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COMPLETE SPECIFICATION

Copolymers and Process for Making them

We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, vormalig Meister Lucius & Brüning, a Company recognised by German law, of 6230 Frankfurt (M)-Hoechst, 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:—

10 This invention relates to copolyacetals.

Polyoxymethylenes of high molecular weight which are suitable for the manufacture of plastics can be obtained by anionic polymerisation of formaldehyde or cationic polymerisation of trioxan, the cyclic trimer of formaldehyde. High-polymer polyoxymethylene constitutes a polyacetal with unstable terminal hemiformal groups. It is thermally decomposed, except for a small proportion, by a so-called zipper reaction in which monomer formaldehyde is formed. In this reaction, a new unstable terminal hemiformal group is formed at the macromolecule on the degradation of a hemiformal molecule.

25 To convert such polyoxymethylenes with terminal hemiformal groups into technically useful plastics it is necessary to stabilise the terminal groups. For this purpose, the terminal groups may, for example, be esterified at 160° C with acetic anhydride. After the esterification, the excess of acetic anhydride and the acetic acid formed must be removed from the polymer by complicated purifying processes. Moreover, the polymers thus stabilised are unstable towards alkalis since they are saponified by them. Furthermore, when a molecule chain which has been stabilised by esterification of the terminal groups is thermally split in the interior part of the chain, a zipper reaction sets in.

40 The latter applies also to products with etherified terminal group. When the terminal groups are etherified it is, moreover, difficult to adjust the polymer to a desired molecular weight. More favourable results in the

stabilisation of polyoxymethylenes are obtained by copolymerising trioxan, for example, with saturated cyclic ethers or cyclic formals such, for example, as ethylene oxide or diethylene glycol formal.

To stabilise the polymers, the unstable terminal groups are decomposed by hydrolysis after the polymerisation, the zipper reaction stopping at the comonomer molecules.

When a molecule chain is thermally split in the processing of the polymer, the decomposition of the chain stops at the next comonomer molecule so that the said copolymers have a much better thermostability than homopolymers of oxymethylene.

As catalysts for the manufacture of the above mentioned copolymers, boron fluoride or its derivatives, for example, etherates, or diazonium fluoroborates are advantageously used.

Copolymers of acetals, especially copolymers having a high content of polyoxymethylene units of high molecular weight and high stability, are successfully used for the manufacture of injection moulded articles which may be used, for example, at elevated temperatures. High molecular weight polymers of the said type that can be used for extrusion processes can be obtained by the known process only with great difficulty and only with the use of extremely pure trioxan.

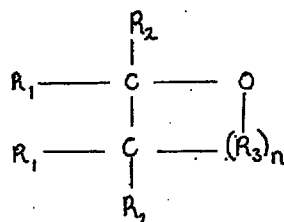
The present invention provides copolyacetals of (A) trioxan, (B) a cyclic ether and/or a cyclic formal and (C) a bifunctional organic compound, especially a diglycidyl ether of an aliphatic diol and/or a diglycidyl ether of a cycloaliphatic diol. Advantageously, the component (A) constitutes from 99.89 to 89 per cent by weight, component (B) constitutes from 0.1 to 10 per cent by weight, and component (C) constitutes from 0.01 to 1 per cent by weight, the percentages being calculated on the total weight of the monomer mixture.

The invention also provides a process for

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the manufacture of the new copolyacetals, which comprises copolymerising the components (A), (B) and (C) by a method known to be suitable for the production of trioxan copolymers. The term "known" method is used herein to mean one known in the literature of the subject.

More especially, the invention provides terpolymers which are distinguished by particularly valuable properties, for example, a high molecular weight and good mechanical properties, and that are obtainable by copolymerising (A) trioxan, (B) a cyclic ether and/or cyclic formal of the formula



in which R_1 and R_2 each represent a hydrogen atom or a lower alkyl radical which may be substituted by halogen, R_3 stands for methylene, oxymethylene, alkyl, halo-alkyl, a substituted methylene radical or an oxymethylene radical substituted by alkyl or halo-alkyl and n is zero, 1, 2 or 3, and (C) a bifunctional compound such as, for example, diglycidyl ether, a diether of 2 mols of glycidide and 1 mol of formaldehyde or a diether of 2 mols of glycidide and 1 mol of an aliphatic diol with 2 to 8 carbon atoms, advantageously 2 to 4 carbon atoms, or a cycloaliphatic diol with 4 to 8 carbon atoms.

As cyclic ethers (B) of the above formula there may advantageously be used, for example, ethylene oxide, dioxolan and diethylene glycol formal. There may also be used dioxan, trimethylene oxide, tetramethylene oxide, pentamethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide, 1,3-butylene oxide, 2,2-di-(chloromethyl)-1,3-propylene oxide. As the bifunctional compound (C) there are preferably used diglycidyl ethers of ethylene glycol, 1,4-butane-diol, 1,3-butane-diol, cyclobutane-1,3-diol, 1,2-propane-diol. Further suitable compounds are the diglycidyl ethers of cyclohexane-1,4-diol and 2 - dimethyl - 4 - dimethyl - cyclobutane-1,3-diol.

By copolymerising according to the process of the invention the components trioxan (A), cyclic ether and/or cyclic formal (B) and one or more of the above mentioned bifunctional compounds (C), for example diglycidyl ether, especially a diether of 2 mols of glycidide and 1 mol of an aliphatic diol with 2 to 4 carbon atoms, in a ratio of 99.89 to 89.0% by weight of trioxan, 0.1 to 10% by weight of cyclic ether and 0.01 to 1% by

weight of bifunctional compound, the percentage figures being calculated on the weight of the total mixture, terpolymers are obtained which are distinguished, in addition to the other properties already mentioned, particularly by the fact of being colourless and by a particularly good extrudability, a processing property very desired in practice. The products are particularly valuable owing to their high molecular weight which is characterised by a melt index within the range of 0.1 to 2.0, determined according to ASTM—D 1238—52 T.

Another advantage of the process of the invention over the previously proposed processes is that it enables high molecular weight products of low melt index to be obtained even with the use of less pure trioxan whereas when in the previous processes such trioxan is used as starting product without the addition of bifunctional compound (C) in accordance with the invention only copolymers having a melt index above 2.0 are obtained.

The polymerisation may be carried out according to known methods, that is in substance, solution or suspension, while using the above mentioned quantitative proportions of the monomers. As solvents there may advantageously be used inert aliphatic or aromatic hydrocarbons, halogenated hydrocarbons or ethers. The polymerisation in substance takes a particularly smooth course.

In some cases it may be advantageous to use the following quantitative proportions: 99.85 to 89.5% by weight of trioxan, 0.1 to 10% by weight of cyclic ether or cyclic formal, and 0.05 to 0.5% by weight of diglycidyl ether, the percentage figures being calculated on the total weight of the monomer mixture.

The molecular weight may be adjusted by means of acetals, for example formaldehyde dimethyl acetal.

The polymerisation is advantageously carried out at temperatures at which trioxan does not crystallise out, that is depending on the solvent used at a temperature within the range of -50 to $+100^\circ\text{C}$ and in the absence of a solvent at a temperature within the range of $+20$ to $+100^\circ\text{C}$.

As catalysts all substances may be used which are capable of initiating a cationic polymerisation, for example, organic or inorganic acids, acid halides and advantageously Lewis acids. Of the latter, boron fluoride and its complex compounds, for example etherates of boron fluoride, are advantageously used. Diazonium fluoroborates are particularly advantageous.

The concentration of the catalyst may vary within wide limits. It depends on the nature of the catalyst and on the intended molecular weight of the terpolymer. The concentration of the catalyst may be within the range of 0.0001 to 1% by weight, calculated on the total monomer mixture, and is advantageously

within the range of 0.001 to 0.1% by weight.

Since the catalysts to be used in the process of the invention tend to decompose the polymer, the catalyst is advantageously neutralised immediately after the polymerisation, for example with ammonia or methanolic or acetic amine solutions.

The unstable terminal hemiacetal groups may be removed in the manner known from other copolymers. Advantageously, the polymer is suspended in aqueous ammonia at temperatures within the range of 100 to 200° C, if desired in the presence of a swelling agent such, for example, as methanol or *n*-propanol. Alternatively, the polymer is dissolved in an alkaline medium at temperatures of above 100° C and subsequently reprecipitated. Examples of suitable solvents are benzyl alcohol, ethylene glycol monoethyl ether or a mixture of 60% of methanol and 40% of water. Examples of suitable compounds having an alkaline reaction are ammonia and aliphatic amines.

It is also possible to thermally stabilise the terminal groups in the absence of a solvent in the melt in the presence of a stabiliser.

The polymer may be stabilised against the action of heat, light and oxygen in the same manner as the known trioxan copolymers. Exemplary of heat stabilisers are polyamides, amides of polybasic carboxylic acids, amidines and urea compounds. Exemplary of stabilisers against oxidation are phenols, advantageously bisphenols and aromatic amines. As light stabilisers alpha-oxybenzophenone derivatives may be used.

The terpolymers of the invention are particularly suitable for the manufacture of films and fibres, especially by the extrusion process, and for the manufacture of hollow articles, especially by the blow moulding process. They may further advantageously be used for making profiles, moulded articles and injection moulded articles.

The following Examples illustrate the invention. In the Examples, the viscosity values are indicated in η_{red} , the value η_{red} being determined at 140° C on a 0.5% solution of the polymer in butyrolactone stabilised with 2% of diphenylamine:—

EXAMPLE 1.

1000 grams of trioxan, 20 grams of ethylene oxide and 1 gram of ethylene glycol diglycidyl ether were mixed at about 80° C in a flask. In the mixture so obtained, 160 milligrams of para-nitrophenyl diazonium fluoroborate were dissolved. The monomer mixture containing the catalyst was introduced into a mould of refined steel which had been scavenged with nitrogen and was placed on a water bath at 70° C. The reaction temperature was measured with a thermo-element. The temperature in the block rose to about 100° C and then decreased again. After one hour the

mould was chilled in cold water and the block was withdrawn and ground.

The polymer was boiled with methanol containing 1% of triethanolamine, washed with methanol and dried. It was then subjected to a heterogeneous hydrolysis in a 1% ammonia solution in a ratio of 1:4. The hydrolysis temperature amounted to 144° C and the pressure to 3.7 atmospheres gauge. The product was then washed again and dried. The melt index was 2.18.

EXAMPLE 2.

879 cc of liquid trioxan were mixed with 20 cc of ethylene oxide and 1 cc of 1,4-butanediol-diglycidyl ether. 160 milligrams of para-nitrophenyl diazonium fluoroborate were dissolved in the monomer mixture and the mixture was then polymerised in a mould of refined steel. In the manner described in Example 1, the polymer was treated with a 1% solution of triethanolamine in methanol, washed with methanol and dried. The polymers obtained by 10 batches with an average extent of conversion of 85% were subjected in a 70-litre vessel for 30 minutes at 141° C to a heterogeneous hydrolysis in a ratio of 1:5 in an aqueous ammonia solution of 1% strength containing 10% of methanol. In the hydrolysis, the product lost 10% of its weight. The polymer had a pure white colour. The melt index amounted to 0.16.

The loss in weight of a product which had been stabilised with 10 milligrams of dicyandiamide and 35 milligrams of 2,2-methylenebis-4-methyl-6-tertiary butylphenol for each 5 grams of polymer, amounted to 0.026% per minute when the product was treated for 45 minutes at 230° C in an air atmosphere.

EXAMPLE 3.

100 grams of trioxan, 3 grams of dioxolan and 0.1 gram of 1,3-butane-diol-diglycidyl ether were polymerised at 70° C with 10 milligrams of para-nitrodiazonium fluoroborate as a catalyst. The polymer was worked up and hydrolysed as described in Example 1. The pure white polymer had a value η_{red} of 0.88. The melt index amounted to 0.80.

EXAMPLE 4.

4 cc of diethylene glycol formal and 0.1 cc of 1,4-butanediol-diglycidyl ether were mixed with 96 cc of liquid trioxan in a screw-top glass bottle and then 0.02 cc of boron fluoride diethyl etherate was added as a catalyst from a finely graduated injection syringe. The polymerisation was carried out at 70° C in a thermostat. The polymer was hydrolysed as described in Example 1 and stabilised as described in Example 2. The melt index was 1.06.

EXAMPLE 5.

100 grams of freshly distilled trioxan, 2 grams of ethylene oxide and 0.5 gram of

diglycidyl ether were polymerised in the presence of 0.1 cc of methylal as a regulator and 10 milligrams of para-nitrophenyl diazonium fluoroborate as a catalyst at an initial temperature of 70° C in a screw-top glass bottle.

After the polymerisation the block was disintegrated and ground and subsequently subjected for 30 minutes at 150° C to a homogeneous hydrolysis in 1 litre of benzyl alcohol in the presence of 10 cc of triethanolamine. After hydrolysis, the polymer was precipitated with methanol, suction-filtered, boiled with methanol, washed and dried. The melt index was 0.9 and the tenfold melt index (the weight of 2.16 kilograms was replaced by a weight of 21.6 kilograms) amounted to 20.6.

EXAMPLE 6.

Freshly distilled trioxan to which 2% by weight of ethylene oxide, 0.05% by weight of 1,4 - butane - diol - diglycidyl ether and 150 ppm methylal had been added was polymerised in a Ko-kneader with the use of 80 ppm of boron fluoride dibutyl etherate as a catalyst. The extent of conversion amounted to 91%.

The product was hydrolysed as described in Example 1, the loss in weight during hydrolysis amounted to 8%. The melt index was 1.5. The loss in weight examined in the manner described in Example 2 was 0.017% per minute.

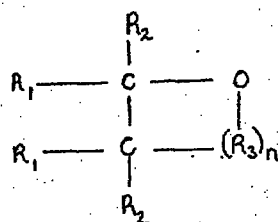
WHAT WE CLAIM IS:—

1. Copolyacetals of (A) trioxan, (B) a cyclic ether and/or a cyclic formal and (C) a bifunctional organic compound.

2. Copolyacetals as claimed in claim 1, wherein component (A) constitutes from 99.89 to 89% by weight, component (B) constitutes from 0.1 to 10% by weight and component (C) constitutes from 0.01 to 1% by weight, the percentages being calculated on the total weight of the monomer mixture.

3. Copolyacetals as claimed in claim 1 or claim 2, wherein component (A) constitutes from 99.85 to 89.5% by weight, component (B) constitutes from 0.1 to 10% by weight and component (C) constitutes from 0.05 to 0.5% by weight, the percentages being calculated on the total weight of the monomer mixture.

4. Copolyacetals as claimed in any one of claims 1 to 3, wherein component (B) is a cyclic ether and/or cyclic formal of the formula



in which R_1 and R_2 each represent a hydrogen atom or a lower alkyl radical which may be substituted by halogen, R_3 stands for methylene, oxymethylene, alkyl, halo-alkyl, a substituted methylene radical or an oxymethylene radical substituted by alkyl or halo-alkyl and n is zero, 1, 2 or 3.

5. Copolyacetals as claimed in any one of claims 1 to 4, wherein component (B) is ethylene oxide, dioxolan or diethylene glycol formal.

6. Copolyacetals as claimed in any one of claims 1 to 5, wherein component (C) is a diglycidyl ether and/or a diether of 2 mols of glycidide and 1 mol of an aliphatic diol and/or a cycloaliphatic diol.

7. Copolyacetals as claimed in claim 6, wherein the diether is that of an aliphatic diol containing 2 to 8 carbon atoms.

8. Copolyacetals as claimed in claim 6 or claim 7, wherein the diether is that of a cycloaliphatic diol containing 4 to 8 carbon atoms.

9. Copolyacetals as claimed in claim 6 or claim 7, wherein component (C) is ethylene glycol diglycidyl ether, 1,4-butane-diol-diglycidyl ether or 1,3 - butane - diol - diglycidyl ether.

10. Copolyacetals as claimed in any one of claims 1 to 9, which have a melt index within the range of 0.1 to 2.0.

11. Copolyacetals as claimed in any one of claims 1 to 10, wherein the terminal groups have been additionally stabilised in a known manner.

12. Copolyacetals as claimed in any one of claims 1 to 11 which have been additionally stabilised in a known manner against the action of heat, light and oxygen.

13. A copolyacetal as claimed in claim 1 and which is described in any one of the Examples herein.

14. A process for the manufacture of copolyacetals, which comprises copolymerising (A) trioxan, (B) a cyclic ether and/or a cyclic formal and (C) a bifunctional organic compound by a method known to be suitable for the production of trioxan copolymers.

15. A process as claimed in claim 14, which comprises subjecting to a cationic copolymerisation 99.89 to 89% by weight of component (A), 0.1 to 10% by weight of component (B) and 0.01 to 1% by weight of component (C), the percentages being calculated on the total weight of the monomer mixture.

16. A process as claimed in claim 15, wherein there are used 99.85 to 89.5% by weight of component (A), 0.1 to 10% by weight of component (B) and 0.05 to 0.5% by weight of component (C), the percentages being calculated on the total weight of the monomer mixture.

17. A process as claimed in any one of claims 14 to 16, wherein component (B) is as specified in claim 4.

18. A process as claimed in claim 17,



diglycidyl ether were polymerised in the presence of 0.1 cc of methylal as a regulator and 10 milligrams of para-nitrophenyl diazonium fluoroborate as a catalyst at an initial temperature of 70° C in a screw-top glass bottle.

After the polymerisation the block was disintegrated and ground and subsequently subjected for 30 minutes at 150° C to a homogeneous hydrolysis in 1 litre of benzyl alcohol in the presence of 10 cc of triethanolamine. After hydrolysis, the polymer was precipitated with methanol, suction-filtered, boiled with methanol, washed and dried. The melt index was 0.9 and the tenfold melt index (the weight of 2.16 kilograms was replaced by a weight of 21.6 kilograms) amounted to 20.6.

EXAMPLE 6.

Freshly distilled trioxan to which 2% by weight of ethylene oxide, 0.05% by weight of 1,4 - butane - diol - diglycidyl ether and 150 ppm methylal had been added was polymerised in a Ko-kneader with the use of 80 ppm of boron fluoride dibutyl etherate as a catalyst. The extent of conversion amounted to 91%.

The product was hydrolysed as described in Example 1, the loss in weight during hydrolysis amounted to 8%. The melt index was 1.5. The loss in weight examined in the manner described in Example 2 was 0.017% per minute.

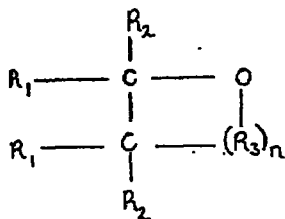
WHAT WE CLAIM IS:—

1. Copolyacetals of (A) trioxan, (B) a cyclic ether and/or a cyclic formal and (C) a bifunctional organic compound.

2. Copolyacetals as claimed in claim 1, wherein component (A) constitutes from 99.89 to 89% by weight, component (B) constitutes from 0.1 to 10% by weight and component (C) constitutes from 0.01 to 1% by weight, the percentages being calculated on the total weight of the monomer mixture.

3. Copolyacetals as claimed in claim 1 or claim 2, wherein component (A) constitutes from 99.85 to 89.5% by weight, component (B) constitutes from 0.1 to 10% by weight and component (C) constitutes from 0.05 to 0.5% by weight, the percentages being calculated on the total weight of the monomer mixture.

4. Copolyacetals as claimed in any one of claims 1 to 3, wherein component (B) is a cyclic ether and/or cyclic formal of the formula



in which R_1 and R_2 each represent a hydrogen atom or a lower alkyl radical which may be substituted by halogen, R_3 stands for methylene, oxymethylene, alkyl, halo-alkyl, a substituted methylene radical or an oxymethylene radical substituted by alkyl or halo-alkyl and n is zero, 1, 2 or 3.

5. Copolyacetals as claimed in any one of claims 1 to 4, wherein component (B) is ethylene oxide, dioxolan or diethylene glycol formal.

6. Copolyacetals as claimed in any one of claims 1 to 5, wherein component (C) is a diglycidyl ether and/or a diether of 2 mols of glycidide and 1 mol of an aliphatic diol and/or a cycloaliphatic diol.

7. Copolyacetals as claimed in claim 6, wherein the diether is that of an aliphatic diol containing 2 to 8 carbon atoms.

8. Copolyacetals as claimed in claim 6 or claim 7, wherein the diether is that of a cycloaliphatic diol containing 4 to 8 carbon atoms.

9. Copolyacetals as claimed in claim 6 or claim 7, wherein component (C) is ethylene glycol diglycidyl ether, 1,4-butane-diol-diglycidyl ether or 1,3 - butane - diol - diglycidyl ether.

10. Copolyacetals as claimed in any one of claims 1 to 9, which have a melt index within the range of 0.1 to 2.0.

11. Copolyacetals as claimed in any one of claims 1 to 10, wherein the terminal groups have been additionally stabilised in a known manner.

12. Copolyacetals as claimed in any one of claims 1 to 11 which have been additionally stabilised in a known manner against the action of heat, light and oxygen.

13. A copolyacetal as claimed in claim 1 and which is described in any one of the Examples herein.

14. A process for the manufacture of copolyacetals, which comprises copolymerising (A) trioxan, (B) a cyclic ether and/or a cyclic formal and (C) a bifunctional organic compound by a method known to be suitable for the production of trioxan copolymers.

15. A process as claimed in claim 14, which comprises subjecting to a cationic copolymerisation 99.89 to 89% by weight of component (A), 0.1 to 10% by weight of component (B) and 0.01 to 1% by weight of component (C), the percentages being calculated on the total weight of the monomer mixture.

16. A process as claimed in claim 15, wherein there are used 99.85 to 89.5% by weight of component (A), 0.1 to 10% by weight of component (B) and 0.05 to 0.5% by weight of component (C), the percentages being calculated on the total weight of the monomer mixture.

17. A process as claimed in any one of claims 14 to 16, wherein component (B) is as specified in claim 4.

18. A process as claimed in claim 17,

wherein component (B) is as specified in claim 5.

19. A process as claimed in any one of claims 14 to 18, wherein component (C) is as specified in claim 6.

20. A process as claimed in claim 19, wherein component (C) is as specified in claim 7.

21. A process as claimed in claim 19 or claim 20, wherein component (C) is as specified in claim 8.

22. A process as claimed in any one of claims 14 to 20, wherein the component (C) is ethylene glycol diglycidyl ether, 1,4-butane-diol-diglycidyl ether or 1,3-butane-diol-diglycidyl ether.

23. A process as claimed in any one of claims 14 to 22, wherein there is used as catalyst boron fluoride or an etherate thereof, or a diazonium fluoroborate.

24. A process as claimed in any one of claims 14 to 23, wherein the copolymerisation is carried out in the presence of a solvent, and at a temperature at which the trioxan does not crystallise out.

25. A process as claimed in any one of claims 14 to 23, wherein the copolymerisation is carried out in the absence of a solvent at a temperature within the range of +20 to +100° C.

26. A process as claimed in claim 14, which is conducted substantially as described in any one of the Examples herein.

27. Copolyacetals whenever obtained by the process claimed in any one of claims 14 to 26.

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