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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Oxymethylene Polymer Production

We, CELANESE CORPORATION OF AMERICA, of 522 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, 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 an improved process for the production of oxymethylene polymers.

Oxymethylene polymers, i.e. polymers containing chains of oxymethylene ($-\text{O}.\text{CH}_2-$) groups, can be produced in a very satisfactory manner by polymerising trioxane alone or with a variety of comonomers in presence of a cationic catalyst consisting of boron fluoride or a boron fluoride-containing complex, see our prior Specifications Nos. 877,820 and 903,668. It has been found, however, that when this process is carried out so as to effect conversion to polymer of 65% or more of the trioxane present, it is difficult to obtain consistently products of good physical properties and processability.

According to the present invention, the polymerisation of trioxane, alone or together with another monomer, using a cationic catalyst consisting of boron fluoride or a boron fluoride-containing complex and continuing the polymerisation until at least 65% of the trioxane is converted into polymer or copolymer, is carried out in presence of from 0.1 to 3.0 moles, per 1000 moles of trioxane initially present, of a chain transfer agent being an acetal, an alcohol, a carboxylic acid or a carboxylic acid anhydride.

By means of the invention it has been found possible to obtain consistently products of excellent physical properties which are of unusually good processability in that they have a melt index noticeably higher than is the case under conditions differing only by the

omission of the chain transfer agent. The "melt index" is a function commonly employed to assess the processability of thermoplastic substances and is determined by heating a sample of the substance to be tested in a standard cylinder to a temperature of 190°C. and forcing it under a load of 2.16 kg through an orifice of 0.0825 inch diameter for a period of 10 minutes and weighing the resin (in grams) passing through the orifice in this period. The test is described in detail in ASTM—D1238—57T.

Catalysts suitable for use in the process of the invention include boron trifluoride itself and boron trifluoride co-ordination complexes with water, with organic compounds in which oxygen or sulphur is the donor atom, or with basic trivalent nitrogen or phosphorus compounds which have ionisation constants in water at 25°C. not higher than 1×10^{-9} . The weight proportion of catalyst (based on boron fluoride content) to trioxane is usually between 0.0002% and 1.00% with from 0.003% to 0.010% being a preferred range for a continuous process and from 0.0002% to 0.007% being preferred in a batch system.

The polymerisation is usually carried out at temperatures between 45° and 115°C. and preferably from 60° to 115°C. The reaction time for polymerisation is usually between 0.25 and 120 minutes. Reaction periods of 0.25 to 3 minutes are preferred for continuous reaction and periods from 10 to 120 minutes for batch reaction. It is often desirable to carry out the polymerisation reaction in the presence of a trioxane solvent such as cyclohexane.

In accordance with an important aspect of the invention, trioxane is copolymerised with a cyclic ether having adjacent carbon atoms to produce copolymers having oxymethylene groups and oxyalkylene groups with adjacent carbon atoms, the copolymerisation preferably being carried out in the presence of not more than 20 weight percent of solvent and prefer-

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ably in the presence of between about 0.5 and about 2 weight percent of solvent when using a continuous reaction method of operation. The preferred copolymers are those made up of oxymethylene and oxyethylene groups, such as may be obtained by copolymerising trioxane with dioxolane or with ethylene oxide, the oxyethylene units comprising between 10 and 1% of the total oxyethylene and oxymethylene units.

As above indicated, the chain transfer agent used may be an acetal, alcohol, carboxylic acid or carboxylic acid anhydride. Suitable acetals include hemiacetals and polyacetals and preferably contain no more than about 18 successive carbon atoms. The polyacetals may be polyoxymethylene dialkyl ethers of the formula $RO(CH_2O)_xR$ where x is an integer from 1 to 10 and R is an alkyl group having up to 18 carbon atoms. For example, dioxymethylene dimethyl ether and trioxymethylene dimethyl ether may be used. Polyoxymethylene diesters of the formula $R.CO.O(CH_2O)_x.CO.R$, where x is an integer from 1 to 20 and R is selected from the group consisting of hydrogen and alkyl groups having up to 18 carbon atoms, may also be used.

Apart from the polyacetals, it is preferred that the acetal be the reaction product of a primary or secondary alcohol having up to 18 carbon atoms with an aldehyde having up to 7 carbon atoms. Formals and acetals (including hemi-formals and hemi-acetals) of unsaturated aliphatic alcohols, such as allyl alcohol; of cyclo-aliphatic alcohols, such as cyclohexanol; and of aromatic alcohols, such as benzyl alcohol may also be used. The formals of aromatic alcohols are subject to secondary reactions, such as boron trifluoride catalysed condensation with formaldehyde (hydroxymethylation) but the reaction products are also effective chain transfer agents.

The alcohols used as chain transfer agents are preferably those having from 1 to 18 carbon atoms, particularly primary and secondary alcohols. Unsaturated alcohols, such as allyl alcohol; monoalkyl ethers of glycols, such as the monomethyl ether of ethylene glycol; chlorinated alcohols, such as ethylene chlorohydrin; and glycols such as ethylene glycol are included. Where glycols are used, some of the glycol may be incorporated into the polymer chain while the remainder acts as a chain transfer agent.

The preferred carboxylic acid chain transfer agents are aliphatic acids having up to 18

carbon atoms, e.g. acetic, propionic, n-butyric, n-valeric, stearic and succinic acids. The corresponding anhydrides may also be employed. Aromatic acids and anhydrides, such as benzoic acid and phthalic anhydride, may also be used despite the fact that they may give rise to secondary reactions, since the products of such reactions are also chain transfer agents. The preferred chain transfer agent is methylal because of its effectiveness as a chain transfer agent, its lack of effect on the activity of the polymerisation catalyst and its compatibility with the catalyst and with the solvent.

The chain transfer agent is added to the polymerisation mixture in proportions between 0.1 and 3.0 moles of chain transfer agent per 1,000 moles of trioxane, and preferably between about 0.3 and about 0.7 moles of chain transfer agent are used per 1,000 moles of trioxane.

The following Example illustrates the invention:—

EXAMPLE

Trioxane and ethylene oxide were copolymerised continuously in an elongated reaction vessel comprising a cylindrical barrel fitted with a screw with interrupted threads and arranged to be rotated and axially reciprocated in the barrel so as to cause teeth arranged in rows on the inner surface of the barrel to pass through the interruptions in the thread of the screw. Such apparatus is described in United States Patent No. 2,505,125 and acts to pass the polymerising material through the barrel while keeping it thoroughly mixed.

The polymerisation took place in the presence of boron fluoride dibutyl etherate as catalyst and cyclohexane as solvent, using various kinds and amounts of chain transfer agent. The general polymerisation conditions were as follows:—

Monomer feed rate, pounds per hour	about 50
Ethylene oxide in monomer, weight percent	2.0
Catalyst concentration (parts per million of BF_3 on trioxane)	about 75
Trioxane/cyclohexane weight ratio	about 60
Screw speed, revolutions per minute	37
Peak temperature	about 190°F.

In the following Table there is given the melt index of each of the products obtained according to the above Example. For comparison there is also given the melt index of a copolymer obtained in the absence of any chain transfer agent but operating otherwise exactly as in the Example.

60

65

70

75

80

85

90

95

100

105

110

Chain Terminating Agent	Concentration, moles per 1000 moles of trioxane	Melt Index
None		2.5
Methylal	0.27	9.5
Methylal	0.81	21.0
Acetal	0.27	4.6
Acetal	0.54	19.5
Formic Acid	0.27	5.4
Acetic Anhydride	0.27	7.4
Methanol	0.27	5.4
Methanol	0.81	16.5

WHAT WE CLAIM IS:—

1. Process for the polymerisation of trioxane, alone or together with another monomer, using a cationic catalyst consisting of boron fluoride or a boron fluoride-containing complex and continuing the polymerisation until at least 65% of the trioxane is converted into polymer or copolymer, wherein the polymerisation is carried out in presence of from 0.1 to 3.0 moles, per 1,000 moles of trioxane initially present, of a chain transfer agent being an acetal, an alcohol, a carboxylic acid or a carboxylic acid anhydride.
2. Process according to Claim 1, wherein the chain transfer agent present is methylal.
3. Process according to Claim 1 or 2, wherein the catalyst used is boron trifluoride dibutyl etherate.
4. Process according to Claim 1, 2 or 3, wherein the trioxane is copolymerised with a

cyclic ether containing adjacent carbon atoms.

5. Process according to Claim 4, wherein the trioxane is copolymerised with a cyclic ether containing oxyethylene units, said cyclic ether being used in such a quantity that in the polymer obtained oxyethylene units form 10 to 1% of the total oxyethylene and oxy-methylene units.

6. Process for the polymerisation of trioxane, alone or together with another monomer, substantially as hereinbefore described.

7. Process for the copolymerisation of trioxane and ethylene oxide, substantially as described in the Example.

8. Polymers and copolymers of trioxane whenever produced by any of the processes claimed in the preceding claims.

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