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(54) POLYOXYMETHYLENE MOULDING COMPOSITIONS

(71) We, DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER, a body corporate organised under the laws of Germany of 9 Weissfrauenstrasse, 6 Frankfurt Main 1, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to moulding compositions based on a polyoxymethylene; a melamine-formaldehyde polycondensate, an antioxidant and, optionally, other conventional additives for polyoxymethylene moulding compositions.

German Offenlegungsschrift No. 1,694,097 describes polyoxymethylene moulding compositions which contain a polyoxymethylene, an antioxidant and from 0.05 to 5% of a water soluble melamine-formaldehyde polycondensate or melamine-dicyanodiamide-formaldehyde mixed polycondensate. Unfortunately, the polycondensates described in this publication are unstable at elevated temperatures and are at least partly split back into melamine and formaldehyde. As a result, some of the melamine escapes during processing. "Efflorescence" and discolouration occurs in the production of mouldings. The polycondensate are also at least partly extracted from finished mouldings by water.

The present invention provides a polyoxymethylene moulding composition comprising a polyoxymethylene, 0.001 to 2% by weight, based on the weight of the polyoxymethylene of an antioxidant and, optionally, at least one other conventional additive for a polyoxymethylene moulding composition, and 0.001 to 30% by weight, based on the total weight of the moulding composition, of a finely divided, crosslinked water-insoluble precipitation polycondensate produced from formaldehyde and melamine in a molar ratio of from 1.2:1 to 10.0:1.

Although infusible and insoluble in molten polyoxymethylenes, the precipitation polycondensates used as stabilisers in accordance with the invention, in conjunction with antioxidants, surprisingly bring about a considerable improvement in the thermal stability of polyoxymethylenes. They are also stable at elevated temperatures and give off hardly any volatile products. Mouldings do not "effloresce", nor are any coatings formed on processing machines. Since in addition no post-crosslinking occurs, soiling or discolouration of the moulding compositions according to the invention is virtually impossible, even in cases where they are worked into polymers containing releaseable formaldehyde.

The finely divided, crosslinked water insoluble precipitation polycondensates have specific surface areas of up to 250 m²/g and most of the primary particles are smaller than 1 µm and, in some cases, smaller than 0.1 µm in diameter. At the same time, they have a nucleating effect upon the polyoxymethylene melt. They are present in the polyoxymethylene moulding compositions according to the invention in quantities of from 0.001 to 30% by weight, preferably in quantities of from 0.01 to 5% by weight and more especially in quantities of from 0.08 to 1.0% by weight.

The precipitation polycondensates may be obtained in known manner by initially reacting formaldehyde and melamine in a molar ratio of from 1.2:1 to 10:1, preferably in a molar ratio of from 1.2:1 to 2.0:1, in aqueous solution or dispersion to form a soluble precondensate which is subsequently crosslinked and precipitated. Production of the soluble precondensate may be carried out within a wide concentration

range, for example from 5 to 45% by weight of polymer former. Condensation is carried out in a weakly alkaline medium at temperatures of preferably from 50°C to 80°C, the melamine passing into solution through addition of formaldehyde. The time which this takes is governed not only by the temperature but also largely by the molar ratio of formaldehyde to melamine. The larger this ratio, the more quickly the melamine passes into solution. At the temperatures indicated above, a homogeneous solution is obtained after 30 to 60 minutes. The precondensate is then acidified with vigorous stirring and heated for 1 to 2 hours to a temperature of from 70°C to 100°C. This results in further condensation, accompanied by crosslinking and precipitation of the crosslinked polycondensate. The crosslinking reaction may also be carried out by gradually introducing the precondensate into acidified hot water. Higher temperatures and longer condensation times than those quoted above may of course also be applied. This may be advisable in cases where the finely divided crosslinked polycondensates are not isolated, but instead are used in the form in which they accumulate, i.e. in the form of an aqueous dispersion. As a result, small quantities of water-soluble condensation products, which may still be present in the reaction mixture, are also crosslinked and become insoluble in water. Crosslinking is preferably carried out at pH values in the range from 5.0 to 6.9 and more especially at pH values in the range from 6.0 to 6.9.

Buffers may be added to make it easier to maintain the required pH-range. In cases where it is intended to use the finely divided crosslinked polycondensates in the form of a dispersion (i.e. in the form in which they accumulate after polycondensation), it may be advisable to keep the salt content of the dispersion as small as possible by using as little as possible, if any, additional base (besides melamine and, optionally, other basic co-condensable compounds) during the precondensation phase. Melamine dissolves in aqueous formaldehyde solution, even in the absence of an additional base, when the ratio of formaldehyde to melamine is no greater than about 4.

It is of particular advantage to add one or more protective colloids during the actual production of the precondensate, but especially before crosslinking. Suitable protective colloids are, for example, tragacanth, agar-agar, starch, methyl cellulose, polyvinyl alcohol, copolymers of acrylonitrile, sodium acrylate and acrylamide, copolymers of styrene and maleic acid, ethylene oxide-propylene oxide block copolymers, ethoxylated fatty alcohols, alkali metal salts of polyoxycarboxylic acids, of methacrylic acid-methacrylic acid methyl ester copolymers and of carboxymethylated starch. Particularly preferred protective colloids are gelatin and carboxymethyl cellulose (in the form of its sodium salt) and mixtures thereof. The protective colloids are best used in quantities of from 0.1 to 10% by weight and preferably in quantities of from 0.5 to 5.0% by weight, based on the weight of the formaldehyde and the melamine. The quantity used is governed not only by the effectiveness of the protective colloids, but above all by the concentration of the polymer formers. With increasing concentration, the precipitations become more coarse for the same amount of protective colloid (based on the polymer formers). This effect may be counteracted by increasing the amount of protective colloid. Even with concentrations of 20% of melamine and formaldehyde, the precipitation polycondensation reaction still gives very finely divided products in cases where particularly effective protective colloids, for example sodium carboxymethyl cellulose, are used. In some cases, the protective colloids are partly incorporated into the polycondensate.

The melamine participates almost completely in the crosslinking reaction. By contrast, the conversion of the formaldehyde drops with decreasing concentration and with increasing molar ratio of formaldehyde to melamine. For a concentration of 20% of polymer formers in the mixture and for a molar ratio of formaldehyde to melamine of 2, about 95% of the formaldehyde are incorporated whereas only about 70% are incorporated for a molar ratio of formaldehyde to melamine of 6.

In the finely divided, crosslinked water insoluble precipitation polycondensates used in accordance with the invention, up to 20 mol % of the melamine may be replaced by one or more other co-condensable substances. Examples of substances such as these are amidine compounds, such as dicyanodiamide or 2,5-diamino-1,3,4-triazole; urea and urea derivatives, for example ethylene urea; amides such as malonamide or isophthalic acid diamide; aliphatic amines, such as monoethanolamine or diethanolamine; aromatic amines such as *o*-toluidine, *p*-toluidine or *p*-phenylene diamine; aminoamides, such as *p*-aminobenzamide; phenol and sterically hindered phenols, such as 2,4-di-*tert*-butyl phenol; hydrazine and hydrazides, for example *N,N'*-bis-(3',5'-di-*tert*-butyl-4'-hydroxy phenyl)-propionyl hydrazine. Mixed polycondensates such as these are produced in the manner described using a starting mixture of a suitable com-

position. In some cases, longer condensation times and/or higher reaction temperatures may be necessary.

The precipitation polycondensates may be incorporated into the polyoxymethylene in the form of the dispersion obtained during their production, optionally after adjustment of the pH value to the required range, in the form of a centrifuge-moist product, in the form of a dispersion of the filtered and washed product, in the form of a dry powder, optionally after wet or dry grinding, in the form of a concentrate (master batch) after mixing and, optionally, homogenisation with a polyoxymethylene or any other polymer compatible with polyoxymethylene.

Incorporation into the polyoxymethylene may be carried out either in batches or, preferably, continuously in kneading machines, best at temperatures above the melting point of the polyoxymethylene. The addition is made directly or after mixing in suitable apparatus, optionally accompanied or followed by drying.

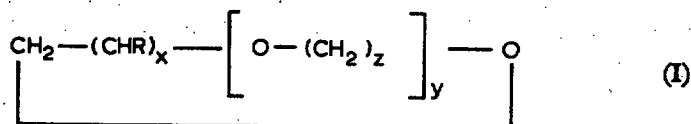
In some cases, it may be of advantage to add basic substances, for example amines, alkali metal hydroxides, alkaline earth metal hydroxides, salts, especially alkali metal and/or alkaline earth metal salts of weak monobasic or polybasic inorganic or organic acids, during incorporation of the precipitation polycondensates into the polyoxymethylenes. Additives such as these are preferably used in dissolved form. They may be added either to the precipitation polycondensate itself or to its dispersion, or alternatively may even be simultaneously mixed into the polyoxymethylene. The quantity of basic additives to be used is governed *inter alia* by the acid content not only of the precipitation polycondensates and other additives used but also of the polyoxymethylene itself, and also by the amount of acid formed, if any, during incorporation. It may readily be determined by tests. Excessive additions of basic substances adversely affect the stability of the finished moulding compositions, whereas with additions that are too small the degradation of any unstable fractions present does not take place quickly enough.

The polyoxymethylenes forming the main constituent of the moulding compositions according to the invention may be homopolymers of formaldehyde or trioxane or copolymers of trioxane. They may have a linear structure, although they may also be branched or crosslinked. They may be used either individually or in the form of mixtures.

In the context of the invention, homopolymers of formaldehyde or trioxane are polymers of which the terminal semi-acetal hydroxyl groups are chemically stabilised against degradation, for example by esterification or etherification. Copolymers of trioxane are copolymers of trioxane and at least one compound copolymerisable with trioxane.

Examples of compounds copolymerisable with trioxane are, for example, cyclic ethers with 3 to 5 ring members and preferably with 3 ring members; cyclic acetals different from trioxane, especially formals, with 5 to 11 and preferably with 5 to 8 ring members; and linear polyacetals, especially polyformals. The above-mentioned co-components are used in quantities of from 0.01 to 20% by weight, preferably in quantities of from 0.1 to 10% by weight and more especially in quantities of from 1 to 5% by weight.

Suitable comonomers are, in particular, compounds corresponding to the formula



in which R represents a hydrogen atom, an alkyl radical with 1 to 6 carbon atoms, preferably with 1, 2 or 3 carbon atoms which may be substituted by 1, 2 or 3 halogen atoms, preferably chlorine atoms, an alkoxymethyl radical containing 2 to 6 carbon atoms, preferably 2, 3 and 4 carbon atoms, a phenyl radical or a phenoxyethyl radical, x is an integer from 1 to 3, in which case y=0, y is an integer from 1 to 3, in which case x=0 and z=2, and z is an integer from 3 to 6, preferably 3 or 4, in which case x=0 and y=1.

Suitable cyclic ethers are, above all, epoxides, for example ethylene oxide, styrene oxide, propylene oxide and epichlorohydrin, also glycidyl ethers of monohydric or polyhydric alcohols or phenols.

Suitable cyclic acetals are, above all, cyclic formals of aliphatic or cycloaliphatic α,ω -diols with 2 to 8, preferably 2, 3 or 4 carbon atoms of which the carbon chain may be interrupted by an oxygen atom at intervals of 2 carbon atoms, for example glycol

formal (1,3-dioxolane), propane diol formal (1,3-dioxane), butane diol formal (1,3-dioxepane) and diglycol formal (1,3,6-trioxocane), also 4-chloromethyl-1,3-dioxolane, hexane diol formal (1,3-dioxonane) and butene diol formal (1,3-dioxo-5-cycloheptene). However, diformals, for example diglycerol diformal, are also suitable, especially for the production of terpolymers of trioxane.

Suitable linear polyacetals are both homopolymers and copolymers of the above-defined cyclic acetals and also linear condensates of aliphatic or cycloaliphatic α,ω -diols with aliphatic aldehydes or thioaldehydes, preferably formaldehyde. Homopolymers of cyclic formals of aliphatic α,ω -diols with 2 to 8 carbon atoms, preferably with 2, 3 or 4 carbon atoms, for example poly(1,3-dioxolane), poly(1,3-dioxane) and poly(1,3-dioxepane), are particularly suitable.

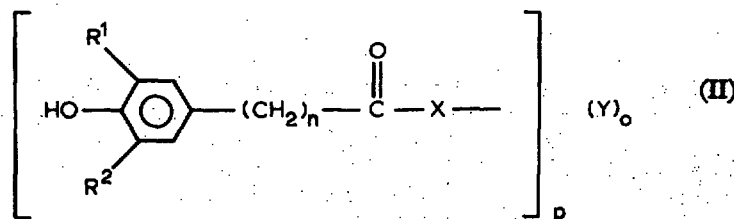
The values for the viscosity number of the polyoxymethylenes used in accordance with the invention (measured on a solution of the polymer in dimethyl formamide containing 2% by weight of diphenylamine at a temperature of 135°C in a concentration of 0.5 g/100 ml) should in general amount to at least 30 (ml/g). The crystallite melting points of the polyoxymethylenes are in the range from 140 to 180°C and preferably in the range from 150 to 170°C, whilst their densities are from 1.38 to 1.45 g · ml⁻¹, preferably from 1.40 to 1.43 g · ml⁻¹ (as measured in accordance with DIN 53 479).

The preferably binary or ternary trioxane copolymers used in accordance with the invention are obtained in known manner by polymerising the monomers in the presence of cationically active catalysts at temperatures in the range from 0°C to 150°C and preferably at temperatures in the range from 70°C to 140°C (cf. for example German Auslegeschrift No. 1,420,283).

The catalysts used are, for example, Lewis acids, for example boron trifluoride and antimony pentafluoride, and complex compounds of Lewis acids, preferably etherates, for example boron trifluoride diethyl etherate and boron trifluoride di-tert-butyl etherate. Other suitable catalysts are proton acids, for example perchloric acid, and salt-like compounds, for example triphenylmethyl hexafluorophosphate, triethyl oxonium tetrafluoroborate, acetyl perchlorate or esters of perchloric acid, for example methoxy methyl perchlorate or tert-butyl perchlorate. In order to regulate molecular weight, it is possible to use any substance which is known to act as a chain transfer agent in the polymerisation of trioxane. Polymerisation may be carried out in bulk, suspension or solution. In order to remove unstable fractions, the copolymers may be subjected to a thermal or hydrolytic controlled partial degradation down to primary terminal hydroxyl groups (cf. German Auslegeschriften 1,445,273 and 1,445,294). However, it is particularly preferred directly to use the crude copolymers and to carry out any degradation necessary during incorporation of the precipitation polycondensate.

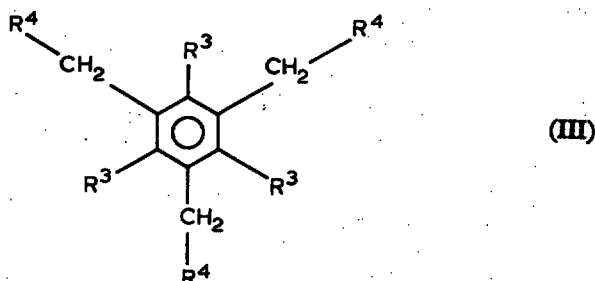
The homopolymers of formaldehyde or trioxane used in accordance with the invention are also obtained in known manner by catalytically polymerising the monomer (cf. for example German Auslegeschrift No. 1,037,705 and German Auslegeschrift No. 1,137,215).

For protection against the damaging effect of atmospheric oxygen, especially at elevated temperatures, the moulding compositions according to the invention must also contain an antioxidant. It is preferred to use phenolic antioxidants, above all those containing from 2 to 6 hydroxy phenyl radicals in the molecule. Particularly suitable compounds correspond to the formula

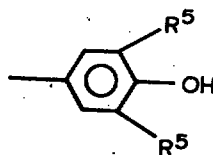


in which R¹ represents a methyl radical or a branched alkyl radical containing from 3 to 8 carbon atoms, R² represents a branched alkyl radical containing from 3 to 8 carbon atoms, X is an oxygen atom or the group —NH—, Y is a difunctional to hexafunctional, straight-chain or branched aliphatic radical of which the chain may be interrupted by a cyclohexylene or phenylene radical, oxygen or sulphur atoms, n=0 or an integer from 1 to 6, preferably 2, o=1 and p is an integer from 2 to 6 or,

where X=—NH—, o may even have the value zero whilst p=2. Other suitable compounds correspond to the formula:



in which each R³ is an alkyl radical with 1 to 4 carbon atoms, each R⁴ represents the radical



and each R⁵ is a branched alkyl radical containing from 3 to 8 carbon atoms. Examples of the antioxidants used in accordance with the invention are ethane diol - bis - 3-(3',5' - di - tert. - butyl - 4' - hydroxyphenyl) - propionate, 2,2 - dimethylpropane diol - bis - 3' - (3'',5'' - di - tert. - butyl - 4'' - hydroxyphenyl) - propionate, hexane diol - bis - (3,5 - di - tert. - butyl - 4 - hydroxybenzoate), N,N' - ethylene - bis - (3,5 - di - tert. - butyl - 4 - hydroxybenzamide). Particularly suitable antioxidants are N,N' - bis - 3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl) - propionyl hydrazine, hexane diol - bis - 3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl) - propionate, N,N-hexamethylene - bis - 3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl) - propionamide, tetrakis - [methylene - 3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl) - propionate] - methane and 1,3,5 - trimethyl - 2,4,6 - tris - (3',5' - di - tert. butyl - 4' - hydroxybenzyl) - benzene. The antioxidants are used in quantities of from 0.001 to 2% by weight and preferably in quantities of from 0.1 to 1.0% by weight, based on the weight of the polyoxymethylene.

Finally, the moulding compositions according to the invention may also contain other conventional additives for polyoxymethylene moulding compositions in the quantities normally used. Examples of additives such as these are other heat stabilisers, for example condensation products of carboxylic acid amides, such as oxalic acid, malonic acid, isophthalic acid, terephthalic acid diamide and trimesic acid triamide, substantially involatile s-triazine derivatives, such as Melam, Melem and Melon; UV-absorbers and light stabilisers, for example 2 - (2' - hydroxyphenyl) - benz - triazoles, 2,4 - bis - (2' - hydroxyphenyl) - 6 - alkyl - s - triazines, 4 - hydroxybenzophenones, 1,3 - bis - (2' - hydroxybenzoyl) - benzene derivatives and oxalic acid diamides, such as oxalic acid dianilide; fillers and/or reinforcing agents in powder, fibre, flake or any other suitable form, for example metals, metal alloys, metal oxides, carbonates and silicates, such as iron, aluminium, copper, aluminium oxide, titanium dioxide, precipitated silica, calcium carbonate, kaolin, mica, asbestos, or glass, carbon, organic polymers, such as cellulose, polyamides, polyesters, polyacrylonitrile, polyvinyl alcohol, polyurethanes, butadiene polymers, copolymers and terpolymers; lubricants, for example graphite, molybdenum disulphide, polytetrafluoroethylene; processing aids, for example fatty acid esters, amides and salts; nucleating agents, for example talcum antimony trioxide, finely divided pyrogenic silica, finely divided pyrogenic silica hydrophobised by reaction at the OH-groups or 2,4-diamino-6-hydroxy-s-triazine; pigments or dyes such as barium sulphate, lithopone, cadmium dyes, chromium oxide dyes, phthalocyanine dyes; acid acceptors such as polynuclear aromatic amines, basic oxides, hydroxides and salts; flameproofing agents, for example red phosphorus.

The moulding compositions according to the invention are produced by mixing the components, which are best largely present in powder or granulate form, followed by homogenisation. However, individual components may also be added in solution or in dispersed form either in the mixing apparatus or in the homogenising apparatus.

In cases where polyoxymethylenes, which have been produced by the bulk (co)polymerisation of trioxane in the form of relatively large blocks, are used, it is of considerable advantage to spray a dispersion of the precipitation polycondensate onto the still hot polymer immediately after polymerisation and before, during or after size reduction. In this way, the polymer is rapidly cooled and damage through oxidation prevented.

Mixing is normally carried out at room temperature, preferably at a temperature in the range from 15°C to 30°C whilst homogenisation is carried out in any heatable mixers, for example mixing rolls, calenders, kneaders or extruders, at a temperature above the crystallite melting point of the polyoxymethylene, i.e. at a temperature of from 150 to 250°C and preferably at a temperature of from 170 to 220°C. The cross-linked melamine-formaldehyde polycondensates undergo deagglomeration during mixing and above all during homogenisation. In the finished moulding composition, most of the particles of the crosslinked melamine-formaldehyde polycondensates have a size of less than 10 µm, preferably less than 5 µm and more especially less than 2 µm.

The invention is illustrated by the following Examples. The solidification time quoted in some of the Examples is determined by heating 3.0 mg samples at a rate of 40°C/minute to a temperature of 190°C in a differential scanning calorimeter (Perkin Elmer DSC 2), leaving them at that temperature for 5 minutes, subsequently cooling them to 149°C, again at a rate of 40°C/minute, and keeping them at that temperature. The time required to reach the maximum of the heat of crystallisation liberated, counting from the moment the temperature of 149°C is reached, is measured by stopwatch.

Production of a trioxane copolymer

A mixture of 2500 g of trioxane, 69 g of 1,3-dioxepane and 4 g of butylal is intensively mixed at 80°C with 15 ml of a solution of t-butylperchlorate in 1,2-dimethoxyethane (0.2 g/l) and then polymerised in an open vessel filled to a level of approximately 5 cm. After 4 minutes, the polymerisation reaction is terminated by grinding the hot polymer block and quenching the ground material in desalted water. The copolymer is then filtered off, washed and dried for 3 hours at 65°C/20 Torr.

Example 1

a) Production of a melamine-formaldehyde polycondensate

A mixture of 162 g of a 37% formaldehyde solution (2 moles of formaldehyde), 50 ml of desalted water and 2 g of a 50% aqueous solution of monoethanolamine dihydrogen phosphate is adjusted to pH 7.0 by the addition of 2N NaOH. 63 g of melamine (0.5 mole) are then added, followed by heating with stirring to 60°C. After the melamine has dissolved, the pH value amounts to 7.4. After 30 minutes, the precondensate is added dropwise with intensive stirring to a solution heated to 75°C of 2.5 g of sodium carboxymethyl cellulose (average degree of substitution 0.2, viscosity as a 2% by weight solution measured according to Hoeppler at 20°C: 29 cP) in 2000 ml of desalted water, of which the pH-value has been adjusted to 6.0 by the addition of 10% sulphuric acid. After 21 minutes, the dropwise addition is over, the temperature is then increased to 90°C and the condensation reaction continued for 1.5 hours at that temperature. The pH-value is then adjusted to 7.5 by the addition of 2N NaOH, after which the product is filtered while still hot, washed with water and acetone and the polycondensate dried at 80°C/20 Torr. Yield: 88 g of MF polycondensate.

b) Production of a moulding composition according to the invention:

1000 g of copolymer, 4 g of MF polycondensate, 4 g of hexane diol - bis - 3-(3',5' - di - tert. - butyl - 4' - hydroxyphenyl) - propionate and 6 ml of an aqueous 0.1% sodium carbonate solution are mixed in a fluid mixer. The mixture is then homogenised in a twin-screw extruder vented through 4 vents, extruded into strands, cooled in a water bath and finally granulated. The screw speed is 150 r.p.m., the mass temperature is in the range from 200 to 220°C in the first three zones, in the range from 210 to 215°C in the fourth zone and approximately 210°C before the die. The dried granulate undergoes a weight loss of 3.6% when heated in air for 2 hours to 220°C. The solidification time is 11.2 seconds. The stability of the product is considerably better and its solidification time considerably shorter than the corresponding values of a comparison product without the melamine-formaldehyde polycondensate.

Comparison Test 1

1000 g of copolymer and 4 g of hexane diol - bis - 3 - (3',5' - di - tert. - butyl-

4' - hydroxyphenyl) - propionate are mixed, homogenised, extruded and further processed in the same way as described in Example 1b). The comparison product undergoes a weight loss of 7.1% when heated in air for 2 hours to 220°C. The solidification time is 44.8 seconds.

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Example 2

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1000 g of copolymer and 1 g of MF polycondensate, produced in accordance with Example 1a) and 4 g of hexane diol - bis - 3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl) - propionate, and 2 ml of an aqueous 0.1% sodium carbonate solution are homogenised, extruded and further processed in the same way as described in Example 1b). The product undergoes a weight loss of 5.1% when heated in air for 2 hours to 220°C. The solidification time is 23.8 seconds.

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Example 3

a) Production of a melamine-formaldehyde polycondensate:

A precondensate is produced in the same way as described in Example 1a) and is run over a period of 22 minutes with vigorous stirring into a solution heated to 75°C and adjusted to pH 6 of 2.5 g of gelatin (DAB 7) in 1090 ml of desalted water. Further processing is carried out in the same way as described in Example 1a). Yield 101.5 g.

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b) Production of a moulding composition according to the invention:

1000 g of copolymer, 4 g of MF polycondensate, 4 g of hexane diol - bis - 3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl)propionate and 6 ml of an aqueous 0.1% sodium carbonate solution are homogenised, extruded and further processed in the same way as described in Example 1b).

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The product undergoes a weight loss of 2.3% when heated in air for 2 hours to 220°C. The solidification time is 24.0 seconds.

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Example 4

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a) Production of a melamine-formaldehyde polycondensate:

A mixture of 126 g of melamine (1 mole), 324 g of a 37% formaldehyde solution (4 moles of formaldehyde), 2000 ml of desalted water and 6 g of polyvinyl alcohol (degree of hydrolysis 98—99 mole percent, viscosity of a 4% aqueous solution in a Hoeppler viscosimeter DIN 53015 at 20°C: approximately 4 cP) is adjusted to pH 9 with 2N NaOH and stirred for 30 minutes at 75°C. A pH value of 6.0 is then adjusted by the addition of 10% sulphuric acid, the temperature is increased to 90°C after the beginning of precipitation and the polycondensation reaction continued at that temperature for a period of 1.5 hours. Further working up is carried out in the same way as described in Example 1a). Yield: 190 g.

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b) Production of a moulding composition according to the invention:

1000 g of copolymer, 4 g of MF polycondensate, 4 g of hexane diol - bis - 3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl)propionate and 1 ml of an aqueous 0.1% sodium carbonate solution are homogenised, extruded and further processed in the same way as described in Example 1b).

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The product undergoes a weight loss of 2.2% when heated in air for 2 hours to 220°C. The solidification time is 17.8 seconds.

Example 5

a) Production of a melamine-formaldehyde polycondensate

A mixture of 126 g of melamine (1 mole), 324 g of a 37% formaldehyde solution (4 moles of formaldehyde), 2000 ml of desalted water, 0.5 g of polyvinyl alcohol (degree of hydrolysis 98—99 mole percent, viscosity of a 4% aqueous solution in a Hoeppler viscosimeter DIN 53 015 at 20°C; approximately 4 cP) and 0.5 g of an ethylene oxide-propylene oxide block copolymer (MW 4100) of 50% by weight of polyoxyethylene and 50% by weight of polyoxypropylene (produced by the addition of ethylene oxide to polyoxypropylene of MW 2050) is adjusted to pH 9 with 2N NaOH and stirred for 30 minutes at 75°C. Precipitation and working up are carried out in the same way as in Example 4a). Yield: 185 g.

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b) Production of a moulding composition according to the invention:

1000 g of copolymer, 4 g of MF polycondensate, 4 g of hexane diol - bis - 3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl)propionate and 1 ml of an aqueous 0.1% sodium carbonate solution are homogenised, extruded and further processed in the same way as described in Example 1b).

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The product undergoes a weight loss of 3.1% when heated in air for 2 hours to 220°C. Its solidification time is 36.4 seconds.

Example 6

a) Production of a melamine-formaldehyde polycondensate:

A mixture of 126 g of melamine (1 mole), 130 g of a 37% formaldehyde solution (1.6 moles of formaldehyde), 713 ml of desalted water, 3.24 g of gelatin (DAB 7) and 0.8 g of sodium carboxymethyl cellulose (average degree of substitution 0.7, viscosity as a 2% solution, as measured according to Hoeppler at 20°C: 29 cP) is adjusted to pH 8.5 by the addition of 2 ml of 10% KOH, followed by heating with stirring for 30 minutes to 75°C. The pH-value, which is now 8.0, is lowered to 6.5 by the addition of 4 ml of 10% sulphuric acid. After 7 minutes, the mixture becomes clouded. The temperature is increased to 90°C and condensation continued for 1.5 hours. Thereafter, the suspension has a pH-value of 5.4. The pH is adjusted to 7.5 by the addition of 2.5 ml of 10% KOH, after which the product is filtered while hot, washed until neutral and dried at 80°C/20 Torr. Yield: 157 g.

b) Production of a moulding composition according to the invention:

1000 g of copolymer, 4 g of MF polycondensate, 4 g of N,N'-hexamethylene-bis-3-(3',5'-di-tert.-butyl-4'-hydroxyphenyl)propionamide and 4 ml of an aqueous 0.1% sodium carbonate solution are homogenised, extruded and further processed in the same way as described in Example 1b). The product obtained undergoes a weight loss of 0.91% when heated in air for 2 hours to 220°C. Its stability is far better than that of a comparison product without the melamine-formaldehyde polycondensate.

Comparison Test 2

1000 g of copolymer and 4 g of N,N'-hexamethylene-bis-3-(3',5'-di-tert.-butyl-4'-hydroxyphenyl)propionamide are homogenised, extruded and further processed in the same way as described in Example 1b). The comparison product undergoes a weight loss of 9.4% when heated in air for 2 hours to 220°C.

Example 7

a) Production of a melamine-formaldehyde polycondensate:

A mixture of 63 g of melamine (0.5 mole), 162 g of a 37% formaldehyde solution (2 moles of formaldehyde) and 1500 ml of desalted water is heated with stirring for 30 minutes to 60°C. It then has a pH-value of 7.1. After the temperature has been increased to 75°C, the precondensate is mixed with intensive stirring with a solution of 5 g of gelatin (DAB 7) in 450 ml of desalted water which also has a temperature of 75°C. The mixture has a pH-value of 6.35. After 3 to 4 minutes, the mixture turns cloudy, the temperature is increased to 95°C and the polycondensation reaction continued for 1.5 hours. Thereafter the suspension has a pH-value of 5.5. A pH of 7.5 is adjusted by the addition of 2 ml of 10% KOH, after which the product is filtered, washed until neutral and dried at 80°C/20 Torr. Yield: 92.5 g.

b) Production of a moulding composition according to the invention:

1000 g of copolymer, 8 g of MF polycondensate, 4 g of hexane diol-bis-3-(3',5'-di-tert.-butyl-4'-hydroxyphenyl)propionate and 10 ml of an aqueous 0.1% sodium carbonate solution are homogenised, extruded and further processed in the same way as in Example 1b). The product obtained undergoes a weight loss of 2.4% when heated in air for 2 hours to 220°C. Its solidification time is 17.4 seconds.

Example 8

a) Production of a melamine-formaldehyde polycondensate:

A mixture of 189 g of melamine (1.5 moles), 243 g of a 37% formaldehyde solution (3.0 moles of formaldehyde) and 750 ml of desalted water, is heated with stirring for 30 minutes to 60°C, after which it has a pH-value of 7.2. After the temperature has been increased to 75°C, the precondensate is mixed with a solution of 5.6 g of gelatin (DAB 7) and 1.4 g of sodium carboxymethyl cellulose (average degree of substitution 0.7, viscosity as a 2% solution, measured according to Hoeppler at 20°C: 29 cP) in 510 ml of desalted water, which also has a temperature of 75°C. The mixture has a pH-value of 6.8. After 8 to 9 minutes, the mixture clouds, the temperature is then increased to 95°C and the polycondensation reaction continued for another 1.5 hours. Thereafter the suspension has a pH-value of 6.5. The weight of the mixture is then adjusted to exactly 1600 g by the addition of desalted water, after which the mix-

ture is divided, one half being worked up in the same way as in Example 7a). Yield, based on the mixture as a whole: 248 g. Concentration of MF polycondensate in the suspension: 15.5%.

b) Production of a moulding composition according to the invention:

1000 g of copolymer, 25.8 g of a suspension of the MF polycondensate (15.5%), 4 g of hexane diol - bis - 3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl) - propionate and 2 ml of an aqueous 0.1% sodium carbonate solution are homogenised, extruded and further processed in the same way as in Example 1b). The product undergoes a weight loss of 2.7% when heated in air for 2 hours to 220°C.

Example 9

a) Production of a melamine-formaldehyde polycondensate:

A mixture of 126 g of melamine (1 mole), 3.05 g of ethanolamine (0.05 mole), 108 g of 37% formaldehyde solution (1.33 mole of formaldehyde) and 600 ml of desalted water is heated with stirring for 30 minutes to approximately 60°C, after which it has a pH-value of 7.7. After the temperature has been increased to 75°C, the precondensate is mixed with a solution of 3.4 g of gelatin (DAB 7) and 0.85 g of sodium carboxymethyl cellulose (average degree of substitution 0.7, viscosity as a 2% solution, measured according to Hoeppler at 20°C: 29 cP) in 185 ml of desalted water, which also has a temperature of approximately 75°C. The pH-value of the mixture is reduced from 7.4 to 6.34 by the addition with vigorous stirring of 15 ml of 10% sulphuric acid. 6 minutes later, the mixture turns cloudy. The polycondensation reaction is continued for 1.5 hours at about 90 to 95°C. The pH-value is then raised from 5.95 to 7.3 by the addition of 10 ml of 10% KOH, followed by filtration, washing until neutral and drying. Yield: 151 g.

b) Production of a moulding composition according to the invention:

1000 g of copolymer, 4 g of MF polycondensate, 4 g of N,N' - hexamethylene-bis - 3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl)propionamide and 3 ml of an aqueous 0.1% sodium carbonate solution are homogenised, extruded and further processed in the same way as in Example 1b). The product obtained undergoes a weight loss of 0.8% when heated in air for 2 hours to 220°C.

Example 10

a) Production of a melamine-formaldehyde polycondensate:

A mixture of 126 g of melamine (1 mole), 108 g of a 37% formaldehyde solution (1.33 moles of formaldehyde) and 500 ml of desalted water is heated with stirring for 30 minutes to about 75°C, and then mixed with a solution of 3.15 g of gelatin (DAB 7) and 0.8 g of sodium carboxymethyl cellulose (average degree of substitution 0.7, viscosity as a 2% solution, measured according to Hoeppler at 20°C: 29 cP) in 230 ml of water which has substantially the same temperature. A pH-value of 6.4 is adjusted by the addition of 2 ml of 10% sulphuric acid. The temperature is then increased to 90-95°C and polycondensation continued for 1.5 hours. The pH-value is raised from 5.35 to 7.8 by the addition of 3 ml of 10% KOH, followed by filtration, washing until neutral and drying. Yield 157 g.

b) Production of a moulding composition according to the invention:

1000 g of copolymer, 4 g of MF polycondensate, 4 g of tetrakis - [methylene-3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl)propionate] - methane and 2 ml of a 0.1% sodium carbonate solution, are homogenised, extruded and further processed in the same way as in Example 1b). The product obtained undergoes a weight loss of 3.3% when heated in air for 2 hours to 220°C. Its stability is significantly better than that of a comparison product without the melamine-formaldehyde polycondensate.

Comparison Test 3

1000 g of copolymer and 4 g of tetrakis - [methylene - 3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl) - propionate] - methane are homogenised, extruded and further processed in the same way as in Example 1b). The comparison product undergoes a weight loss of 6.3% when heated in air for 2 hours to 220°C.

Example 11

a) Production of a melamine-formaldehyde polycondensate:

A mixture of 101 g of melamine (0.8 mole), 390 g of a 37% formaldehyde solution (4.8 moles of formaldehyde), 500 ml of desalted water and 0.5 ml of 10%

KOH is stirred under heat, kept at 60°C for about 30 minutes and then tempered at 75°C. The precondensate is then mixed with a solution, adjusted to substantially the same temperature, of 4.9 g of gelatin (DAB 7) and 1.25 g of sodium carboxymethyl cellulose (average degree of substitution 0.7, viscosity as a 2% solution, measured according to Hoeppler at 20°C: 29 cP) in 490 ml of desalted water. The mixture which has a pH of 6.25 becomes cloudy after 6 minutes. The polycondensation reaction is continued for 1.5 hours at 90 to 95°C. During this time, the pH value drops to 5.85. The product is then filtered while hot, washed with desalted water and dried. Yield 173 g.

b) Production of a moulding composition according to the invention:

1000 g of copolymer, 4 g of MF polycondensate, 4 g of 1,3,5 - trimethyl-2,4,6 - tris - (3',5' - di - tert. - butyl - 4' - hydroxybenzyl) - benzene and 4 ml of a 0.1% sodium carbonate solution are homogenised, extruded and further processed in the same way as in Example 1b). The product obtained undergoes a weight loss of 3.1% when heated in air for 2 hours to 220°C. Its stability is far better than that of a comparison product without the melamine-formaldehyde polycondensate.

Comparison Test 4

1000 g of copolymer and 4 g of 1,3,5 - trimethyl - 2,4,6 - tris - (3',5' - di - tert. - butyl - 4' - hydroxybenzyl) - benzene are homogenised, extruded and further processed in the same way as in Example 1b). The comparison product undergoes a weight loss of 11.5% when heated in air for 2 hours to 220°C.

Example 12

a) Production of a melamine-formaldehyde polycondensate:

A mixture of 252 g of melamine (2.0 moles), 211 g of a 37% formaldehyde solution (2.6 moles of formaldehyde) and 1000 ml of desalted water is heated while stirring for 30 minutes (final temperature 90°C), after which it has a pH-value of 7.5. The precondensate is then mixed with a solution heated to about 60—70°C of 6.6 g of gelatin (DAB 7), 1.65 g of sodium carboxymethyl cellulose (average degree of substitution 0.7, viscosity as a 2% solution, measured according to Hoeppler at 20°C: 29 cP), 3.8 ml of 10% sulphuric acid and 515 ml of desalted water. The mixture has a pH-value of 6.5. The mixture turns cloudy after about 5 minutes. The polycondensation reaction is continued for 1.5 hours at temperatures of from 90°C to 100°C. Thereafter the suspension, which has a pH-value of 5.8, is adjusted to pH 8.1 by the addition of 5 ml of 10% KOH and filtered while hot. The polycondensate is thoroughly washed and then dried. Yield 296 g.

b) Production of a moulding composition according to the invention:

6000 g of copolymer, 24 g of MF polycondensate, 24 g of hexane diol - bis - 3-(3',5' - di - tert. - butyl - 4' - hydroxyphenyl)propionate and 24 ml of an aqueous 0.1% sodium carbonate solution are mixed, extruded and further processed in the same way as in Example 1b). After extrusion, the coating which has formed over the inspection window of the first vacuum socket is weighed, in addition its nitrogen content is determined. Weight of the coating: 9.2 mg. Nitrogen content: 0.0%.

Volatile but readily condensable products in the granulate are determined as follows: 10 g of granulate are heated for 2 hours in a sublimation apparatus at approximately 0.8 Torr in an aluminium block heated to 250°C. The internal temperature reaches about 217 to 220°C. The coating formed over the cooling finger is weighed and tested for nitrogen. Weight of the coating: 9.4 mg; nitrogen content 0.55%.

The solidification behaviour of the granulate is determined by the described DSC method. Solidification time: 35.0 seconds.

Comparison Test 5

a) Production of a water-soluble melamineformaldehyde polycondensate:

Following the procedure of Example 2 of DT-OS 1,694,097, 10 g of melamine, 2 g of triethanolamine and 6 ml of 30% formalin are boiled for 30 minutes in 150 ml of water. The solids content of the aqueous solution, determined by drying for 5 hours at 65°C/20 Torr amounts to 7.9%.

b) Production of a moulding composition using the polycondensate described above:

2000 g of copolymer are mixed with 101 g of an aqueous solution of the melamine-formaldehyde polycondensate (corresponding to 8 g of polycondensate), and the

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water is removed by drying at approximately 65°C/20 Torr. 8 g of hexane diol - bis-3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl)propionate are then mixed in. Mixing and subsequent extrusion and also further processing are carried out in the same way as in Example 1b).

5 After extrusion, the coating which has formed over the inspection window of the first vacuum socket is weighed, in addition its nitrogen content is determined. Weight of the coating: 95 mg; nitrogen content 64.0%.

10 The determination of volatile constituents in 10 g of granulate is carried out in the same way as in Example 12b). Weight of the coating on the cooling finger: 18.3 mg; nitrogen content: 26.6%.

The solidification behaviour of the granulate is determined by the DSC method described above. Solidification time: 49.8 seconds.

Comparison of the results of Example 12 and Comparison Test 5:

15		Melamine sublimate from 1 kg of POM on extruder inspection window	Melamine sublimate from 10 g of POM (sublimation test)	Solid time (secs.)	15
	Example 12	0.0 mg	0.08 mg	35.0	
	Comparison Test 5	45.6 mg	7.30 mg	49.8	

20 The quantities quoted are calculated from the nitrogen content of the coating. 20

WHAT WE CLAIM IS:—

25 1. A polyoxymethylene moulding composition comprising a polyoxymethylene, 0.001 to 2% by weight, based on the weight of the polyoxymethylene, of an anti-oxidant and 0.001 to 30% by weight, based on the total weight of the moulding composition, of a finely divided crosslinked water-insoluble precipitation polycondensate produced from formaldehyde and melamine in a molar ratio of from 1.2:1 to 10.0:1. 25

30 2. A polyoxymethylene moulding composition as claimed in Claim 1 also containing at least one other conventional additive for a polyoxymethylene moulding composition. 30

3. A modification of a polyoxymethylene moulding composition as claimed in Claim 1 or 2, wherein up to 20 mole percent of the melamine in the finely divided crosslinked water-insoluble precipitation polycondensate is replaced by other co-condensable substances. 30

35 4. A polyoxymethylene moulding composition substantially as hereinbefore described with particular reference to any of the Examples. 35

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water is removed by drying at approximately 65°C/20 Torr. 8 g of hexane diol - bis-3 - (3',5' - di - tert. - butyl - 4' - hydroxyphenyl)propionate are then mixed in. Mixing and subsequent extrusion and also further processing are carried out in the same way as in Example 1b).

After extrusion, the coating which has formed over the inspection window of the first vacuum socket is weighed, in addition its nitrogen content is determined. Weight of the coating: 95 mg; nitrogen content 64.0%.

The determination of volatile constituents in 10 g of granulate is carried out in the same way as in Example 12b). Weight of the coating on the cooling finger: 18.3 mg; nitrogen content: 26.6%.

The solidification behaviour of the granulate is determined by the DSC method described above. Solidification time: 49.8 seconds.

Comparison of the results of Example 12 and Comparison Test 5:

	Melamine sublimate from 1 kg of POM on extruder inspection window	Melamine sublimate from 10 g of POM (sublimation test)	Solid time (secs.)
Example 12	0.0 mg	0.08 mg	35.0
Comparison Test 5	45.6 mg	7.30 mg	49.8

The quantities quoted are calculated from the nitrogen content of the coating.

WHAT WE CLAIM IS:—

1. A polyoxymethylene moulding composition comprising a polyoxymethylene, 0.001 to 2% by weight, based on the weight of the polyoxymethylene, of an anti-oxidant and 0.001 to 30% by weight, based on the total weight of the moulding composition, of a finely divided crosslinked water-insoluble precipitation polycondensate produced from formaldehyde and melamine in a molar ratio of from 1.2:1 to 10.0:1.

2. A polyoxymethylene moulding composition as claimed in Claim 1 also containing at least one other conventional additive for a polyoxymethylene moulding composition.

3. A modification of a polyoxymethylene moulding composition as claimed in Claim 1 or 2, wherein up to 20 mole percent of the melamine in the finely divided crosslinked water-insoluble precipitation polycondensate is replaced by other co-condensable substances.

4. A polyoxymethylene moulding composition substantially as hereinbefore described with particular reference to any of the Examples.

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