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(54) Title: POLYACETAL MOLDED ARTICLES STABILIZED AGAINST DISCOLORATION

(57) Abstract: Polyacetal molded articles are effectively stabilized against unwanted discoloration comprising by incorporating a synergistic combination of antioxidants selected from the group consisting of (i) Pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate]; and (ii) at least one compound selected from the group consisting of tris-(4-t-butyl-2,6-dimethyl-3-hydroxybenzyl) isocyanurate, ethylene-1,2-bis-(oxyethylene(3-t-butyl-4-hydroxy-5-methylhydrocinnamate), hexamethylene-1,6-bis-(3,5-di-t-butyl-4-hydroxyhydrocinnamate) and the monoacrylate ester of 2,2'-methylenebis(6-tert-butyl-4-methylphenol); or (iii) Hexamethylene-1, 6-bis-(3,5-di-t-butyl-4-hydroxyhydrocinnamate); and (iv) at least one compound selected from the group consisting of ethylene-1,2-bis-(oxyethylene(3-t-butyl-4-hydroxy-5-methylhydrocinnamate)) and tris-(4-t-butyl-2,6-dimethyl-3-hydroxybenzyl) isocyanurate.

Polyacetal molded articles stabilized against discoloration

The present invention relates to polyacetal resin molded articles stabilized against color formation. More particularly, the present invention relates to polyacetal resin molded articles that comprise a synergistic mixture of (i) pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] and (ii) at least one compound selected from the group consisting of tris-(4-t-butyl-2,6-dimethyl-3-hydroxybenzyl) isocyanurate, ethylene-1,2-bis-(oxyethylene(3-t-butyl-4-hydroxy-5-methylhydrocinnamate)), hexamethylene-1,6-bis-(3,5-di-t-butyl-4-hydroxyhydrocinnamate) and the monoacrylate ester of 2,2'-methylenebis(6-tert-butyl-4-methylphenol), or (iii) hexamethylene-1,6-bis-(3,5-di-t-butyl-4-hydroxyhydrocinnamate) and (iv) at least one compound selected from the group consisting of ethylene-1,2-bis-(oxyethylene(3-t-butyl-4-hydroxy-5-methylhydrocinnamate)) and tris-(4-t-butyl-2,6-dimethyl-3-hydroxybenzyl) isocyanurate.

The polyacetal-molded articles of the present invention exhibit excellent thermal aging resistance, excellent initial and long-term color stability and excellent anti-mold deposit properties. The polyacetal molded articles of the present invention can be advantageously used for various applications, for example for mechanical parts which will be used under high temperature conditions for a prolonged period of time (for example, mechanical parts employed in association with automobile engines).

Polyacetal resins not only have an excellent balance of mechanical strength, chemical resistance and sliding properties, but can also be easily processed. By virtue of these advantages, polyacetal resins are widely used as engineering plastic materials for a wide variety of applications including mechanical parts, such as mechanical parts for electric and electronic equipment as well as automobiles.

When a polyacetal resin is used in the above-mentioned fields, it is necessary that the polyacetal resin have good thermal aging resistance and initial and long-term color stability. Further, from the viewpoint of improving molding productivity, it is important that the polyacetal resin have good anti-mold deposit properties.

U.S. Patent Specification No. 3,743,614 and British Patent Specification 1 425 771 disclose a method for improving the thermal aging resistance of a polyacetal resin by adding an aliphatic carboxylic acid metal salt.

U.S. Patent Specification No. 5,364,900 discloses polyacetal resin compositions comprising hindered phenol antioxidants and ion adsorbents.

U.S. Pat. No. 5,948,844 discloses polyacetal resin compositions comprising terminal-stabilized polyacetal resin and at least one certain aliphatic carboxylic acid metal salt.

It has unexpectedly been found that specific hindered phenolic antioxidant combinations are synergistic towards providing thermal aging resistance and initial and long-term color stability to polyacetal resins.

According to the present invention, there is provided a polyacetal molded article stabilized against discoloration comprising

- (a) A polyacetal resin; and
- (b) An effective stabilizing amount of a synergistic combination of
 - (i) Pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate]; and
 - (ii) At least one compound selected from the group consisting of tris-(4-t-butyl-2,6-dimethyl-3-hydroxybenzyl) isocyanurate, ethylene-1,2-bis-(oxyethylene(3-t-butyl-4-hydroxy-5-methylhydrocinnamate)), hexamethylene-1,6-bis-(3,5-di-t-butyl-4-hydroxyhydrocinnamate) and the monoacrylate ester of 2,2'-methylenebis(6-tert-butyl-4-methylphenol); or
- (c) An effective stabilizing amount of a synergistic combination of
 - (iii) Hexamethylene-1,6-bis-(3,5-di-t-butyl-4-hydroxyhydrocinnamate) and
 - (iv) At least one compound selected from the group consisting of ethylene-1, 2-bis-(oxyethylene (3-t-butyl-4-hydroxy-5-methylhydrocinnamate)) and tris-(4-t-butyl-2, 6-dimethyl-3-hydroxybenzyl) isocyanurate.

Pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], CAS # 6683-19-8, is commercially available as Irganox[®] 1010; tris-(4-t-butyl-2, 6-dimethyl-3-hydroxybenzyl) isocyanurate, CAS #40601-76-1, is available as Irganox[®] 3790; ethylene-1, 2-bis-(oxyethylene (3-t-butyl-4-hydroxy-5-methylhydrocinnamate)), CAS # 36443-68-2, is available as Irganox[®] 245; hexamethylene-1, 6-bis-(3,5-di-t-butyl-4-hydroxyhydrocinnamate), CAS # 35074-77-2, is available as Irganox[®] 259; the monoacrylate ester of 2,2'-methylenebis(6-tert-butyl-4-methylphenol), CAS # 61167-58-6, is available as Irganox[®] 3052. IRGANOX is a trademark of Ciba Specialty Chemicals.

The polyacetal molded articles of the present invention have excellent thermal aging resistance and excellent initial and long-term color stability, so that it solves the problems which are encountered when a shaped article produced from a conventional polyacetal resin com-

position is used in a high-temperature atmosphere, namely, the problems of low mechanical properties (due to unsatisfactory thermal aging resistance) and poor appearance (due to unsatisfactory initial or long-term color stability). Initial color stability refers to the initial color of the extruded molded article. Long-term color stability refers to the color of the molded article after thermal exposure. In the context of this invention "discoloration" refers to unwanted initial color of the molded article (formed on extrusion) as well as unwanted color formation of the molded article in-use (formed on thermal exposure), for instance as an automobile part. The polyacetal-molded articles of the present invention are suitable used for mechanical parts, for instance mechanical parts employed in association with automobile engines.

The amount of component (b) or (c) relative to component (a) is in the range from about 0.05 to about 5.0% by weight, for example about 0.1 to about 2.0% or about 0.1 to about 1.0% by weight, based on the weight of component (a).

The ratio of component (i) to (ii) is from about 1:9 to about 9 :1, for example about 1:4 to about 4:1, for instance about 1:3 to about 3:1, or about 1:2 to about 2:1, or about 1:1. The ratio of component (iii) to (iv) is defined as for (i) to (ii).

Examples of polyacetal resins of the present invention include those obtained by a method in which an oxymethylene homopolymer consisting essentially of oxymethylene units is produced from a formaldehyde monomer or a cyclic oligomer of formaldehyde, such as formaldehyde trimer (trioxane) or a formaldehyde tetramer (tetraoxane), and those obtained by a method in which an oxymethylene-oxyalkylene copolymer, containing about 0.1 to about 50.0%, for example about 20.0% or less by weight of oxyalkylene units having 2 to 8 carbon atoms, is produced from a mixture of the above-mentioned formaldehyde monomer or oligomer and a cyclic formal. Examples of cyclic formals as comonomers include ethylene oxide, propylene oxide, epichlorohydrine, 1,3-dioxolane 1,4-butanediol, a glycol formal and a diglycol formal. Examples of polyacetal resins include an oxymethylene-oxyalkylene copolymer comprising a branched molecular chain, and an oxymethylene-containing block copolymer, such as a block copolymer comprising more than 50.0% by weight of a polyoxymethylene (POM) block and less than 50.0% by weight of a polymer block (containing 50.0% by weight or more of recurring oxymethylene units) other than the POM block. Examples of configurations of such oxymethylene block copolymers include A-B-A and A-B configurations, wherein A represents a POM block and B represents a polymer block other than the POM block (containing 50.0% by weight or more of recurring oxymethylene units), the amount of the B block being less than 50.0% by weight of the block copolymer.

The polyacetal homopolymer and copolymer resins of the present invention with unstable termini containing hydroxyl groups may be stabilized by known methods, for example by conversion to esters, ethers, urethanes and the like. The unstable termini may also be removed by hydrolysis.

With respect to the method for producing the polyacetal resin of the present invention, there is no particular limitation. Raw material monomers are copolymerized in the presence of a catalyst to obtain a crude polyacetal resin. The polymerization may be conducted by bulk polymerization. Either of a batch wise method and a continuous method can be employed. As a batch type polymerization apparatus, a generally known reaction vessel having a stirrer can be used. As a continuous type polymerization apparatus, a self-cleaning type mixer, such as a co-kneader, a twin-screw continuous extrusion kneader or a twin-paddle type continuous mixer, can be used. The polymerization can be conducted for example from about 60 to about 200°C, for instance from about 60 to about 120°C, under atmospheric pressure.

Examples of polymerization catalysts to be used in the polymerization reaction include boron trifluoride, boron trifluoride hydrate, and coordination compounds of an oxygen- or sulfur-containing organic compound with boron trifluoride, which may be either in gaseous form or in the form of a solution thereof in a suitable organic solvent. Of the above polymerization catalysts, the coordination compounds of an oxygen- or sulfur-containing organic compound with boron trifluoride, specifically, boron trifluoride diethyl ether and boron trifluoride dibutyl ether, are specific examples. With respect to the amount of the polymerization catalyst, the catalyst is used in an amount of from about 1×10^{-6} to about 1×10^{-3} mol, for instance about 5×10^{-6} to about 1×10^{-4} mol per mol of the total of the trioxane and cyclic ether.

Because the obtained crude polyacetal resin contains an active polymerization catalyst, it may be necessary to deactivate the polymerization catalyst. A method of deactivating the polymerization catalyst either in water containing a basic substance or in an organic solvent containing a basic substance may be used. Further, a method of deactivating a catalyst by adding a basic substance to a crude polyacetal resin in a molten state in an extruder may be used. Examples of basic substances to be used for deactivating a polymerization catalyst include hydroxides, inorganic weak acid salts, and organic acid salts of alkali metals or alkaline earth metals. Of these, hydroxides, carbonates, phosphates, silicates, borates, formates, acetates, stearates, palmitates, propionates, oxalates and the like of lithium, sodium, potassium, magnesium, calcium, strontium and barium are specific examples. Further, ammonia and amine compounds, such as triethylamine and tributylamine, may be used as a catalyst deactivator.

In the present invention, if desired, various customary additives, which are usually incorporated in a polyacetal resin, can be used without any particular restriction. For example, at least one additive selected from the group consisting of additional antioxidants, polymers containing a formaldehyde-reactive nitrogen atom, formic acid scavengers, light stabilizers and mold release agents can be incorporated in the polyacetal molded articles. Light stabilizers are for example ultraviolet light absorbers (UVA's) and sterically hindered amines (HALS). The amount of the additives is generally from 0.1 to 5.0 parts by weight, per 100 parts by weight of the polyacetal-molded article.

Accordingly, a further subject of the present invention is a polyacetal resin molded article stabilized against discoloration comprising

- (a) A polyacetal resin;
- (b) An effective stabilizing amount of a synergistic combination of
 - (i) Pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate]; and
 - (ii) At least one compound selected from the group consisting of tris(4-t-butyl-2,6-dimethyl-3-hydroxybenzyl) isocyanurate, ethylene-1,2-bis-(oxyethylene(3-t-butyl-4-hydroxy-5-methylhydrocinnamate)), hexamethylene-1,6-bis-(3,5-di-t-butyl-4-hydroxyhydrocinnamate) and the monoacrylate ester of 2,2'-methylenebis(6-tert-butyl-4-methylphenol); or
- (c) An effective stabilizing amount of a synergistic combination of
 - (iii) Hexamethylene-1,6-bis-(3,5-di-t-butyl-4-hydroxyhydrocinnamate); and
 - (iv) At least one compound selected from the group consisting of ethylene-1,2-bis-(oxyethylene(3-t-butyl-4-hydroxy-5-methylhydrocinnamate)) and tris-(4-t-butyl-2,6-dimethyl-3-hydroxybenzyl) isocyanurate; and
- (d) One or more additives selected from the group consisting of antioxidants, polymers containing a formaldehyde-reactive nitrogen atom, formic acid scavengers, ultraviolet light absorbers, hindered amine light stabilizers and mold release agents.

Additional antioxidants are for example hindered phenols selected from the group consisting of n-octadecyl-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)-propionate, n-octadecyl-3-(3'-methyl-5'-t-butyl-4'-hydroxyphenyl)-propionate, n-tetradecyl-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)-propionate, 1,4-butanediol-bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate], 3,9-bis[2-(3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy)-1,1-dimethylethyl]2,4,8,10-tetraoxaspiro(5,5)undecane, N,N'-bis-3-(3',5'-di-t-butyl-t-butyl-4-hydroxyphenol)propionyl hexamethylenediamine, N,N'-tetramethylenebis-3-(3'-methyl-5'-t-butyl-4-hydroxyphenol)propionyl-

dia mine, N,N'-bis-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionyl]hydrazine, N-salicyloyl-N'salicylidenehydrazine, 3-(N-salicyloyl)amino-1,2,4-triazole and N,N'-bis[2-{3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionyloxy}ethyl]oxyamide.

It is contemplated that the molded polyacetal articles comprising the presently defined binary synergistic combination of antioxidants may also comprise one or both of the other antioxidants selected from the group consisting of pentaerythritol tetrakis [3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate], tris-(4-*t*-butyl-2,6-dimethyl-3-hydroxybenzyl) isocyanurate, ethylene-1,2-bis-(oxyethylene(3-*t*-butyl-4-hydroxy-5-methylhydrocinnamate)), hexamethylene-1,6-bis-(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate) and the monoacrylate ester of 2,2'-methylenebis(6-*t*-butyl-4-methylphenol).

As a polymer containing a formaldehyde-reactive nitrogen atom, a polyamide resin, such as nylon 4,6, nylon 6, nylon 6,6, nylon 6,10, nylon 6,12 and nylon 12, and a co polyamide resin, such as nylon 6/6,6/6,10 and nylon 6/6,12, can be mentioned. Further examples of polymers containing a formaldehyde-reactive nitrogen atom include a homopolymer of acrylamide or a derivative thereof, and a copolymer of acrylamide or a derivative thereof with another vinyl monomer, such as a poly- β -alanine, which is obtained by polymerizing acrylamide or a derivative thereof with another vinyl monomer in the presence of a metal alcoholate. These polymers containing a formaldehyde-reactive nitrogen atom can be used individually or in combination. When the polyacetal-molded articles contain a polymer containing a formaldehyde-reactive nitrogen atom, the polyacetal composition exhibits remarkably high retention of strength at a thermal aging resistance test in which the resin composition is heated at 150°C for 1,000 hours.

Examples of formic acid scavengers include an amino-substituted triazine compound, an addition product between an amino-substituted triazine compound and formaldehyde, and a polycondensate between an amino-substituted triazine compound and formaldehyde.

Illustrative examples of amino-substituted triazine compounds 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, benzoguanamine (2,4-diamino-6-phenyl-*sym*-triazine), 2,4-diamino-6-methyl-*sym*-triazine, 2,4-diamino-6-butyl-*sym*-triazine, 2,4-diamino-6-benzyloxy-*sym*-triazine, 2,4-diamino-6-butoxy-*sym*-triazine, 2,4-diamino-6-cyclo-hexyl-*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'-tetracyanoethylbenzoguanamine.

Examples of addition products between an amino-substituted triazine compound and formaldehyde include N-methylolmelamine, N,N'-dimethylolmelamine and N,N',N''-trimethylolmelamine.

Examples of polycondensates between an amino-substituted triazine compound and formaldehyde include a polycondensate between melamine and formaldehyde.

The above amino-substituted triazine compounds, addition products between an amino-substituted triazine compound and formaldehyde, and polycondensates between an amino-substituted triazine compound and formaldehyde can be used individually or in combination.

Examples of light stabilizers include hydroxyphenylbenzotriazole, hydroxyphenyltriazine, oxalic anilide and hydroxybenzophenone ultraviolet light absorbers (UVA's) and sterically hindered amine light stabilizers.

Light stabilizers are for example:

2-(2-Hydroxyphenyl)-2H-benzotriazoles, for example known commercial hydroxyphenyl-2H-benzotriazoles and benzotriazoles as disclosed in *United States Patent Specification Nos.* 3,004,896; 3,055,896; 3,072,585; 3,074,910; 3,189,615; 3,218,332; 3,230,194; 4,127,586; 4,226,763; 4,275,004; 4,278,589; 4,315,848; 4,347,180; 4,383,863; 4,675,352; 4,681,905; 4,853,471; 5,268,450; 5,278,314; 5,280,124; 5,319,091; 5,410,071; 5,436,349; 5,516,914; 5,554,760; 5,563,242; 5,574,166; 5,607,987; 5,977,219 and 6,166,218 such as 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3,5-di-t-butyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(2-hydroxy-5-t-butylphenyl)-2H-benzotriazole, 2-(2-hydroxy-5-t-octylphenyl)-2H-benzotriazole, 5-chloro-2-(3,5-di-t-butyl-2-hydroxyphenyl)-2H-benzotriazole, 5-chloro-2-(3-t-butyl-2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3-sec-butyl-5-t-butyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(2-hydroxy-4-octyloxyphenyl)-2H-benzotriazole, 2-(3,5-di-t-amyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(3,5-bis- α -cumyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-(ω -hydroxy-octa-(ethyleneoxy)carbonyl-ethyl)-phenyl)-2H-benzotriazole, 2-(3-dodecyl-2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-octyloxycarbonyl)ethylphenyl)-2H-benzotriazole, dodecylated 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-octyloxycarbonyl)ethylphenyl)-5-chloro-2H-benzotriazole, 2-(3-tert-butyl-5-(2-(2-ethylhexyloxy)-carbonyl)ethyl)-2-hydroxyphenyl)-5-chloro-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-methoxycarbonyl)ethylphenyl)-5-chloro-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-methoxycarbonyl)ethylphenyl)-2H-benzotriazole, 2-(3-t-butyl-5-(2-(2-ethylhexyloxy)carbonyl)ethyl)-2-hydroxyphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-isooctyloxycarbonyl)ethylphenyl)-2H-benzotriazole, 2,2'-methylene-bis(4-t-octyl-(6-2H-benzotriazol-2-yl)phenol), 2-(2-

hydroxy-3- α -cumyl-5-t-octylphenyl)-2H-benzotriazole, 2-(2-hydroxy-3-t-octyl-5- α -cumylphenyl)-2H-benzotriazole, 5-fluoro-2-(2-hydroxy-3,5-di- α -cumylphenyl)-2H-benzotriazole, 5-chloro-2-(2-hydroxy-3,5-di- α -cumylphenyl)-2H-benzotriazole, 5-chloro-2-(2-hydroxy-3- α -cumyl-5-t-octylphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-isooctylloxycarbonyl-ethyl)phenyl)-5-chloro-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3- α -cumyl-5-t-octylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-5-t-octylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3,5-di-t-octylphenyl)-2H-benzotriazole, methyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyhydrocinnamate, 5-butylsulfonyl-2-(2-hydroxy-3- α -cumyl-5-t-octylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3- α -cumyl-5-t-butylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3,5-di-t-butylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3,5-di- α -cumylphenyl)-2H-benzotriazole, 5-butylsulfonyl-2-(2-hydroxy-3,5-di-t-butylphenyl)-2H-benzotriazole and 5-phenylsulfonyl-2-(2-hydroxy-3,5-di-t-butylphenyl)-2H-benzotriazole;

2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives;

Esters of substituted and unsubstituted benzoic acids, as for example 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl) resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate;

Acrylates and malonates, for example, α -cyano- β,β -diphenylacrylic acid ethyl ester or isooctyl ester, α -carbomethoxy-cinnamic acid methyl ester, α -cyano- β -methyl-p-methoxy-cinnamic acid methyl ester or butyl ester, α -carbomethoxy-p-methoxy-cinnamic acid methyl ester, N-(β -carbomethoxy- β -cyanovinyl)-2-methyl-indoline, Sanduvor[®] PR25, dimethyl p-methoxybenzylidenemalonate (CAS# 7443-25-6), and Sanduvor[®] PR31, di-(1,2,2,6,6-pentamethylpiperidin-4-yl) p-methoxybenzylidenemalonate (CAS #147783-69-5);

Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide, mixtures of o- and p-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides;

tris-Aryl-o-hydroxyphenyl-s-triazines, for example known commercial tris-aryl-o-hydroxyphenyl-s-triazines and triazines as disclosed in, WO 96/28431, EP 434608, EP 941989, GB 2,317,893, United States Patent Specification Nos. 3,843,371; 4,619,956; 4,740,542;

5,096,489; 5,106,891; 5,298,067; 5,300,414; 5,354,794; 5,461,151; 5,476,937; 5,489,503; 5,543,518; 5,556,973; 5,597,854; 5,681,955; 5,726,309; 5,942,626; 5,959,008; 5,998,116 and 6,013,704, for example 4,6-bis-(2,4-dimethylphenyl)-2-(2-hydroxy-4-octyloxyphenyl)-s-triazine, Cyasorb[®] 1164, Cytec Corp, 4,6-bis-(2,4-dimethylphenyl)-2-(2,4-dihydroxyphenyl)-s-triazine, 2,4-bis(2,4-dihydroxyphenyl)-6-(4-chlorophenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-hydroxyethoxy)phenyl]-6-(4-chlorophenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-hydroxy-4-(2-hydroxyethoxy)phenyl)-6-(2,4-dimethylphenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-hydroxyethoxy)phenyl]-6-(4-bromophenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-acetoxyethoxy)phenyl]-6-(4-chlorophenyl)-s-triazine, 2,4-bis(2,4-dihydroxyphenyl)-6-(2,4-dimethylphenyl)-s-triazine, 2,4-bis(4-biphenyl)-6-(2-hydroxy-4-octyloxycarbonylethylideneoxyphenyl)-s-triazine, 2-phenyl-4-[2-hydroxy-4-(3-sec-butyloxy-2-hydroxypropyloxy)phenyl]-6-[2-hydroxy-4-(3-sec-amxyloxy-2-hydroxypropyloxy)phenyl]-s-triazine, 2,4-bis(2,4-dimethylphenyl)-6-[2-hydroxy-4-(3-benzyloxy-2-hydroxypropyloxy)phenyl]-s-triazine, 2,4-bis(2-hydroxy-4-n-butyloxyphenyl)-6-(2,4-di-n-butyloxyphenyl)-s-triazine, 2,4-bis(2,4-dimethylphenyl)-6-[2-hydroxy-4-(3-nonyloxy*-2-hydroxypropyloxy)-5- α -cumylphenyl]-s-triazine (* denotes a mixture of octyloxy, nonyloxy and decyloxy groups), methylenebis-{2,4-bis(2,4-dimethylphenyl)-6-[2-hydroxy-4-(3-butyloxy-2-hydroxypropoxy)phenyl]-s-triazine}, methylene bridged dimer mixture bridged in the 3:5', 5:5' and 3:3' positions in a 5:4:1 ratio, 2,4,6-tris(2-hydroxy-4-isooctyloxycarbonylisopropylideneoxyphenyl)-s-triazine, 2,4-bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-hexyloxy-5- α -cumylphenyl)-s-triazine, 2-(2,4,6-trimethylphenyl)-4,6-bis[2-hydroxy-4-(3-butyloxy-2-hydroxypropyloxy)phenyl]-s-triazine, 2,4,6-tris[2-hydroxy-4-(3-sec-butyloxy-2-hydroxypropyloxy)phenyl]-s-triazine, mixture of 4,6-bis-(2,4-dimethylphenyl)-2-(2-hydroxy-4-(3-dodecyloxy-2-hydroxypropoxy)-phenyl)-s-triazine and 4,6-bis-(2,4-dimethylphenyl)-2-(2-hydroxy-4-(3-tridecyloxy-2-hydroxypropoxy)-phenyl)-s-triazine, Tinuvin[®] 400, Ciba Specialty Chemicals Corp., 4,6-bis-(2,4-dimethylphenyl)-2-(2-hydroxy-4-(3-(2-ethylhexyloxy)-2-hydroxypropoxy)-phenyl)-s-triazine and 4,6-diphenyl-2-(4-hexyloxy-2-hydroxyphenyl)-s-triazine;

Sterically hindered amine stabilizers, for example 4-hydroxy-2,2,6,6-tetramethylpiperidine, 1-allyl-4-hydroxy-2,2,6,6-tetramethylpiperidine, 1-benzyl-4-hydroxy-2,2,6,6-tetramethylpiperidine, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl) succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl) nitrilotriacetate, tetrakis(2,2,6,6-

tetramethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl) malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) succinate, linear or cyclic condensates of N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidin-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, a condensation product of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane, a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro[4,5]decane and epichlorohydrine, 1,1-bis(1,2,2,6,6-pentamethyl-4-piperidyl)oxycarbonyl)-2-(4-methoxyphenyl)ethene, N,N'-bis-formyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine, diester of 4-methoxy-methylene-malonic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperidyl)]-siloxane, reaction product of maleic acid anhydride- α -olefin-copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine;

The sterically hindered amine may also be one of the compounds described in GB-A-2 301 106 as component I-a), I-b), I-c), I-d), I-e), I-f), I-g), I-h), I-i), I-j), I-k) or I-l), in particular the light stabilizer 1-a-1, 1-a-2, 1-b-1, 1-c-1, 1-c-2, 1-d-1, 1-d-2, 1-d-3, 1-e-1, 1-f-1, 1-g-1, 1-g-2 or 1-k-1 listed on pages 68 to 73 of said GB-A-2301106;

The sterically hindered amine may also be one of the compounds described in EP-A-0 782 994, for example compounds as described in Examples 1-12 or D-1 to D-5; and Sterically hindered amines substituted on the N-atom by a hydroxy-substituted alkoxy group, for example compounds such as 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine, 1-(2-hydroxy-2-methylpropoxy)-4-hexadecanoyloxy-2,2,6,6-

tetramethylpiperidine, the reaction product of 1-oxyl-4-hydroxy-2,2,6,6-tetramethylpiperidine with a carbon radical from t-amylalcohol, 1-(2-hydroxy-2-methylpropoxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine, 1-(2-hydroxy-2-methylpropoxy)-4-oxo-2,2,6,6-tetramethylpiperidine, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) adipate, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) succinate, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) glutarate and 2,4-bis{N-[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl]-N-butylamino}-6-(2-hydroxyethylamino)-s-triazine.

The above-mentioned hindered amine light stabilizers can be used individually or in combination, and also be used in combination with the above-mentioned ultraviolet light absorbers.

As a mold release agent, at least one member selected from the group consisting of a fatty acid ester, a polyalkylene glycol and an amido group-containing aliphatic compound can be used. The term "fatty acid ester" mentioned herein means a fatty acid ester which is obtained from a polyhydric alcohol and a fatty acid, preferably one which is obtained by the reaction of at least one type of a saturated or unsaturated fatty acid having 10 or more carbon atoms with a polyhydric alcohol having 2 to 6 carbon atoms. Examples of polyhydric alcohols usable for producing fatty acid esters include ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, butanediol, pentanediol, hexanediol, glycerol, diglycerol, triglycerol, threitol, erythritol, pentaerythritol, arabitol, ribitol, xylitol, sorbite, sorbitan, sorbitol and mannitol. Examples of fatty acids include capric, lauric, myristic, palmitic, stearic, 12-hydroxystearic, arachic, behenic, lignoceric, cerotic, montanic, melissic and ceroplastic acid. Examples of unsaturated aliphatic carboxylic acids include undecylenic, oleic, elaidic, cetoleic, erucic, brassidic, sorbic, linoleic, linolenic, arachidonic, propiolic and stearolic acid, natural fatty acids containing these unsaturated aliphatic carboxylic acids, and a mixture thereof. The above-mentioned fatty acids may or may not be substituted with a hydroxyl group. Of the above-mentioned fatty acid esters, a fatty acid ester that is obtained by the reaction of a fatty acid selected from the group consisting of palmitic, stearic, behenic and montanic acid, with a polyhydric alcohol selected from the group consisting of glycerol, pentaerythritol, sorbitan and sorbitol, is preferred. The above-mentioned fatty acid esters may or may not contain a hydroxyl group. For example, the fatty acid esters can be any of a monoester, a diester and a triester. Further, the fatty acid ester may contain a hydroxyl group, which is blocked with boric acid or the like. Preferred examples of fatty acid esters include glycerol monopalmitate, dipalmitate, tripalmitate, monostearate, distearate,

Examples of amido group-containing aliphatic compounds include ethylenebisstearylamine, ethylenebislaurylamine, ethylenebisoleylamine and ethylenebiserucic acid amide. These amide group-containing aliphatic compounds can be used individually or in combination.

With respect to the form of the additives, the additives may be added in a powdery form or in a molten form.

With respect to the method for producing the polyacetal-molded articles of the present invention, there is no particular limitation. Generally, a polyacetal resin composition of the present invention can be obtained by melt-kneading in an extruder a polyacetal resin and the synergistic combinations of components (b) or (c) and, if desired, further optional additives. The extruder may be a single-screw extruder or may be a twin-screw extruder. The components (b) or (c) and optional further additives may be added to a reaction system during the polymerization reaction for producing a polyacetal resin.

Hindered phenol antioxidants of components (b) or (c) may be added to comonomers, such as ethylene oxide, propylene oxide, epichlorohydrin, 1,3-dioxolane and 1,4-butanediol, prior to reaction of a formaldehyde monomer or oligomer with a cyclic formaldehyde.

The individual compounds of components (i) and (ii) or (iii) and (iv) may be added to the monomers, comonomers or polyacetal either separately or together. They may be added for instance as solid particles or in the molten state. The individual compounds may be added in the form of a master batch.

The extrusion temperature is not particularly restricted, and, in general, it can be appropriately selected in the range of from about 170 to about 240°C.

With respect to the method for preparing the molded articles of the present invention, there is no particular limitation. The polyacetal-molded articles of the present invention can be obtained by conventionally known methods, such as extrusion molding, injection molding, compression molding, vacuum forming, blow molding or foam molding.

It is contemplated that terminal-stabilized polyacetal resins and aliphatic carboxylic acid metal salts with occluded metal compounds and surface attached metal compounds may be employed in this invention. These components are disclosed in *U.S. Patent Specification No. 5,948,844*, the relevant parts of which are hereby incorporated by reference.

It is contemplated that ion adsorbents as disclosed in *U.S. Patent Specification No. 5,364,900* may be employed in the resin compositions of the present invention. The disclosure of *U.S. Patent Specification No. 5,364,900* is hereby incorporated by reference.

The following Examples illustrate the invention in more detail. They are not to be construed as limiting the instant invention in any manner whatsoever. Additive structures are as defined in the specification.

Abbreviations: min: minute(s); rpm: rotations per minute; h: hour(s)

Example 1

Polyoxymethylene copolymer pellets are blended with additives by using a Turbula mixer for 15-20 min. Total formulation size is 1000 g. The mixtures are then extruded with a 27 mm Leistritz twin-screw extruder. The extrusion is conducted under conditions such that the zone temperatures are 165, 170, 180, and 190°C, the melt temperature is 199°C, the melt pressure is 650-800 psi, and the feeder speed is 100 rpm. The resin composition obtained is pelletized by a cutter. The pelletized resin composition is dried for 3 hours in a vacuum oven (at 82°C, nitrogen bleed) prior to injection molding. BOY 50M injection molder is employed with zone temperatures of 182, 188, 193°C, nozzle temperature of 199°C, mold temperature of 90°C, to obtain plaque specimen of 2" x 2" x 0.06". These specimens are then placed in Blue M circulating air oven to be aging at 130 and 140°C. Color measurement is done on these oven aged specimens by using a DCI SF600 spectrophotometer. Yellowness Index (YI) is reported in the following tables. Total levels of additives are 0.5% by weight based on the overall formulation. The results are compiled in Tables 1 – 7:

Table 1

POM Plaques Oven Aged At 130°C					
Additive	Initial	Days			
		1	2	3	7
A (IRGANOX 1010)	30.1	31.6	33.0	34.4	40.1
B (IRGANOX 3790)	24.8	28.5	30.2	31.8	38.0
1:1 Ratio of A,B (expected)	20.5 (27.4)	24.3 (30.1)	26.3 (31.6)	28.5 (33.1)	36.3 (39.1)
1:1 Ratio of A,B (expected)	13.9 (25.9)	21.1 (29.1)	23.7 (30.8)	26.2 (32.2)	35.7 (38.4)

Table 2

POM Plaques Oven Aged At 140°C					
Additive	Initial	Days			
		1	2	3	7
A (IRGANOX 1010)	30.0	31.4	36.8	45.4	56.4
B (IRGANOX 3790)	25.0	28.6	33.6	41.8	56.1
1:1 Ratio of A,B (expected)	20.5 (27.5)	24.3 (30.0)	30.7 (35.2)	42.3 (43.6)	55.5 (56.2)
1:1 Ratio of A,B (expected)	14.0 (26.0)	20.7 (29.2)	27.8 (34.2)	38.6 (42.5)	54.5 (56.2)

Table 3

POM Plaques Oven Aged At 130°C					
Additive	Initial	Days			
		1	2	3	7
A (IRGANOX 1010)	13.1	16.4	17.8	19.7	27.7
B (IRGANOX 3790)	14.6	19.8	22.8	27.2	45.8
1:1 Ratio of A,B (expected)	11.1 (13.8)	14.2 (18.1)	15.5 (20.3)	17.5 (23.4)	25.5 (36.8)
3:1 Ratio of A,B (expected)	12.8 (13.5)	16.1 (17.2)	17.4 (19.0)	19.3 (21.6)	26.6 (32.2)
4:1 Ratio of A,B (expected)	12.3 (13.4)	15.5 (17.1)	16.8 (18.8)	18.7 (21.2)	26.6 (31.3)

Table 4

POM Plaques Oven Aged At 140°C					
Additive	Initial	Days			
		1	2	3	7
A (IRGANOX 1010)	13.1	16.3	20.5	33.2	48.8
B (IRGANOX 3790)	14.6	20.9	29.4	49.4	71.8
1:1 Ratio of A,B (expected)	11.1 (13.8)	14.0 (18.6)	17.5 (25.0)	29.0 (41.3)	45.0 (60.3)
3:1 Ratio of A,B (expected)	12.9 (13.5)	16.0 (17.4)	19.6 (22.7)	31.0 (37.2)	46.1 (54.6)
4:1 Ratio of A,B (expected)	12.4 (13.4)	15.5 (17.2)	19.4 (22.3)	31.2 (36.4)	46.9 (53.4)

It is seen that the combination of Irganox® 1010 and Irganox 3790® is synergistic towards preventing color formation in POM molded plaques.

Table 5

POM Plaques Oven Aged At 130°C					
Additive	Initial	Days			
		1	2	3	7
A (IRGANOX 1010)	13.1	16.4	17.8	19.7	27.7
B (IRGANOX 245)	12.0	14.0	14.9	16.1	21.3
C (IRGANOX 259)	11.3	15.6	17.7	20.9	32.0
1:1 Ratio of A,B (expected)	10.9 (12.6)	13.4 (15.2)	14.3 (16.4)	15.7 (17.9)	21.2 (24.5)
1:1 Ratio of A,C (expected)	10.7 (12.2)	13.5 (16.0)	14.5 (17.8)	16.1 (20.3)	22.2 (29.8)

Table 6

POM Plaques Oven Aged At 140°C					
Additive	Initial	Days			
		1	2	3	7
A (IRGANOX 1010)	13.1	16.3	20.5	33.2	48.8
B (IRGANOX 245)	12.1	13.9	16.0	24.5	39.1
C (IRGANOX 259)	11.4	14.8	20.3	38.8	59.2
1:1 Ratio of A,B (expected)	11.0 (12.6)	13.3 (15.1)	16.0 (18.2)	25.4 (28.8)	38.9 (44.0)
1:1 Ratio of A,C (expected)	10.9 (12.2)	13.7 (15.6)	16.6 (20.4)	26.7 (36.0)	40.3 (54.0)

It is seen that the combination of Irganox[®] 1010 and Irganox 245[®] or Irganox[®] 259 is synergistic towards preventing color formation in POM molded plaques.

Table 7

POM Plaques Oven Aged At 130°C					
Additive	Initial	Days			
		1	2	3	7
A (IRGANOX 1010)	13.1	16.4	17.8	19.7	27.7
B (IRGANOX 3052)	12.3	16.5	17.6	18.9	23.5
1:1 Ratio of A,B (expected)	12.3 (12.7)	15.7 (16.4)	16.8 (17.7)	18.2 (19.3)	23.5 (25.6)

It is seen that the combination of Irganox[®] 1010 and Irganox 3052[®] is synergistic towards preventing color formation in POM molded plaques.

Example 2

Plaques are prepared as in Example 1. Initial color (YI) of the injection-molded plaques is measured on a spectrophotometer as in Example 1. Total levels of additives are 0.5 weight percent, based on the overall weight of the formulation. YI measurements are shown below.

Additive	YI
A (IRGANOX 259)	33.8
B (IRGANOX 245)	18.9
C (IRGANOX 3790)	24.8
1:1 Ratio of A,B (expected)	17.9 (26.4)
1:1 Ratio of A,C (expected)	22.0 (29.3)
1:1 Ratio of A,C (expected)	22.4 (26.6)

It is seen that the combinations of Irganox[®] 259 with either Irganox[®] 245 or Irganox[®] 3790 are synergistic towards preventing color formation in POM molded articles.

CLAIMS

1. A polyacetal molded article stabilized against discoloration comprising
 - (a) A polyacetal resin; and
 - (b) An effective stabilizing amount of a synergistic combination of
 - (i) Pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate]; and
 - (ii) At least one compound selected from the group consisting of tris-(4-tert-butyl-2,6-dimethyl-3-hydroxybenzyl) isocyanurate, ethylene-1,2-bis-(oxyethylene(3-tert-butyl-4-hydroxy-5-methylhydrocinnamate)), hexamethylene-1,6-bis-(3,5-di-tert-butyl-4-hydroxyhydrocinnamate) and the monoacrylate ester of 2,2'-methylenebis(6-tert-butyl-4-methylphenol); or
 - (c) An effective stabilizing amount of a synergistic combination of
 - (iii) Hexamethylene-1,6-bis-(3,5-di-tert-butyl-4-hydroxyhydrocinnamate) and
 - (iv) At least one compound selected from the group consisting of ethylene-1,2-bis-(oxyethylene (3-tert-butyl-4-hydroxy-5-methylhydrocinnamate)) and tris-(4-tert-butyl-2,6-dimethyl-3-hydroxybenzyl) isocyanurate.
2. A polyacetal molded article according to claim 1 in which components (b) or (c) are present from about 0.05 to about 5.0% by weight, based on the weight of component (a).
3. A polyacetal molded article according to claim 1 in which components (b) or (c) are present from about 0.1 to about 2.0% by weight, based on the weight of component (a).
4. A polyacetal molded article according to claim 1 in which the polyacetal resin is an oxymethylene homopolymer or an oxymethylene-oxyalkylene copolymer.
5. A polyacetal molded article according to claim 1 further comprising one or more additives selected from the group consisting of additional antioxidants, polymers containing a formaldehyde-reactive nitrogen atom, formic acid scavengers, ultraviolet light absorbers, hindered amine light stabilizers and mold release agents.
6. A polyacetal molded article according to claim 5 comprising one or more additives selected from the group consisting of hydroxyphenylbenzotriazoles, hydroxyphenyltriazines and hindered amine light stabilizers.
7. A polyacetal molded article according to claim 1 in which the ratio (i):(ii) or (iii):(iv) is from about 1:9 to about 9:1.

8. A polyacetal molded article according to claim 7 in which the ratio (i):(ii) or (iii):(iv) is from about 1:4 to about 4:1.
9. A polyacetal molded article according to claim 1 in which the ratio (i):(ii) or (iii):(iv) is about 1:1.
10. A polyacetal molded article according to claim 1, which comprises
 - (i) Pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] and
 - (ii) tris-(4-t-Butyl-2,6-dimethyl-3-hydroxybenzyl) isocyanurate.

INTERNATIONAL SEARCH REPORT

National Application No
PCT/EP 02/04461A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K5/134 C08K5/3492 C08L59/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 216 052 A (ATTINGER-SORATO CARLA ET AL) 1 June 1993 (1993-06-01) claims 1,8,12,13 examples 4,6 ---	1,4-6,10
X	EP 0 619 344 A (ASAHI CHEMICAL IND) 12 October 1994 (1994-10-12) claims 1,3 ---	1,4-6
X	DATABASE WPI Section Ch, Week 199241 Derwent Publications Ltd., London, GB; Class A28, AN 1992-335432 XP002211560 & JP 04 239048 A (TORAY IND INC), 26 August 1992 (1992-08-26) abstract --- -/--	1,5,6

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

° Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/04461

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 198 28 797 A (BASF AG) 30 December 1999 (1999-12-30) claims 1,8 ---	1,4-6
X	EP 0 435 649 A (POLYPLASTICS CO) 3 July 1991 (1991-07-03) claims 1,2 ---	1,4-6
A	EP 0 827 979 A (IDEMITSU KOSAN CO) 11 March 1998 (1998-03-11) claims 1,19 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/04461

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 5216052	A	01-06-1993	BE 1005299 A3	22-06-1993
			CA 2072717 A1	02-01-1993
			DE 4221068 A1	14-01-1993
			FR 2678616 A1	08-01-1993
			GB 2257140 A , B	06-01-1993
			IT 1255191 B	20-10-1995
			JP 3062977 B2	12-07-2000
			JP 5230050 A	07-09-1993
			KR 218594 B1	01-09-1999
			NL 9201164 A	01-02-1993
EP 0619344	A	12-10-1994	CN 1093725 A , B	19-10-1994
			DE 69419060 D1	22-07-1999
			DE 69419060 T2	03-02-2000
			EP 0619344 A2	12-10-1994
			HK 1000578 A1	24-03-2000
			JP 2808078 B2	08-10-1998
			JP 6340792 A	13-12-1994
			KR 133012 B1	13-04-1998
			US 5364900 A	15-11-1994
			JP 4239048	A
DE 19828797	A	30-12-1999	DE 19828797 A1	30-12-1999
			CN 1307615 T	08-08-2001
			DE 59901554 D1	04-07-2002
			WO 0000547 A1	06-01-2000
			EP 1091999 A1	18-04-2001
			JP 2002519466 T	02-07-2002
			PL 345265 A1	03-12-2001
EP 0435649	A	03-07-1991	JP 2866417 B2	08-03-1999
			JP 3200857 A	02-09-1991
			BR 9006584 A	01-10-1991
			CA 2033041 A1	29-06-1991
			EP 0435649 A1	03-07-1991
			US 5128405 A	07-07-1992
EP 0827979	A	11-03-1998	JP 8302117 A	19-11-1996
			DE 69619669 D1	11-04-2002
			DE 69619669 T2	29-08-2002
			EP 0827979 A1	11-03-1998
			US 6214909 B1	10-04-2001
			WO 9635752 A1	14-11-1996