

Diesel-fuel-resistant moldings

The invention relates to the use of at least one zinc carboxylate
5 B) for increasing the diesel-fuel resistance of moldings made
from polyoxymethylenes A).

The invention further relates to the moldings obtainable as
claimed in the inventive use.

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The high crystallinity of polyacetals gives them good resistance
to numerous chemicals, and particular emphasis is given here to
their high resistance to fuel (including those in which methanol
is present), fats, oils, brake fluids and coolants. Polyacetal,
15 for example, exhibits only slight swelling and therefore high
dimensional stability. The good molding shrinkage of polyacetal
(compared with other engineering thermoplastics) is utilized in
the production of reservoir casings (fuel-extraction equipment),
since the plug connectors integrated into this application have
20 to be highly leakproof. At the same time, the material used for
the reservoir casing has to have high elongation at break in
order to fulfill the crash requirements imposed by legislation.
Here, too, polyacetal is again the material of choice for the
desired high heat resistance in the region of the fuel supply and
25 fuel return systems.

However, these good properties of polyacetals do not apply above
60°C.

30 The trend in the automotive sector toward developing engines
which are ever more powerful but at the same time more economical
has caused specific and unexpected problems in the diesel vehicle
sector. To achieve optimized combustion of diesel fuels the
diesel fuel is atomized at pressures around 1300 bar. This is
35 followed by a sudden pressure reduction to 0 bar. When this
procedure is used in what is known as the common rail system,
short-lived temperatures up to 160°C can occur in the engine
compartment. Consequently, the temperature of all of the parts
which come into contact with the diesel fuel rises markedly, and
40 mixing of cold fuel from the tank with hot fuel from the region
of the engine within the fuel supply and fuel return system
produces temperatures around 90°C. Even in the region of the tank,
it is still possible for temperatures above 90°C to arise, since
the fuel injection system returns excess diesel fuel, which is
45 still hot, into the tank. Under these conditions polyacetal

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decomposes and deposits within the lines, making these brittle and also impassable for the diesel fuel.

In addition, sulfur and/or sulfur compounds are present in diesel fuels and also damage the POM matrix, since in particular acid sulfur compounds are produced in the presence of air and degrade the polymer.

These sulfur compounds are also found in motor vehicle parts in which vulcanized elastomers are present or which are encapsulated within elastomers of this type (e.g. bearing elements in the operating [sic] or steering area, which have elastomer sleeves for dust protection).

Sterically hindered amines (HALS compounds), where appropriate with benzotriazole derivatives, are usually used to increase the UV resistance of POM compositions, and, depending on the application, these may be combined with other UV-stabilizers: see, for example, EP-A 448 038, EP-A 171 941, EP-A 586 988, DE-A 33 15 115, and DE-A 44 04 081.

EP-A 855 424 proposes the use of sterically hindered amines to increase diesel-fuel resistance. The relatively recent applications DE-A 10030553, DE-A 10030635, and DE-A 10030632 propose polyethyleneimines for the purpose.

The addition of zinc compounds to polyoxymethylenes is known, for example from DE-A 19925491, JP-A 11/181232, JP-A 07/150004, and JP-A 07/150005.

It is an object of the present invention, therefore, to provide moldings which are made from polyacetals and which can be used at high long-term service temperatures, and which are resistant to diesel fuels or vulcanized elastomers, with very substantial retention of the abovementioned good service properties.

We have found that this object is achieved by the use, as defined at the outset, of zinc carboxylates. Preferred embodiments are given in the subclaims.

As component A), the molding compositions which may be used according to the invention comprise from 10 to 99.99% by weight, preferably from 30 to 99% by weight, and in particular from 90 to 99% by weight, of a polyoxymethylene homo- or copolymer.

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Polymers of this type are known to the skilled worker and are described in the literature.

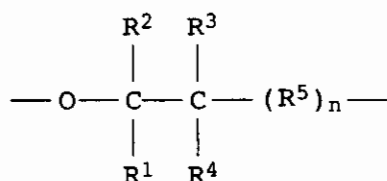
These polymers very generally have at least 50 mol% of -CH₂O- repeat units in their main polymer chain.

The homopolymers are generally prepared by polymerizing formaldehyde or trioxane, preferably in the presence of suitable catalysts.

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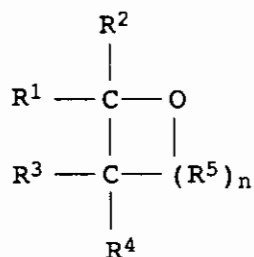
For the purposes of the invention, component A is preferably polyoxymethylene copolymers, especially those which, besides the recurring -CH₂O- units, also have up to 50 mol%, preferably from 0.1 to 20 mol%, in particular from 0.3 to 10 mol%, and very

15 particularly preferably from 2 to 6 mol%, of repeat units



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where R¹ to R⁴, independently of one another, are hydrogen, C₁-C₄-alkyl or halogen-substituted alkyl having from 1 to 4 carbon atoms, and R⁵ is -CH₂-, -CH₂O-, C₁-C₄-alkyl-, or

25 C₁-C₄-haloalkyl-substituted methylene or a corresponding oxymethylene group, and n is from 0 to 3. These groups may be advantageously introduced into the copolymers by ring-opening of cyclic ethers. Preferred cyclic ethers have the formula

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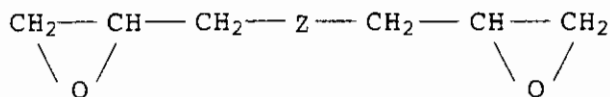
where R¹ to R⁵ and n are as defined above. Mention may be made, merely as examples, of ethylene oxide, propylene 1,2-oxide, butylene 1,2-oxide, butylene 1,3-oxide, 1,3-dioxane,

40 1,3-dioxolane and 1,3-dioxepan as cyclic ethers, and also linear oligo- and polyformals, such as polydioxolane or polydioxepan as comonomers.

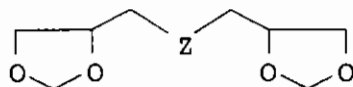
Other suitable components A) are oxymethylene terpolymers,

45 prepared, for example, by reacting trioxane, one of the cyclic ethers described above and a third monomer, preferably bifunctional compounds of the formula

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5 and/or



10 where Z is a chemical bond, -O-, -ORO- (R= C₁-C₈-alkylene or C₂-C₈-cycloalkylene).

Preferred monomers of this type are ethylene diglycide,
diglycidyl ether and diethers made from glycidyl compounds and
15 formaldehyde, dioxane or trioxane in a molar ratio of 2 : 1, and
also diethers made from 2 mol of glycidyl compound and 1 mol of
an aliphatic diol having from 2 to 8 carbon atoms, for example
the diglycidyl ether of ethylene glycol, 1,4-butanediol,
1,3-butanediol, 1,3-cyclobutanediol, 1,2-propanediol or
20 1,4-cyclohexanediol, to mention merely a few examples.

Processes for preparing the homo- and copolymers described above
are known to the person skilled in the art and described in the
literature, and further details are therefore superfluous here.

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The preferred polyoxymethylene copolymers have melting points of
at least 150°C and molecular weights (weight-average) M_w in the
range from 5000 to 250,000, preferably from 7000 to 150,000.

30 Particular preference is given to end-group-stabilized
polyoxymethylene polymers which have C-C bonds at the ends of the
chains.

The component A) used may in particular also be products which
35 comprise a relatively high proportion (generally
> 0.1% by weight) of residual thermally unstable fractions.
Components C) and D) have particularly excellent stabilizing
action on crude polyoxymethylene if they are premixed with the
polyoxymethylene prior to the mixing process.

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As component B), the molding compositions which may be used
according to the invention comprise from 0.01 to 5% by weight,
preferably from 0.1 to 4% by weight, and in particular from 0.1
to 3% by weight, based on components A) to D), of at least one
45 zinc carboxylate. (The total of the percentages by weight of
components A) to D) is always 100%).

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The carboxylic radical preferably has from 2 to 44 carbon atoms, in particular from 3 to 40 carbon atoms. Preferred carboxylic radicals are fatty acid radicals. For the purposes of the present invention, fatty acids, as in Morrison/Boyd Lehrbuch der org.

- 5 Chemie, 3rd edition, 1973, Verlag Chemie GmbH, p. 1138 are mostly straight-chain compounds which may preferably contain from 3 to 18 carbon atoms. Other than the compounds having 3 or 5 carbon atoms, the acids occurring in substantial quantities are generally only those which contain an even number of carbon
10 atoms.

Preferred acids which may be mentioned are montanic acid (a mixture of fatty acids having from 30 to 40 carbon atoms),

- | | |
|-------------------|--|
| 15 propionic acid | $\text{CH}_3\text{CH}_2\text{COOH}$ |
| butyric acid | $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ |
| valeric acid | $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ |
| caproic acid | $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ |
| caprylic acid | $\text{CH}_3(\text{CH}_2)_6\text{COOH}$ |
| 20 capric acid | $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ |
| lauric acid | $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ |
| myristic acid | $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ |
| palmitic acid | $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ |
| stearic acid | $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ |
| 25 oleic acid | cis-9-octadecadienoic acid |
| linoleic acid | cis-cis-9,12-octadecadienoic acid |
| linolenic acid | cis,cis,cis-9,12,15-octadecatrienoic acid |

and also perlargonic acid, margaric acid, succinic acid,

- 30 dodecanedioic acid.

Particularly preferred zinc carboxylates are zinc stearate, zinc oleate, and zinc montanate, zinc palmitate, zinc behenate, zinc citrate, zinc propionate, zinc oxalate, zinc succinate, zinc

- 35 acetate, and mixtures of these. Another preferred zinc carboxylate which may be mentioned is a dibasic zinc stearate produced by a double reaction, and obtainable commercially from the company Bärlocher as zinc soap BII. It is also possible to use polybasic carboxylates. It is, of course, also possible to
40 use mixtures of the abovementioned carboxylates.

As component C), the molding compositions which may be used according to the invention may comprise from 0 to 5% by weight, preferably from 0.01 to 4% by weight, and in particular from 0.1

- 45 to 3% by weight, of a zinc compound other than B). Suitable zinc compounds are

- zinc acetylacetonate
- zinc halides
- zinc carbonate
- zinc hexafluorosilicate
- 5 zinc hydroxide
- zinc hydroxycarbonate
- zinc nitrate
- zinc oxide
- zinc sulfate
- 10 zinc sulfide
- zinc tetrafluoroborate
- zinc titanate (ZnTiO_3)

particularly preferably zinc oxide or zinc sulfide. Processes for
 15 preparation are known to the skilled worker, and no further details in this connection are therefore required.

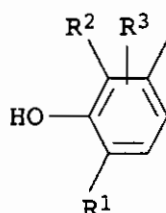
As component D), the molding compositions of the invention may
 comprise from 0 to 70% by weight, preferably from 0 to 30% by
 20 weight of other additives.

Suitable sterically hindered phenols D) are in principle any of
 the compounds which have a phenolic structure and whose phenolic
 ring has at least one bulky group.

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Examples of preferred compounds are those of the formula

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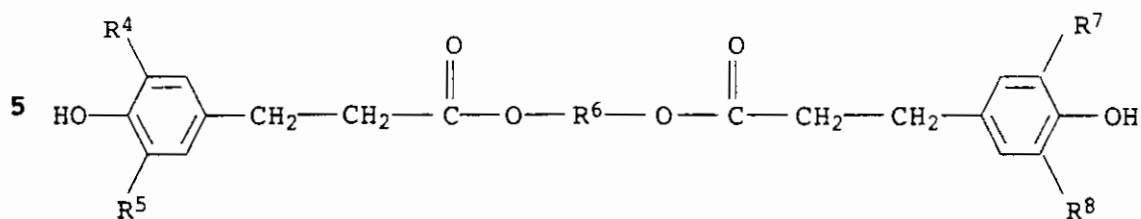
R^1 and R^2 are alkyl, substituted alkyl or a substituted triazole group, where R^1 and R^2 may be identical or different, and R^3 is alkyl, substituted alkyl, alkoxy or substituted amino.

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Antioxidants of the type mentioned are described, for example, in DE-A 27 02 661 (US-A 4 360 617).

Another group of preferred sterically hindered phenols derives
 45 from substituted benzenecarboxylic acids, in particular from substituted benzenepropionic acids.

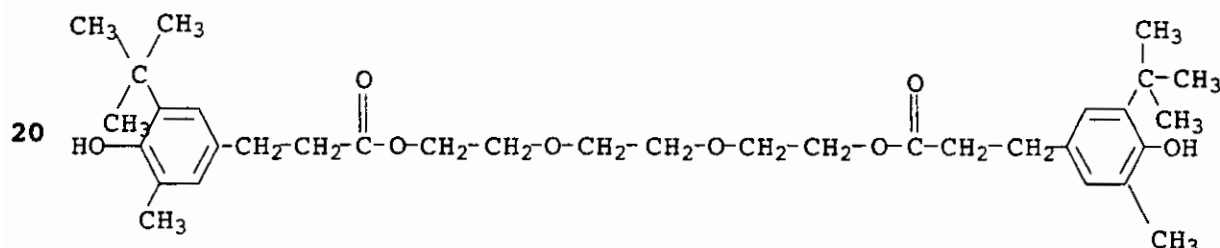
Particularly preferred compounds of this class have the formula



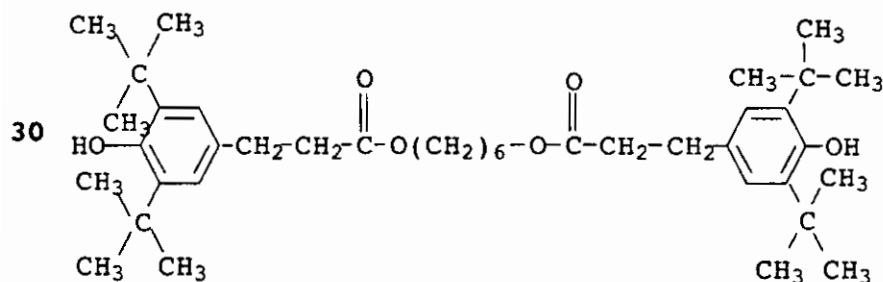
where R^4 , R^5 , R^7 and R^8 , independently of one another, are

- 10 C_1 - C_8 -alkyl which may in turn have substitution (at least one of these is a bulky group) and R^6 is a bivalent aliphatic radical which has from 1 to 10 carbon atoms and may also have C-O bonds in its main chain.

15 Preferred compounds of this formula are



25 (Irganox® 245 from Ciba-Geigy)



35 (Irganox® 259 from Ciba-Geigy)

The examples of sterically hindered phenols which should be mentioned are:

- 40 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 1,6-hexanediol bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], distearyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, 2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-ylmethyl
- 45 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, 3,5-di-tert-butyl-4-hydroxyphenyl-3,5-distearylthiotriazylamine, 2-(2'-hydroxy-3'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole,

2,6-di-tert-butyl-4-hydroxymethylphenol, 1,3,5-trimethyl-
 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene,
 4,4'-methylenebis(2,6-di-tert-butylphenol), 3,5-di-tert-
 butyl-4-hydroxybenzylidimethylamine and N,N'-hexamethylenebis-
 5 3,5-di-tert-butyl-4-hydroxyhydrocinnamide.

Compounds which have proven especially effective and which are
 therefore preferably used are 2,2'-methylenebis(4-methyl-6-tert-
 butylphenol), 1,6-hexanediol bis(3,5-di-tert-butyl-4-hydroxy-
 10 phenyl]propionate (Irganox® 259), pentaerythritol tetrakis-
 [3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] and the
 Irganox® 245 described above from Ciba Geigy, which is
 particularly suitable.

15 The amounts present of the antioxidants (D), which may be used
 individually or as mixtures, are usually up to 2% by weight,
 preferably from 0.005 to 2% by weight, in particular from 0.1 to
 1% by weight, based on the total weight of the molding
 compositions A) to C).

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Sterically hindered phenols which have proven particularly
 advantageous, in particular when assessing color stability on
 storage in diffuse light over prolonged periods, in some cases
 have no more than one sterically hindered group in the ortho
 25 position to the phenolic hydroxyl.

The polyamides which can be used as components D) are known per
 se. Use may be made of partly crystalline or amorphous resins as
 described, for example, in the Encyclopedia of Polymer Science
 30 and Engineering, Vol. 11, John Wiley & Sons, Inc., 1988, pp. 315-
 489. The melting point of the polyamide here is preferably below
 225°C, and particularly preferably below 215°C.

Examples of these are polyhexamethylene azelamide,
 35 polyhexamethylene sebacamide, polyhexamethylene dodecanediamide,
 poly-11-aminoundecanamide and
 bis(p-aminocyclohexyl)methyldodecanediamide, and the products
 obtained by ring-opening of lactams, for example or [sic]
 polylauro lactam. Other suitable polyamides are based on
 40 terephthalic or isophthalic acid as acid component and
 trimethylhexamethylenediamine or bis(p-aminocyclohexyl)propane as
 diamine component and polyamide base resins prepared by
 copolymerizing two or more of the abovementioned polymers or
 components thereof.

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Particularly suitable polyamides which may be mentioned are copolyamides based on caprolactam, hexamethylenediamine, p,p'-diaminodicyclohexylmethane and adipic acid. An example of these is the product marketed by BASF Aktiengesellschaft under the name Ultramid® 1 C.

Other suitable polyamides are marketed by Du Pont under the name Elvamide®.

10 The preparation of these polyamides is also described in the abovementioned text. The ratio of terminal amino groups to terminal acid groups can be controlled by varying the molar ratio of the starting compounds.

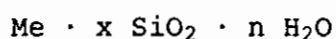
15 The proportion of the polyamide in the molding composition of the invention is up to 2% by weight, by preference from 0.005 to 1.99% by weight, preferably from 0.01 to 0.08% by weight.

The dispersibility of the polyamides used can be improved in some cases by concomitant use of a polycondensation product made from 2,2-di(4-hydroxyphenyl)propane (bisphenol A) and epichlorohydrin.

Condensation products of this type made from epichlorohydrin and bisphenol A are commercially available. Processes for their preparation are also known to the person skilled in the art. Tradenames of the polycondensates are Phenoxy® (Union Carbide Corporation) and Epikote® (Shell). The molecular weight of the polycondensates can vary within wide limits. In principle, any of the commercially available grades is suitable.

30 Other stabilizers which may be present in the polyoxymethylene molding compositions of the invention are one or more alkaline earth metal silicates and/or alkaline earth metal glycerophosphates in amounts of up to 2.0% by weight, preferably from 0.005 to 0.5% by weight and in particular from 0.01 to 0.3% by weight, based on the total weight of the molding compositions. Alkaline earth metals which have proven preferable for forming the silicates and glycerophosphates are calcium and, in particular, magnesium. Useful compounds are calcium glycerophosphate and preferably magnesium glycerophosphate and/or calcium silicate and preferably magnesium silicate. Particularly preferable alkaline earth silicates here are those described by the formula

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where:

Me is an alkaline earth metal, preferably calcium or in particular magnesium,

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x is a number from 1.4 to 10, preferably from 1.4 to 6, and

n is a number greater than or equal to 10, preferably from 0 to 8.

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The compounds are advantageously used in finely ground form. Particularly suitable products have an average particle size of less than 100 μm , preferably less than 50 μm .

15 Preference is given to the use of calcium silicates and magnesium silicates and/or calcium glycerophosphates and magnesium glycerophosphates. Examples of these may be defined more precisely by the following characteristic values:

20 Calcium silicate and magnesium silicate, respectively:

content of CaO and MgO, respectively: from 4 to 32% by weight, preferably from 8 to 30% by weight and in particular from 12 to 25% by weight,

ratio of SiO_2 to CaO and SiO_2 to MgO, respectively (mol/mol) :

25 from 1.4 to 10, preferably from 1.4 to 6 and in particular from 1.5 to 4,

bulk density: from 10 to 80 g/100 ml, preferably from 10 to 40 g/100 ml, and average particle size: less than 100 μm , preferably less than 50 μm and

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Calcium glycerophosphates and magnesium glycerophosphates, respectively:

content of CaO and MgO, respectively: above 70% by weight, preferably above 80% by weight,

35 residue on ashing: from 45 to 65% by weight,

melting point: above 300°C, and

average particle size: less than 100 μm , preferably less than 50 μm .

40 Preferred lubricants D) which may be present in the molding compositions of the invention are, in amounts of up to 5 [lacuna], preferably from 0.09 to 2 [lacuna] and in particular from 0.1 to 0.7 [lacuna], at least one ester or amide of saturated or unsaturated aliphatic carboxylic acids having from
45 10 to 40 carbon atoms, preferably from 16 to 22 carbon atoms, with polyols or with saturated aliphatic alcohols or amines

having from 2 to 40 carbon atoms, preferably from 2 to 6 carbon atoms, or with an ether derived from alcohols and ethylene oxide.

The carboxylic acids may be mono- or dibasic. Examples which may be mentioned are pelargonic acid, palmitic acid, lauric acid, margaric acid, dodecanedioic acid, behenic acid and, particularly preferably, stearic acid, capric acid and also montanic acid (a mixture of fatty acids having from 30 to 40 carbon atoms).

10 The aliphatic alcohols may be mono- to tetrahydric. Examples of alcohols are n-butanol, n-octanol, stearyl alcohol, ethylene glycol, propylene glycol, neopentyl glycol and pentaerythritol, and preference is given to glycerol and pentaerythritol.

15 The aliphatic amines may be mono- to tribasic. Examples of these are stearylamine, ethylenediamine, propylenediamine, hexamethylenediamine and di(6-aminoethyl)amine, and particular preference is given to ethylenediamine and hexamethylenediamine. Correspondingly, preferred esters and amides are glycerol

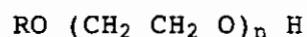
20 distearate, glycerol tristearate, ethylenediammonium distearate, glycerol monopalmitate, glycerol trilaurate, glycerol monobehenate and pentaerythritol tetrastearate.

It is also possible to use mixtures of different esters or amides or esters with amides combined, in any desired mixing ratio.

Other suitable compounds are polyether polyols and polyester polyols which have been esterified with mono- or polybasic carboxylic acids, preferably fatty acids, or have been etherified. Suitable products are available commercially, for example Loxiol® EP 728 from Henkel KGaA.

Preferred ethers derived from alcohols and ethylene oxide have the formula

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where R is alkyl having from 6 to 40 carbon atoms and n is an integer greater than or equal to 1.

40 R is particularly preferably a saturated C₁₆-C₁₈ fatty alcohol with n ≈ 50, obtainable commercially from BASF as Lutensol® AT 50.

The novel molding compositions may comprise from 0 to 5% by weight, preferably from 0.001 to 5% by weight, particularly preferably from 0.01 to 3% by weight and in particular from 0.05 to 1% by weight, of a melamine-formaldehyde condensate. This is

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preferably a crosslinked, water-insoluble precipitation condensate in finely divided form. The molar ratio of formaldehyde to melamine is preferably from 1.2:1 to 10:1, in particular from 1.2:1 to 2:1. The structure of condensates of this type and processes for their preparation are found in DE-A 25 40 207.

The novel molding compositions may comprise from 0.0001 to 1% by weight, preferably from 0.001 to 0.8% by weight, and in particular from 0.01 to 0.3% by weight, of a nucleating agent as component D).

Possible nucleating agents are any known compounds, for example melamine cyanurate, boron compounds, such as boron nitride, silica, pigments, e.g. Heliogen® Blue (copper phthalocyanine pigment; registered trademark of BASF Aktiengesellschaft), or branched polyoxymethylenes, which in these small amounts have a nucleating action.

Talc in particular is used as a nucleating agent and is a hydrated magnesium silicate of the formula $Mg_3[(OH)_2/Si_4O_{10}]$ or $MgO \cdot 4SiO_2 \cdot H_2O$. This is termed a three-layer phyllosilicate and has a triclinic, monoclinic or rhombic crystal structure and lamellar appearance. Other trace elements which may be present are Mn, Ti, Cr, Ni, Na and K, and some of the OH groups may have been replaced by fluoride.

Particular preference is given to the use of talc in which 100% of the particle sizes are $< 20 \mu m$. The particle size distribution is usually determined by sedimentation analysis and is preferably:

$< 20 \mu m$	100% by weight
$< 10 \mu m$	99% by weight
$< 5 \mu m$	85% by weight
$< 3 \mu m$	60% by weight
$< 2 \mu m$	43% by weight

Products of this type are commercially available as Micro-Talc I.T. extra (Norwegian Talc Minerals).

Examples of fillers which may be mentioned, in amounts of up to 50% by weight, preferably from 5 to 40% by weight, are potassium titanate whiskers, carbon fibers and preferably glass fibers. The glass fibers may, for example, be used in the form of glass wovens, mats, nonwovens and/or glass filament rovings or chopped glass filaments made from low-alkali E glass and having a

diameter of from 5 to 200 μm , preferably from 8 to 50 μm . After they have been incorporated, the fibrous fillers preferably have an average length of from 0.05 to 1 μm , in particular from 0.1 to 0.5 μm .

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Examples of other suitable fillers are calcium carbonate and glass beads, preferably in ground form, or mixtures of these fillers.

10 Other additives which may be mentioned are amounts of up to 50% by weight, preferably from 0 to 40% by weight, of impact-modifying polymers (also referred to below as elastomeric polymers or elastomers).

15 Preferred types of such elastomers are those known as ethylene-propylene (EPM) and ethylene-propylene-diene (EPDM) rubbers.

EPM rubbers generally have practically no residual double bonds,
20 whereas EPDM rubbers may have from 1 to 20 double bonds per 100 carbon atoms.

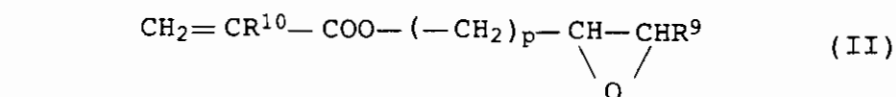
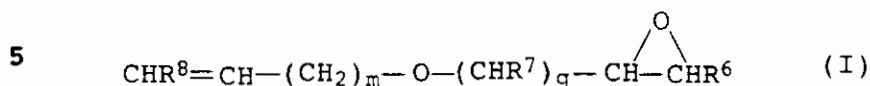
Examples which may be mentioned of diene monomers for EPDM rubbers are conjugated dienes, such as isoprene and butadiene,
25 non-conjugated dienes having from 5 to 25 carbon atoms, such as 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, 2,5-dimethyl-1,5-hexadiene and 1,4-octadiene, cyclic dienes, such as cyclopentadiene, cyclohexadienes, cyclooctadienes and dicyclopentadiene, and also alkenylnorbornenes, such as
30 5-ethylidene-2-norbornene, 5-butyldiene-2-norbornene, 2-methallyl-5-norbornene and 2-isopropenyl-5-norbornene, and tricyclobutenes, such as 3-methyl-tricyclo[5.2.1.0^{2,6}]-3,8-decadiene, or mixtures of these. Preference is given to 1,5-hexadiene-5-ethylidenenorbornene [sic] and dicyclopentadiene.
35 The diene content of the EPDM rubbers is preferably from 0.5 to 50% by weight, in particular from 1 to 8% by weight, based on the total weight of the rubber.

EPDM rubbers may preferably have also been grafted with other
40 monomers, e.g. with glycidyl (meth)acrylates, with (meth)acrylic esters, or with (meth)acrylamides.

Copolymers of ethylene with esters of (meth)acrylic acid are another group of preferred rubbers. The rubbers may also contain
45 monomers having epoxy groups. These monomers containing epoxy groups are preferably incorporated into the rubber by adding, to

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the monomer mixture, monomers having epoxy groups and the formula I or II



where R^6 to R^{10} are hydrogen or alkyl having from 1 to 6 carbon atoms, and m is an integer from 0 to 20, g is an integer from 0 to 10 and p is an integer from 0 to 5.

15 R^6 to R^8 are preferably hydrogen, where m is 0 or 1 and g is 1. The corresponding compounds are allyl glycidyl ether and vinyl glycidyl ether.

20 Preferred compounds of the formula II are acrylic and/or methacrylic esters having epoxy groups, for example glycidyl acrylate and glycidyl methacrylate.

The copolymers are advantageously composed of from 50 to 98% by weight of ethylene, from 0 to 20% by weight of monomers having epoxy groups, the remainder being (meth)acrylic esters.

Particular preference is given to copolymers made from

30 from 50 to 98% by weight, in particular from 55 to 95% by weight, of ethylene, in particular from 0.3 to 20% by weight of glycidyl acrylate, and/or

35 from 0 to 40% by weight, in particular from 0.1 to 20% by weight of glycidyl methacrylate, and

40 from 1 to 50% by weight, in particular from 10 to 40% by weight of *n*-butyl acrylate and/or 2-ethylhexyl acrylate.

Other preferred (meth)acrylates are the methyl, ethyl, propyl, 45 isobutyl and tert-butyl esters.

15

Besides these, comonomers which may be used are vinyl esters and vinyl ethers.

The ethylene copolymers described above may be prepared by
5 processes known per se, preferably by random copolymerization at high pressure and elevated temperature. Appropriate processes are well known.

Preferred elastomers also include emulsion polymers whose
10 preparation is described, for example, by Blackley in the monograph "Emulsion Polymerization". The emulsifiers and catalysts which may be used are known per se.

In principle it is possible to use homogeneously structured
15 elastomers or those with a shell construction. The shell-type structure is determined, inter alia, by the sequence of addition of the individual monomers. The morphology of the polymers is also affected by this sequence of addition.

20 Monomers which may be mentioned here, merely as examples, for the preparation of the rubber fraction of the elastomers are acrylates, such as n-butyl acrylate and 2-ethylhexyl acrylate, and corresponding methacrylates, and butadiene and isoprene, and also mixtures of these. These monomers may be copolymerized with
25 other monomers, such as styrene, acrylonitrile, vinyl ethers and with other acrylates or methacrylates, such as methyl methacrylate, methyl acrylate, ethyl acrylate or propyl acrylate.

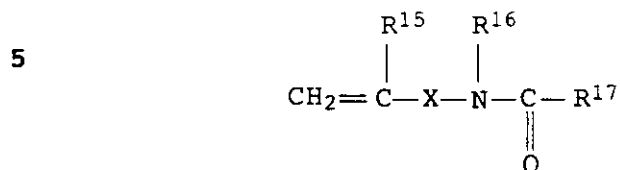
The soft or rubber phase (with a glass transition temperature of
30 below 0°C) of the elastomers may be the core, the outer envelope or an intermediate shell (in the case of elastomers whose structure has more than two shells). When elastomers have more than one shell it is also possible for more than one shell to be composed of a rubber phase.

35 If one or more hard components (with glass transition temperatures above 20°C) are involved, besides the rubber phase, in the structure of the elastomer, these are generally prepared by polymerizing, as principal monomers, styrene, acrylonitrile,
40 methacrylonitrile, α -methylstyrene, p-methylstyrene, or acrylates or methacrylates, such as methyl acrylate, ethyl acrylate or methyl methacrylate. Besides these, it is also possible to use relatively small proportions of other comonomers.

45 It has proven advantageous in some cases to use emulsion polymers which have reactive groups at their surfaces. Examples of groups of this type are epoxy, amino and amide groups, and also

16

functional groups which may be introduced by concomitant use of monomers of the formula



10 where:

R^{15} is hydrogen or C_1 - C_4 -alkyl,,

R^{16} is hydrogen, C_1 - C_8 -alkyl or aryl, in particular phenyl,

15 R^{17} is hydrogen, C_1 - C_{10} -alkyl, C_6 - C_{12} -aryl or $-\text{OR}^{18}$

R^{18} is C_1 - C_8 -alkyl or C_6 - C_{12} -aryl, if desired with substitution by O- or N-containing groups,

20 X is a chemical bond, C_1 - C_{10} -alkylene or C_6 - C_{12} -arylene, or



[lacuna]

The graft monomers described in EP-A 208 187 are also suitable
30 for introducing reactive groups at the surface.

Other examples which may be mentioned are acrylamide, methacrylamide and substituted acrylates or methacrylates, such as (N-tert-butylamino)ethyl methacrylate,
35 (N,N-dimethylamino)ethyl acrylate, (N,N-dimethylamino)methyl acrylate and (N,N-diethylamino)ethyl acrylate.

The particles of the rubber phase may also have been crosslinked. Examples of crosslinking monomers are 1,3-butadiene,
40 divinylbenzene, diallyl phthalate, butanediol diacrylate and dihydrodicyclopentadienyl acrylate, and also the compounds described in EP A 50 265.

It is also possible to use the monomers known as graft-linking
45 monomers, i.e. monomers having two or more polymerizable double bonds which react at different rates during the polymerization. Preference is given to the use of those compounds in which at

least one reactive group polymerizes at about the same rate as the other monomers, while the other reactive group (or reactive groups), for example, polymerize(s) significantly more slowly. The different polymerization rates give rise to a certain

- 5 proportion of unsaturated double bonds in the rubber. If another phase is then grafted onto a rubber of this type, at least some of the double bonds present in the rubber react with the graft monomers to form chemical bonds, i.e. the phase grafted on has at least some degree of chemical bonding to the graft base.

10

Examples of graft-linking monomers of this type are monomers containing allyl groups, in particular allyl esters of ethylenically unsaturated carboxylic acids, for example allyl acrylate, allyl methacrylate, diallyl maleate, diallyl fumarate
15 and diallyl itaconate, and the corresponding monoallyl compounds of these dicarboxylic acids. Besides these there is a wide variety of other suitable graft-linking monomers. For further details reference may be made here, for example, to US-A 4 148 846.

20

The proportion of these crosslinking monomers in component D) is generally up to 5% by weight, preferably not more than 3% by weight, based on D).

- 25 Some preferred emulsion polymers are listed below. Mention is made firstly of graft polymers with a core and with at least one outer shell and the following structure:

30

Monomers for the core	Monomers for the envelope
1,3-butadiene, isoprene, n-butyl acrylate, ethylhexyl acrylate or a mixture of these, where appropriate together with crosslinking monomers 35	Styrene, acrylonitrile, (meth)acrylates, where appropriate having reactive groups, as described herein

- 40 Instead of graft polymers whose structure has more than one shell it is also possible to use homogeneous, i.e. single-shell, elastomers made from 1,3-butadiene, isoprene and n-butyl acrylate or from copolymers of these. These products, too, may be prepared by concomitant use of crosslinking monomers or of monomers having
45 reactive groups.

The elastomers D) described may also be prepared by other conventional processes, e.g. by suspension polymerization.

Other suitable elastomers which may be mentioned are

5 thermoplastic polyurethanes, as described in EP-A 115 846, EP-A 115 847, and EP-A 117 664, for example.

It is, of course, also possible to use mixtures of the rubber types listed above.

10

The molding compositions of the invention may also comprise other conventional additives and processing aids. Merely by way of example, mention may be made here of additives for scavenging formaldehyde (formaldehyde scavengers), plasticizers, coupling
15 agents, and pigments. The proportion of additives of this type is generally within the range from 0.001 to 5% by weight.

As component D), the molding compositions of the invention may comprise, based on the total weight of components A) to D), from
20 0 to 2% by weight, preferably from 10 ppm to 1.5% by weight, and in particular from 0.001 to 1% by weight, of an alkali metal compound and/or alkaline earth metal compound.

Use may generally be made of any of the alkaline earth metal
25 and/or alkali metal cations, preference being given to lithium cations, sodium cations, potassium cations, and calcium cations.

For the purposes of the present invention, alkali metal compounds and/or alkaline earth metal compounds are inorganic or organic
30 salts which have give an alkaline reaction in aqueous solution or suspension.

Examples of inorganic salts are carbonates, hydrogen carbonates, hydroxides, oxides, and phosphates, particular preference being
35 given to alkali metal carbonates, such as potassium carbonate and sodium carbonate.

Examples of organic salts are alkoxides of C₂-C₁₂ alcohols, phenoxides, and salts of carboxylic acids having from 2 to 12
40 carbon atoms, particular preference being given to citrates, oxalates, and tartrates.

Particular preference is given to alkali metal hydroxides, in particular potassium hydroxide and sodium hydroxide, which are
45 preferably added in the form of an aqueous solution of from 10 to 70% strength, preferably from 40 to 60% strength, during the

preparation of the POM molding compositions, preferably being fed together with the carbon black.

- The thermoplastic molding compositions of the invention are
- 5 prepared by mixing the components in a manner known per se, and there is therefore no need to give any detailed information in this connection. It is advantageous to mix the components in an extruder.
- 10 In one preferred preparation method, component B), and also, where appropriate, component(s) C) and D) may preferably be applied at room temperature to the pellets of A) and then extruded.
- 15 In another preferred embodiment, B) is added to the thermoplastic melt A) by means of a solution or dispersion and/or emulsion, preferably an aqueous solution. This usually has a solids content of from 0.005 to 5%, preferably from 0.1 to 1%.
- 20 The thermoplastic molding compositions which may be used according to the invention have a balanced property profile. Moldings produced therefrom are suitable for high long-term service temperatures and are diesel-fuel-resistant. Moldings of this type are therefore particularly suitable for application as
- 25 moldings in a diesel engine or diesel engine compartment, or as bearing elements in the power train or steering area of a motor vehicle.

Examples

30

The components used were as follows:

Component A)

- 35 Polyoxymethylene copolymer made from 98.8% by weight of trioxane and 1.2% by weight of butanediol formal. The product comprised about 3% by weight of residual unconverted trioxane and 5% by weight of thermally unstable fractions. After degradation of the thermally unstable fractions, the copolymer had a melt volume
- 40 rate of 11 cm³/10 min (190°C, 2.16 kg applied weight, to ISO 1133).

Components B)

- 45 Component B/1

Zinc stearate (Liga 101 from Peter Greven Fett-Chemie).

20

Component B/2

Zinc soap B II from Baerlocher. According to the manufacturer's information, this is a dibasic zinc stearate produced by a double reaction.

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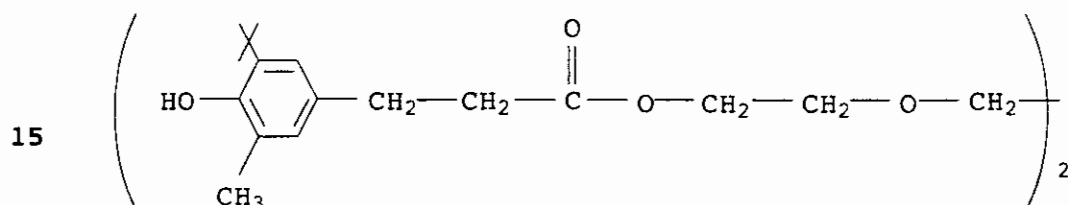
Component C

ZnO (zinc white indirectly from the company Wihart)

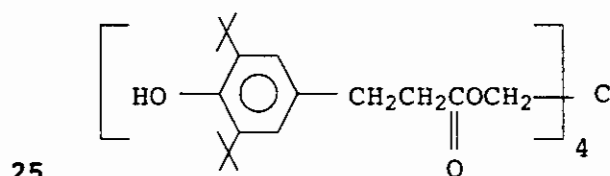
Component D

10

D/1: Irganox® 245 from the company Ciba-Geigy:



20 D/2:



Irganox® 1010 (Ciba Geigy)

D/3

30 Polyamide oligomer with a molecular weight of about 3000, prepared from caprolactam, hexamethylenediamine, adipic acid, and propionic acid (as molecular weight regulator) as in Ex. 5-4 of US-A 3 960 984 ("PA-dicapped")

35 D/4

Synthetic Mg silicate (Ambosol® from the company Société Nobel, Bozel, Puteaux) with the following properties:

40

Content of MgO:	≥ 14.8% by weight
Content of SiO ₂ :	≥ 59% by weight
Ratio SiO ₂ : MgO	2.7 mol/mol
Bulk density:	20-30 g/100 ml
Loss on ashing:	<25% by weight

45

D/5

A melamine-formaldehyde condensate as used in example 1 of DE-A 25 40 207.

5 D/6 Glycerol distearate (Loxiol® P 1206 from Cognis).

Each POM mixture comprised, as processing aid, 0.35% by weight of component D/1, 0.1% by weight of component D/2, 0.04% by weight of component D/3, 0.05% by weight of component D/4, 0.20% by weight of component D/5, and 0.15 % of component D/6.

To prepare the mixtures, component A was mixed with the amounts given in table 1 of components B/1 or B/2 and the amounts described above of components D/1, D/2, D/3, D/4, D/5, and D/6, and compounded in a twin-screw extruder at 220°C, devolatilized, and extruded and pelletized. Injection-molded test specimens were then produced at 190°C.

The resistance of polyacetal materials to hot diesel fuel was determined in the laboratory, using the change in weight of standardized test specimens. For better simulation of practical conditions and to shorten test times, use was made of test specimens of 1 mm thickness, obtained by comminuting the type 1A test specimens of 4 mm thickness provided in ISO 527 by a factor of 4 (these being given the abbreviated term "quarter ISO specimens" below).

The results of aging of the polyacetal test specimens in hot diesel fuel depend on a wide variety of parameters, in particular on the following:

- aging temperature
- shape of test specimen
- ratio number of test specimens/diesel fuel volume
- 35 - nature of diesel fuel (even with standardized reference fuels there are often considerable variations in the results observed from batch to batch)
- frequency of change of diesel fuel
- supply of air or oxygen.

40

It has been found that to obtain conclusive and useful results it is essential for specimens made from POM reference materials of known performance to be aged with test specimens. The POM reference material used was Ultraform® S 1320 003, which has been used successfully in the tank sector.

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The structure and parameters used for the examples and comparative examples below were as follows:

- autoclave manufactured from V2A stainless steel, volume
- 5 3 liters, half filled with reference fuel CEC-RF 90-A-92 from Haltermann, Hamburg, Germany
- per autoclave, 60 injection-molded quarter ISO specimens (15 from a particular batch of uncolored Ultraform S1320 003 and 15 from materials of each of three other formulations)
- 10 – aging temperature 100°C
- no change of fuel
- weight change observed by weighing, on each occasion, 5 test specimens from all of the formulations present in the autoclave, at room temperature; after removal from the
- 15 autoclave the test specimens were carefully freed from adherent residues of fuel, using absorbent paper, and cooled to room temperature
- at the juncture at which the test specimens manufactured from the reference material have lost 40% of their initial weight,
- 20 the weight loss for the other formulations present in the autoclave was likewise determined; the quotient calculated from weight loss reference material/weight loss formulation at this juncture gave the characteristic value k_1 for the material.

25

If $k_1 > 1$, the resistance of the reference fuel has been exceeded, the higher k_1 , the better the resistance.

The makeups of the molding compositions and the results of the

30 tests are given in the table.

Example	B/1 [% by weight]	B/2 [% by weight]	C [% by weight]	k_1
35 1	1	—	—	3.2
2	2	—	—	9.3
3	—	1	—	4.2
4	—	2	—	8.4
40 5	0.5	—	1	14
6	1	—	1	19

45

We claim:

1. The use of at least one zinc carboxylate B) for increasing
5 the diesel-fuel resistance of moldings made from
polyoxymethylenes A).
2. The use as claimed in claim 1, where the carboxylic radical
of component B) has from 2 to 44 carbon atoms.
- 10 3. The use as claimed in claim 1 or 2, where component B) is
composed of zinc stearate, zinc oleate, zinc montanate, zinc
palmitate, zinc behenate, zinc citrate, zinc propionate, zinc
oxalate, zinc succinate, zinc acetate, or a mixture of these.
- 15 4. The use as claimed in any of claims 1 to 3, where the
polyoxymethylenes may comprise up to 5% by weight of zinc
compounds C) other than B).
- 20 5. The use as claimed in any of claims 1 to 4, where the
polyoxymethylenes A) may also comprise from 0 to 70% by
weight, based on the molding compositions made from A) to D),
of other additives.
- 25 6. The use as claimed in any of claims 1 to 5, where the amount
of component B) is from 0.01 to 5% by weight, based on A) to
D).
- 30 7. The use as claimed in any of claims 1 to 6, where the amount
of component C) is from 0.01 to 5% by weight, based on A) to
D).
- 35 8. A diesel-fuel-resistant molding obtainable as claimed in any
of use claims 1 to 7.
9. A hot-diesel-fuel-resistant molding for the motor vehicle
engine, or an engine compartment element or bearing element
for the power train or steering area of a motor vehicle,
obtainable as claimed in any of use claims 1 to 7.
- 40 10. Fuel-extraction equipment, a rollover valve, a diesel fuel
line, a negative-pressure valve, a holder for a diesel fuel
pump, a pump housing, an internal part for a diesel fuel
pump, or in particular a rotor or stator in an electric
45 motor, obtainable as claimed in any of use claims 1 to 7.