 As the fatty acid ester, an ester of the above fatty acid is used. Preferable fatty acid esters
20 are those obtained from a fatty acid selected from palmitic acid, stearic acid, behenic acid and montanic acid and a polyhydric alcohol selected from glycerine, pentaerythritol, sorbitan and sorbitol. These fatty acid esters may or may not have a hydroxyl group(s).
25 That is, these fatty acid esters may be monoesters or diesters or triesters. The remaining hydroxyl group(s) may be blocked with boric acid or the like. Preferable

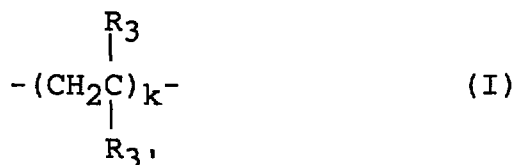
examples of the fatty acid ester are glycerine
monopalmitate, glycerine dipalmitate, glycerine
tripalmitate, glycerine monostearate, glycerine
distearate, glycerine tristearate, glycerine
5 monobehenate, glycerine dibehenate, glycerine
tribehenate, glycerine monomontanate, glycerine
dimontanate, glycerine trimontanate, pentaerythritol
monopalmitate, pentaerythritol dipalmitate,
pentaerythritol tripalmitate, pentaerythritol
10 tetrapalmitate, pentaerythritol monostearate,
pentaerythritol distearate, pentaerythritol
tristearate, pentaerythritol tetrastearate,
pentaerythritol monobehenate, pentaerythritol
dibehenate, pentaerythritol tribehenate,
15 pentaerythritol tetrabehenate, pentaerythritol
monomontanate, pentaerythritol dimontanate,
pentaerythritol trimontanate, pentaerythritol
tetramontanate, sorbitan monopalmitate, sorbitan
dipalmitate, sorbitan tripalmitate, sorbitan
20 monostearate, sorbitan distearate, sorbitan
tristearate, sorbitan monobehenate, sorbitan
dibehenate, sorbitan tribehenate, sorbitan
monomontanate, sorbitan dimontanate, sorbitan
trimontanate, sorbitol monopalmitate, sorbitol
25 dipalmitate, sorbitol tripalmitate, sorbitol
monostearate, sorbitol distearate, sorbitol
tristearate, sorbitol monobehenate, sorbitol
dibehenate, sorbitol tribehenate, sorbitol

monomontanate, sorbitol dimontanate and sorbitol trimontanate. The fatty acid ester whose hydroxyl group(s) is (are) blocked with boric acid or the like includes a boric acid ester of a glycerine-fatty acid ester disclosed in JP-A-49-60762. These fatty acid esters can be used singly or in combination of two or more of them.

As the polyoxyalkylene glycol, there are a first group compound, a second group compound and a third group compound. The first group compound is a polycondensate of an alkylene glycol monomer and includes, for example, polyethylene glycol, polypropylene glycol, polyethylene glycol and polypropylene glycol. The polymerization degree of the first group compound is preferably 5-1,000, more preferably 10-500. The second group compound of the polyoxyalkylene glycol is an ether formed between the first group compound and an aliphatic alcohol and includes, for example, polyethylene glycol oleyl ether (the number of ethylene oxide polymerized: 5-50), polyethylene glycol cetyl ether (the number of ethylene oxide polymerized: 5-20), polyethylene glycol stearyl ether (the number of ethylene oxide polymerized: 5-30), polyethylene glycol lauryl ether (the number of ethylene oxide polymerized: 5-30), polyethylene glycol tridecyl ether (the number of ethylene oxide polymerized: 5-30), polyethylene glycol nonylphenyl

ether (the number of ethylene oxide polymerized: 2-100) and polyethylene glycol octylphenyl ether (the number of ethylene oxide polymerized: 4-50). The third group compound of the polyoxyalkylene glycol is an ester
5 formed between a polyoxyalkylene glycol as the first group compound and a higher fatty acid and includes, for example, polyethylene glycol monolaurate (the number of ethylene oxide polymerized: 2-30), polyethylene glycol monostearate (the number of
10 ethylene oxide polymerized: 2-50) and polyethylene glycol monooleate (the number of ethylene oxide polymerized: 2-10). Of three polyoxyalkylene glycols, the first group compound is preferred.

The olefin compound having an average
15 polymerization degree of 10-500 is an olefin compound constituted by at least one kind of the olefin units represented by the following general formula:



wherein R_3 and R_3 are each selected from the group consisting of a hydrogen atom, an alkyl group, an aryl
20 group and an ether group and may be the same or different, and k is an integer of 10-500. The alkyl group includes, for example, an ethyl group, a propyl

group, a butyl group, a hexyl group, an octyl group, a decyl group, a lauryl group, a cetyl group and a stearyl group. The aryl group includes, for example, a phenyl group, a p-nonylphenyl group, a benzyl group, a p-octylphenyl group, a p-nonylphenyl group, a benzyl group, a p-butylbenzyl group, a tolyl group and a xylyl group. The ether group includes, for example, an ethyl ether group, a propyl ether group and a butyl ether group.

10 The preferable olefin units are those olefin units represented by the following formulas (II) to (IV):

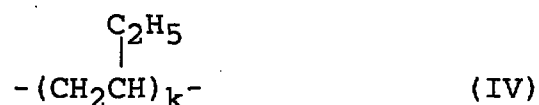
polyethylene unit



polypropylene unit



15 hydrogenated 1,2-polybutadiene unit



wherein k is an integer of 10-500.

The olefin compound usable in the present invention may be a compound constituted by one kind of the above-mentioned olefin units, or a compound

constituted by two or more kinds of said olefin units. The olefin compound may be constituted, for example, by polyethylene units and polypropylene units. Olefin compounds having a block copolymer structure or a graft
5 copolymer structure are also included in the olefin compound according to the present invention.

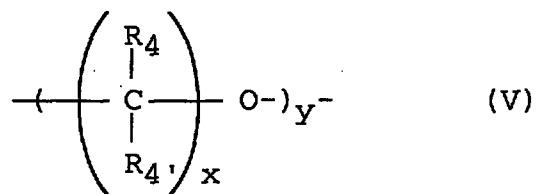
As to the structure of the olefin compound, a linear structure is preferred rather than a graft copolymer structure. The monomer constituting the
10 olefin compound includes, for example, olefin monomers such as ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, 2-methyl-1-butene, 3-methyl-1-butene, 2,3-dimethyl-2-butene, 1-hexene, 1-heptene, 1-octene, 1-nonene and 1-decene, etc. and
15 diolefin monomers such as allene, methylallene, butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,5-hexadiene, etc.

The olefin compound used in the present invention may be a compound obtained by copolymerizing
20 two or more of these olefin monomers and diolefin monomers.

When the olefin compound is a compound obtained by polymerizing a diolefin monomer, it is preferable to reduce the carbon-carbon unsaturated
25 bonds of the compound as low as possible by an ordinary hydrogenation method before using it in the present polyacetal resin composition, so that the composition can have improved thermal stability.

The average polymerization degree k of the olefin units constituting the olefin compound is 10-500, preferably 15-300, more preferably 20-100. When k is smaller than 10, the long-term lubricity of the resulting polyacetal resin composition is reduced, the moldability of the composition is adversely affected; and the mold is easily stained. When k is larger than 500, the initial lubricity of the composition is greatly reduced.

As a preferable olefin compound, an ether group-modified olefin compound may be used. The ether group mentioned herein is constituted by a polyalkylene oxide unit represented by the following general formula (V):



wherein R_4 and $R_{4'}$, which may be the same or different, may be bonded to the same carbon atom or the different carbon atoms and are each selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group; x is an integer of 2-6 and y is an integer of 1-1,000. The polyalkylene oxide unit constituting the ether group is preferably the same as the polyalkylene oxide unit constituting one end of the

polyacetal resin molecule of the present resin composition, in view of the sliding property of the composition.

The silicone oil usable in the present invention is dimethylpolysiloxane or a dimethyl polysiloxane derivative in which the methyl groups of dimethylpolysiloxane are partially replaced by at least one selected from the group consisting of hydrogen, a phenyl group, a halogenated phenyl group, a halogenated alkyl groups and the like. These polysiloxanes are silicone oils with no intermolecular cross-linking structure. These silicone oils can be used singly or in combination of two or more of them. Preferred as the silicone oil are dimethylpolysiloxane or a copolymer of dimethylsiloxane with methylphenylsiloxane, the both having an average polymerization degree of 1,000-5,000. The average polymerization degree is more preferably 3,000-5,000. The above copolymer preferably contains 1-20 mole % of a methylphenylsiloxane unit.

The one member selected from the group consisting of an reinforcing agent, an electroconductive material, a thermoplastic resin and a thermoplastic elastomer, usable in the present invention is used in an amount of 0.1-60 parts by weight per 100 parts by weight of the above-mentioned polyacetal resin composition. When the amount is less than 0.1 part by

weight, no addition effect of the member is obtained. When the amount is more than 60 parts by weight, the properties inherently possessed by the polyacetal resin are reduced and its thermal stability is lowered. Each
5 member constituting the above group is described by citing the specific examples.

The reinforcing agent includes an inorganic filler, a glass fiber, glass beads and a carbon fiber.

The inorganic filler includes talc, mica,
10 wollastonite, asbestos, clay, bentonite, diatomaceous earth, a ceramic fiber, rock wool, etc. Talc and wollastonite are particularly preferred.

The inorganic filler, the glass fiber, the glass beads and the carbon fiber has been preferably
15 subjected to a surface treatment with an emulsion of a silane coupling agent-containing polyurethane. The silane coupling agent is preferably an aminoalkylsilane such as γ -aminopropyltrimethoxysilane, γ -aminopropyltriethoxysilane, γ -(N-aminoethyl)aminobutyl-
20 triethoxysilane, γ -(N-methylethyl(N-aminoethyl)aminoiminobutyltriethoxysilane, bis- γ -N-propyldiethylaminopropyldimethoxysilane, bis- β -(N-aminoethyl)diethoxysilane, β -N-ethylaminoethyltrimethoxysilane, γ -propyl(N-aminoethyl)aminotri-
25 methoxysilane, β -N-ethylaminoethyltri- β -methoxyethoxysilane or the like.

The isocyanate compound constituting the urethane of the polyurethane emulsion is preferably a

non-yellowing diisocyanate such as hexamethylene diisocyanate, lysine diisocyanate, hydrated 2,4-toluylene diisocyanate, hydrated 4,4-diphenylmethane diisocyanate, dicyclohexyldimethylmethane, p,p'-
5 diisocyanate, diethylfumarate diisocyanate, isophorone diisocyanate, hydrated xylylene diisocyanate or the like; or an aromatic polyisocyanate such as 2,4-toluylene diisocyanate, 4,4'-diphenylmethane diisocyanate, xylylene isocyanate, p-phenylmethane
10 isocyanate, naphthalene-1,5-diisocyanate, triphenylmethane triisocyanate, polymethylene polyphenyl isocyanate or the like.

The polyhydroxy compound constituting the urethane of the polyurethane emulsion includes a
15 polyester obtained from a carboxylic acid (e.g. adipic acid, sebacic acid, maleic acid or dimer acid) and a hydroxy compound (e.g. ethylene glycol, propylene glycol, butylene glycol or trimethylolpropane); a polyol in which an alkylene oxide (e.g. ethylene oxide,
20 propylene oxide or tetrahydrofuran) is added to a diol formed by the ring opening of the above alkylene oxide or to a polyhydric alcohol (e.g. glycerine, neopentyl glycol, trimethylolpropane or sorbitol); and an unsubstituted polyol such as ethylene glycol, propylene
25 glycol, butylene glycol, hexamethylene glycol, trimethylolpropane, trimethylolethane, glycerine, 1,2,6-hexanetriol, pentaerythritol or the like.

As the electroconductive material, an carbon black, a metal powder or a metal fiber is used. The electroconductive carbon black is preferably one having small particle diameters or one having a large surface area and a well-developed chain structure, more preferably one having a dibutyl phthalate (hereinafter referred to as DBP) absorption of 200 ml/100 g or more. Such a carbon black includes, for example, Toka Black #4500 (DBP absorption: 230 ml/100 g, a product of Tokai Carbon Co., Ltd.), #450 #3750 (DBP absorption: 245 ml/100 g, a product of Mitsubishi Chemical Industries, Ltd.), ketzen Black EC (DBP absorption: 480 ml/100 g, a product of Lion-Akzo Co., Ltd.) and Brintex XE2 (DBP absorption: 370 ml/100 g, a product of Degussa). The metal used in the metal powder or the metal fiber is iron, nickel, copper, silver, stainless steel or the like.

The thermoplastic resin includes a polyolefin resin, an acrylic resin, a styrene resin, a polycarbonate resin, an uncured epoxy resin, etc.

The polyolefin resin includes a polyolefin, an olefin-vinyl compound copolymer, and their modification products. The polyolefin includes, for example, a high-density polyethylene, low-density polyethylene, polypropylene, polybutene-1 and poly-4-methylpentene-1. The olefin-vinyl compound copolymer includes, for example, a copolymer between an olefin

such as ethylene, propylene, butene or the like and a vinyl compound such as vinyl acetate, vinyl formate, methyl acrylate, butyl methacrylate, acrylonitrile, butyl vinyl ether, isobutyl vinyl ether or the like.

- 5 The modification products refer to those polymers obtained by reacting the above polyolefin resin with a reagent such as peroxide or the like to allow the polyolefin resin to have a polar group such as carboxyl group or the like added thereto. They, for example,
- 10 include polyolefin resins having added thereto an unsaturated organic acid such as maleic acid, itaconic acid, acrylic acid, methacrylic acid or the like; an anhydride of unsaturated organic acid such as maleic anhydride, itaconic anhydride, citraconic anhydride or
- 15 the like; an ester of unsaturated organic acid such as monomethyl maleate, methyl acrylate or the like; an amide of unsaturated organic acid such as fumaric monoamide, acrylic amide or the like; an imide of unsaturated organic acid such as itaconic imide or the
- 20 like; polystyrene; a styrene copolymer; polymethylmethacrylate. Among them, low-density polyethylene having grafted thereon polystyrene or a styrene-acrylonitrile copolymer is particularly preferred.

As the acrylic resin, any of an methacrylic acid ester homopolymer and a methacrylic acid ester

25 copolymer can be used. A homopolymer of an alkyl methacrylate having 1-6 alkyl group carbon atoms is

preferred and a polymethyl methacrylate is particularly preferred. As the methacrylic acid ester copolymer, there can be used a copolymer obtained by copolymerizing two or more alkyl methacrylates having 1-6 alkyl group carbon atoms, particularly a copolymer between methyl methacrylate and an alkyl methacrylate having 2-6 alkyl group carbon atoms or a copolymer between methyl methacrylate and an alkyl acrylate having 1-6 alkyl group carbon atoms. As the acrylic resin, there can also be used a graft copolymer obtained by graft-polymerizing, onto a homopolymer or a random or block copolymer both of an alkyl methacrylate having 1-6 alkyl group carbon atoms, an alkyl methacrylate or acrylate having 1-6 alkyl group carbon atoms, preferably an alkyl acrylate having 1-6 alkyl group carbon atoms. A particularly preferable graft copolymer is one obtained by graft-polymerizing an alkyl methacrylate having 2-6 alkyl group carbon atoms or an alkyl acrylate having 1-6 alkyl group carbon groups, onto the main chain of polymethyl methacrylate, a random or block copolymer between methyl methacrylate and an alkyl acrylate having 2-6 alkyl group carbon atoms, or a random or block copolymer between methyl methacrylate and an alkyl acrylate having 1-6 alkyl group carbon atoms. The acrylic resin further includes a multi-phase polymer consisting of a rubbery core and a methacrylic acid ester polymer shell. The monomer

units constituting the rubbery core include conjugated dienes such as butadiene, isoprene, chloroprene and the like; and alkyl acrylates having 2-8 alkyl group carbon atoms, such as ethyl acrylate, propyl acrylate, butyl
5 acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate and the like. These monomers can be used singly or in combination of two or more of them.

The styrene resin includes polystyrene, poly(α -methylstyrene), a styrene and/or α -methyl-
10 styrene-acrylonitrile copolymer, a styrene and/or α -methylstyrene-acrylonitrile-butadiene terpolymer or tetrapolymer, etc.

The polycarbonate resin is derived from an aromatic dihydric phenol, an alicyclic or aliphatic
15 hydrocarbon having two hydroxyl groups in the molecule, or a mixture thereof. The aromatic dihydric phenol includes, for example, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, 2,2-bis(3-bromo-4-hydroxyphenyl)propane, 4,4'-dihydroxydiphenyl
20 ether and 4,4'-dihydroxydiphenyl sulfide. The alicyclic hydrocarbon having two hydroxyl groups in the molecule includes, for example, 2,2-bis(4-hydroxycyclohexyl)propane, 2,2-bis(4-hydroxy-3,5-dibromocyclohexyl)propane, 2,2-bis(4-hydroxycyclo-
25 hexyl)butane, 4,4'-dihydroxydicyclohexyl ether and 4,4'-dihydroxydicyclohexyl sulfide. The aliphatic hydrocarbon having two hydroxyl groups in the molecule

includes, for example, 1,3-propanediol, 1,4-butanediol and 1,6-hexanediol.

The polycarbonate resin can be obtained by reacting one of the above compound(s) with phosgene or
5 diphenyl carbonate.

As the uncured epoxy resin, a mono- or polyfunctional glycidyl derivative is used preferably. Examples thereof are 2-ethylhexyl glycidyl ether, 2-methyloctyl glycidyl ether, lauryl glycidyl ether,
10 stearyl glycidyl ether, behenyl glycidyl ether, ethylene glycidyl ether, polyethylene glycidyl ether (the number of ethylene oxide units: 2-30), propylene glycol diglycidyl ether, polyethylene glycidyl ether (the number of propylene oxide units: 2-30), neopentyl
15 glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerine diglycidyl ether, glycerine triglycidyl ether, bisphenol A diglycidyl ether, sorbitan monoester diglycidyl ether, pentaerythritol triglycidyl ether, pentaerythritol tetraglycidyl ether,
20 diglycerine tetraglycidyl ether and a condensate of cresol novolac and epichlorohydrin (epoxy equivalents: 100-400, softening point: 20-150°C).

The thermoplastic elastomer is used to improve impact resistance (e.g. Izod impact strength)
25 and includes a polyurethane elastomer, a polyester elastomer, a polystyrene elastomer and a polyamide elastomer.

The polyurethane elastomer includes those obtained by combining a urethane as hard segment obtained by reacting a diisocyanate (e.g. 4,4'-diphenylmethane diisocyanate or 4,4'-dicyclohexylmethane diisocyanate) with a glycol (e.g. ethylene glycol or tetramethylene glycol) and, as a soft segment, a polyester diol (e.g. polyethylene adipate or polybutylene adipate) or a polyether diol (e.g. polypropylene glycol or polytetramethylene glycol). Of these polyurethane elastomers, particularly preferable is a polyurethane synthesized from 4,4'-diphenylmethane diisocyanate, tetramethylene glycol and polytetramethylene glycol.

The polyester elastomer includes those obtained by combining polyester as hard segment, such as polyethylene terephthalate, polybutylene terephthalate, modified polyethylene terephthalate, polyethylene-butylene terephthalate or the like and a polyether as soft segment, such as polypropylene glycol, polytetramethylene glycol or the like. Of these polyester elastomers, particularly preferable are a polybutylene terephthalate-polytetramethylene glycol block copolymer and a polyethylene-butylene terephthalate-polytetramethylene glycol block copolymer.

The polystyrene elastomer includes those obtained by combining a polystyrene as hard segment

and, as a soft segment, a diene polymer (e.g. polybutadiene or polyisoprene) or a hydrogenated diene polymer (e.g. hydrogenated polybutadiene or hydrogenated polyisoprene). Of these polystyrene
5 elastomers, particularly preferable are a polystyrene-polybutadiene block copolymer and a polystyrene-hydrogenated polybutadiene block copolymer.

The polyamide elastomer includes those obtained by combining a polyamide as hard segment, such
10 as nylon 6, nylon 6-6, nylon 6-10, nylon 11, nylon 12 or the like and, as a soft segment, a polyether (e.g. polypropylene glycol or polytetramethylene glycol) or a polyester (e.g. polyethylene adipate or polybutylene succinate). Of these polyamide elastomers,
15 particularly preferable are a nylon 6-polypropylene glycol block copolymer and a nylon 6-polytetramethylene glycol block copolymer.

The pigment usable in the present invention is used in an amount of 0.01-5 parts by weight per 100
20 parts by weight of the above-mentioned polyacetal resin composition. When the amount is more than 5 parts by weight, the resulting polyacetal resin composition has remarkably deteriorated thermal stability. The pigment includes an inorganic pigment and an organic pigment.
25 The inorganic pigment refers to one generally used for coloring of resins and includes, for example, zinc sulfide, zinc oxide, titanium oxide, barium sulfate,

titan yellow, iron oxide, ultramarine, cobalt blue, a sintered pigment, a carbonic acid salt, a phosphoric acid salt, an acetic acid salt, carbon black, acetylene black and lamp black. The organic pigment includes
5 pigments of condensed azo type, isoindoline type, diazo type, monoazo type, anthraquinone type, heterocyclic type, perynone type, quinacridone type, thioindigo type, perylene type, dioxazine type, phthalocyanine type, etc.

10 The polyacetal resin composition of the present invention may contain other additives such as nucleating agent, thermosetting resin and the like in such amounts as not to impair the intended effects of the present invention.

15 The present resin composition can be molded by a method such as hot-runner molding or the like, in which a resin to be molded is required to have high thermal resistance, and is suitable for use in tape recorder, video tape recorder (VTR), keyboard switch,
20 gear, cam, roller, side board, cam gear, key system, chassis, switch board, etc. The present resin composition is particularly suitable for use in outsert or insert molding and gas injection molding, in which precise dimension and excellent dimensional stability
25 are required.

 The present invention is hereinafter described in more detail by way of Examples and

Comparative Examples. However, the present invention is not restricted thereto.

In the followings, % and ppm are by weight in all cases.

5 The terms and measurement methods used in Examples are as follows.

Polyacetal oligomer content

Ten grams of a polyacetal resin composition sample was placed in an autoclave. Thereto was added
10 100 ml of a 15% aqueous methanol solution adjusted to pH 10 with ammonia water. The mixture was subjected to an extraction treatment at 120°C for 4 hours. When the mixture temperature decreased to 100-80°C, the mixture was filtered to remove the solid polymer. The filtrate
15 was allowed to stand at room temperature (10-30°C) for 24-48 hours. The resulting white precipitate was collected by centrifugation and weighed, and the weight was converted into ppm by weight. In Examples, each acetal oligomer was measured for number-average
20 molecular weight Mn at 40°C by GPC using two HFIP80M columns, hexafluoroisopropanol as a solvent and SHODEX RI as a detector, and their Mns (PMMA-reduced) were as low as 5,000 or less.

Comonomer content of polyacetal oligomer

25 A polyacetal oligomer was measured for proton NMR spectrum by the method described in JP-A-6-34583

(Asahi Chemical Industry Co., Ltd.). The comonomer content of the polyacetal oligomer was quantitatively determined from the observed peak area of the predetermined signal, and expressed as molar ratio of ethylene oxide units to methylene oxide units.

Fluorine content

Five grams of a polyacetal resin composition sample was hydrolyzed in 15 g of 1 N hydrochloric acid, and the fluorine content was measured by the use of a fluorine ion meter (HORIBA N-8F) and expressed by ppm by weight.

Flowability

Each sample having a composition shown in Table 1 was molded by the use of a molding machine using a spiral die of 1 mm (thickness) and 6 mm (width), under the following molding conditions, to measure the length of the sample filled. The flowability of the sample was expressed by the flow length (mm).

Molding conditions:

Cylinder temperature: 200°C

Injection pressure: 980 kgf/cm²

Die temperature: 80°C

Thermal stability

An obtained sample was molded into a test

piece by the use of a 3-ounce molding machine whose cylinder temperature was set at 220°C. In this molding, there was measured a maximum residence time (min) until silver streak(s) began to appear on the test piece surface.

Examples 1-6 (present invention) and Example 8 (comparison)

A 5-liter kneader having two blades, provided with a jacket through which a heat medium could be passed, was kept at 65-90°C. Thereinto were fed 2 kg of trioxane, 1.14 ml of methylal (a molecular weight modifier) and 75 g of 1,3-oxolane (a comonomer). To the mixture was added 8.0×10^{-6} to 2.0×10^{-5} mole, per mole of the mixture, of boron trifluoride-diethyl ether, and polymerization was started. In the polymerization, the inflow of water and oxygen present in the atmosphere was minimized. Twenty minutes later, methylal was added in an amount of 1,000 parts by weight per 100 parts by weight of the obtained polymer (polyacetal resin), to conduct stirring and washing at 20-60°C. Thereafter, the contents in the kneader were washed with acetone, followed by drying, to prepare samples of different oligomer contents and different fluorine contents. To each sample as base polymer were added, as additives, 0.3 part by weight of triethylene glycol-bis-(3-tert-butyl-5-methyl-4-hydroxyphenyl)-

propionate, 0.1 part by weight of a β -alanine copolymer, 0.2 part by weight of calcium stearate containing 15 ppm pf calcium ion, and 0.5 part by weight of glycerine monostearate. Each of the resulting
5 resin compositions was subjected to granulation using a twin-screw extruder and measured for flowability and thermal stability. The results are shown in Table 1.

Example 7 (present invention) and Example 9
(comparison)

10 To the base polymer of Example 5 (present invention) was added the oligomer having a molecular weight Mn of 4,700, obtained from the measurement of acetal oligomer content, and the mixture was used as a new base polymer. To each of these new base polymers
15 were added the same additives as in Example 1 (present invention). Each of the resulting resin compositions were subjected to granulation and measured in the same manner as in Example 1. The results are shown in Table 1.

20 Examples 10 and 11 (comparison)

Polymerization was conducted in the same manner as in Example 1 (present invention) except that the amount of the comonomer 1,3-dioxolane was changed to 18 g (Example 10) or 280 g (Example 11). To each of
25 the resulting base polymers were added the same

additives as in Example 1. Each of the resulting resin compositions were subjected to granulation and measured in the same manner as in Example 1. The results are shown in Table 1.

5 Example 12 (comparison)

Polymerization was conducted in the same manner as in Example 1 except that the amount of boron trifluoride-diethyl ether was changed to 4.0×10^{-6} mole. To the resulting base polymer were added the
10 same additives as in Example 1. The resulting resin composition was subjected to granulation and measured in the same manner as in Example 1. The results are shown in Table 1.

Example 13 (comparison)

15 Polymerization was conducted in the same manner as in Example 1 except that the comonomer was changed to ethylene oxide and the amount of boron trifluoride-diethyl ether complex was changed to 8.0×10^{-5} mole. To the resulting base polymer were added
20 the same additives as in Example 1. The resulting resin composition was subjected to granulation and measured in the same manner as in Example 1. The results are shown in Table 1.

Example 14 (comparison)

25 To the base polymer of Example 6 was added

the oligomer obtained from the measurement of polyacetal oligomer content, and each of the resulting mixture was used as a new base polymer. Then, the same measurements as in Example 1 were conducted. The
5 results are shown in Table 1.

Examples 15-47

To the base polymer of Example 1 (present invention), Example 8 (comparison) or Example 14 (comparison) were added the same additives as in
10 Example 1. Thereto was (were) added a compounding agent(s) shown in Table 2. Each of the resulting resin compositions was subjected to granulation and measured in the same manner as in Example 1. The results are shown in Table 2.

Table 1

	Base polymer					Flow-ability (mm)	Thermal stability (min)
	Oligomer		Fluorine content (ppm)				
	Content (ppm)	Content of comonomer units (mole %)					
Example 1 (present invention)	580	2.7	6.0	175	145		
" 2 (")	350	2.8	4.0	170	140		
" 3 (")	580	2.6	3.5	172	135		
" 4 (")	340	2.7	7.8	178	132		
" 5 (")	450	2.8	5.5	175	135		
" 6 (")	1000	2.7	9.0	160	120		
" 7 (")	1000	2.8	5.5	170	130		
" 8 (comparison)	45	2.7	2.0	110	140		
" 9 (")	6200	2.8	5.5	175	90		
" 10 (")	520	0.6	7.0	165	115		
" 11 (")	530	11.0	11.0	172	110		
" 12 (")	530	2.8	2.5	115	135		
" 13 (")	1100	2.7	19.0	175	60		
" 14 (")	7300	2.7	19.0	174	60		

Table 2

	Base polymer	Compounding agent(s)	Flow-ability (mm)	Thermal stability (min)
Example 15 (present invention)	Polymer of Example 1 (present invention)	2-[2'-Hydroxy-3,5-bis (α,α' -dimethylbenzyl)- phenyl]-2H-benzotriazole 1.0 part by weight Bis(2,2,6,6-tetramethyl- 4-piperidyl)sebacate 0.5 part by weight	180	140
Example 16 (comparison)	Polymer of Example 8 (comparison)		110	130
Example 17 (comparison)	Polymer of Example 14 (comparison)		180	55
Example 18 (present invention)	Polymer of Example 1 (present invention)	Low-density polyethylene (MI:5) 3 parts by weight Melamine 0.5 part by weight Polyethylene glycol (M.W.: 2,000) 1 part by weight	170	140
Example 19 (comparison)	Polymer of Example 8 (comparison)		100	125
Example 20 (comparison)	Polymer of Example 14 (comparison)		175	50

(cont'd)

Table 2 (Cont'd)

	Base polymer	Compounding agent(s)	Flow-ability (mm)	Thermal stability (min)
Example 21 (present invention)	Polymer of Example 1 (present invention)	Low-density polyethylene-g-polystyrene 5 parts by weight Behenic acid monoglyceride 2 parts by weight	170	135
Example 22 (present invention)	Polymer of Example 8 (comparison)		100	115
Example 23 (present invention)	Polymer of Example 14 (comparison)		175	55
Example 24 (present invention)	Polymer of Example 1 (present invention)	Multi-phase acrylic polymer 20 parts by weight Core: butadiene/ethyl acrylate = 7/3 Shell: methyl methacrylate Core/shell: 6/4	100	125
Example 25 (comparison)	Polymer of Example 8 (comparison)		50	105
Example 26 (comparison)	Polymer of Example 14 (comparison)		100	30

(cont'd)

Table 2 (Cont'd)

	Base polymer	Compounding agent(s)	Flow-ability (mm)	Thermal stability (min)
Example 27 (present invention)	Polymer of Example 1 (present invention)	Polyurethane emulsion Sizing glass fiber 35 parts by weight	45	135
Example 28 (comparison)	Polymer of Example 8 (comparison)		20	120
Example 29 (comparison)	Polymer of Example 14 (comparison)		45	40
Example 30 (present invention)	Polymer of Example 1 (present invention)	ABS resin Styrac IM-15 (a product of Asahi Chemical Industry Co., Ltd.) 20 parts by weight	125	130
Example 31 (comparison)	Polymer of Example 8 (comparison)		70	110
Example 32 (comparison)	Polymer of Example 14 (comparison)		120	40

(cont'd)

Table 2 (Cont'd)

	Base polymer	Compounding agent(s)	Flow-ability (mm)	Thermal stability (min)
Example 33 (present invention)	Polymer of Example 1 (present invention)	Hydrogenated styrene elastomer Tuftec H1052 (a product of Asahi Chemical Industry Co., Ltd.) 30 parts by weight	100	130
Example 34 (comparison)	Polymer of Example 8 (comparison)		60	115
Example 35 (comparison)	Polymer of Example 14 (comparison)		100	55
Example 36 (present invention)	Polymer of Example 1 (present invention)	Polycarbonate resin Iupilon S-2000 (a product of Mitsubishi Gas Chemical Company, Inc.) 10 parts by weight	120	135
Example 37 (comparison)	Polymer of Example 8 (comparison)		65	115
Example 38 (comparison)	Polymer of Example 14 (comparison)		120	50

(cont'd)

Table 2 (Cont'd)

	Base polymer	Compounding agent(s)	Flow-ability (mm)	Thermal stability (min)
Example 39 (present invention)	Polymer of Example 1 (present invention)	Talc 10 parts by weight	110	125
Example 40 (comparison)	Polymer of Example 8 (comparison)		60	105
Example 41 (comparison)	Polymer of Example 14 (comparison)		105	30
Example 42 (present invention)	Polymer of Example 1 (present invention)	Ketzen black EC (a product of Lion-Akzo Co., Ltd.) 5 parts by weight Epoxy resin (AER ECN-200, a product of Asahi Chemical Industry Co., Ltd.) 2 parts by weight	150	125
Example 43 (comparison)	Polymer of Example 8 (comparison)		90	105
Example 44 (comparison)	Polymer of Example 14 (comparison)		145	45

(cont'd)

Table 2 (Cont'd)

	Base polymer	Compounding agent (s)	Flow-ability (mm)	Thermal stability (min)
Example 45 (present invention)	Polymer of Example 1 (present invention)	Ethylene-propylene copolymer 5 parts by weight Ethylene polymerization degree: 60 Propylene polymerization degree: 60	185	140
Example 46 (comparison)	Polymer of Example 8 (comparison)		110	130
Example 47 (comparison)	Polymer of Example 14 (comparison)		185	70



CLAIMS

1. A polyacetal resin composition comprising oxymethylene units as the main constitute, 2-10 mol% of comonomer units, 50-5,000 ppm of a polyacetal oligomer
5 and 3-13 ppm of fluorine.
2. A polyacetal resin composition according to Claim 1, wherein the fluorine content is 3-8 ppm.
3. A polyacetal resin composition comprising:
100 parts by weight of a polyacetal resin
10 composition according to Claim 1,
0.1-10 parts by weight of (A) at least one member selected from the group consisting of an antioxidant, a polymer or compound containing formaldehyde-reactive nitrogen, a formic acid-capturing
15 agent, a weathering stabilizer and a releasent,
0.1-60 parts by weight of (B) at least one member selected from the group consisting of a reinforcing agent, an electroconductive material, a thermoplastic resin and a thermoplastic elastomer, and/
20 or
0.001-5 parts by weight of (C) a pigment.
4. A polyacetal resin composition according to Claim 3, wherein the antioxidant comprises at least one hindered phenol antioxidant.
- 25 5. A polyacetal resin composition according to Claim 3, wherein the polymer or compound containing formaldehyde-reactive nitrogen is at least one member selected from the group consisting of a polyamide



resin, polyacrylamide or a derivative thereof, a copolymer of acrylamide and other vinyl monomer, and an amide compound.

6. A polyacetal resin composition according to
5 Claim 3, wherein the formic acid-capturing agent is at least one member selected from the group consisting of an amino-substituted triazine, a polycondensate of an amino-substituted triazine and formaldehyde, and a hydroxide, inorganic acid salt, carboxylate or alkoxide
10 of an alkali metal or an alkaline earth metal.

7. A polyacetal resin composition according to Claim 3, wherein the weathering agent is at least one member selected from the group consisting of a benzotriazole type substance, an oxalic anilide type
15 substance and a hindered amine type substance.

8. A polyacetal resin composition according to Claim 3, wherein the releasant is at least one member selected from the group consisting of an alcohol, a fatty acid, a fatty acid ester, a polyoxyalkylene
20 glycol, an olefin compound having an average polymerization degree of 10-500, and a silicone oil.

9. A polyacetal resin composition according to Claim 3, wherein the reinforcing agent is at least one member selected from the group consisting of an
25 inorganic filler, a glass fiber, glass beads and a carbon fiber.

10. A polyacetal resin composition according to Claim 3, wherein the electroconductive agent is at



least one member selected from the group consisting of an electroconductive carbon black, a metal powder and a metal fiber.

11. A polyacetal resin composition according to
5 Claim 3, wherein the thermoplastic resin is at least one member selected from the group consisting of an olefin resin, an acrylic resin, a styrene resin, a polycarbonate resin and an uncured epoxy resin.

12. A polyacetal resin composition according to
10 Claim 3, wherein the thermoplastic elastomer is at least one member selected from the group consisting of a polyurethane elastomer, a polyester elastomer, a polystyrene elastomer and a polyamide elastomer.

ABSTRACT

A polyacetal resin composition comprising oxymethylene units as the main constitute, 2-10 mol% of comonomer units, 50-5,000 rpm of a polyacetal oligomer and 3-13 ppm of fluorine. The present invention provides a polyacetal resin composition having excellent flowability and thermal stability in good balance.

2-8341070