

# PATENT SPECIFICATION

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NO DRAWINGS.

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International Classification:—C 08 g.

## COMPLETE SPECIFICATION.

### Improvements in Polymer Production.



Small c

5 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 in-  
vention, for which we pray that a patent  
may be granted to us, and the method by  
which it is to be performed, to be particu-  
10 larly described in and by the following  
statement:—

This invention relates to improvements in  
the production of oxymethylene polymers.  
15 Useful thermoplastic oxymethylene poly-  
mers can be obtained by polymerisation of  
trioxane alone or together with co-mono-  
mers, especially valuable polymers being ob-  
tained by co-polymerising trioxane with a  
20 cyclic ether containing two or more adjacent  
carbon atoms. The polymerisation is ex-  
ceedingly rapid in presence of boron fluor-  
ide-containing catalysts but this has the dis-  
advantage that unless the polymerisation is  
carried out in presence of a large amount of  
25 inert diluent the polymer forms a solid lump  
which must be ground, chopped or pulver-  
ised in order to obtain it in a form conven-  
ient for washing or other subsequent hand-  
ling. The toughness of the polymers makes  
30 their reduction to particle form quite an  
expensive operation. On the other hand, the  
presence of a large amount of diluent is un-  
desirable where the production of polymers  
of high molecular weight with rapid reac-  
35 tion rates is desired.

According to the invention, an oxymethyl-  
ene polymer is obtained directly in powder  
form by carrying out the polymerisation of  
trioxane, or its co-polymerisation with an-  
40 other monomer, in a liquid mixture contain-  
ing at least 50 weight per cent of trioxane  
while subjecting the polymerising material  
simultaneously to shearing and blending, the

blending causing admixture of the polymer-  
ising material at various stages of polymeri- 45  
sation with material in which the polymeri-  
sation has not yet progressed to the same  
degree, and continuing the shearing and  
blending until a product is obtained in which  
at least 65 weight per cent of the trioxane 50  
present is in polymer form.

A particularly satisfactory method of  
carrying out the process of the invention  
consists in feeding the polymerisation mix- 55  
ture into a continuous mixer, comprising a  
barrel provided with rows of teeth along its  
inner surface and a screw fitting in the bar-  
rel, means being provided to both rotate  
and reciprocate the screw so that the teeth 60  
on the barrel pass through interruptions in  
the screw thread. Rotation of the screw  
causes the polymerisation mixture to travel  
through the barrel in a generally helical  
path, while the reciprocation of the screw 65  
causes mixing of the mixture at any point  
with mixture immediately behind it. Throughout its travel through the barrel the  
trioxane polymerises progressively while the  
mixture is constantly subjected to the shear-  
ing action of the screw thread and the in- 70  
wardly projecting teeth on the barrel wall.  
Coils for the circulation of heating or cooling  
fluid within the screw and barrel wall en-  
able the temperature to be maintained with-  
in desired limits. An apparatus sold com- 75  
mercially under the name Ko-Kneader and  
described in United States Patent No.  
2,505,125 operates in the manner set out  
above and is suitable for use in carrying out  
the process of the invention. 80

In using an apparatus of the type de-  
scribed in the previous paragraph, the tri-  
oxane-containing mixture may be introduced  
into the barrel through a hopper but, to  
avoid polymerisation in the hopper, the cata- 85  
lyst should be added to the mixture as it is

[Price 4s. 6d.]

about to enter the barrel or the catalyst may be introduced into the barrel through a separate feed line.

The preferred polymerisation catalysts are boron fluoride and boron fluoride coordination complexes with organic compounds in which oxygen or sulphur is the donor atom, with water or with basic trivalent nitrogen or phosphorus compounds having ionization constants in water at 25° C. not higher than about  $1 \times 10^{-9}$ . Boron fluoride ether complexes, such as boron fluoride dibutyl etherate, give especially satisfactory results.

The catalyst is usually mixed with the trioxane in amounts between 0.0001 and 0.10 weight per cent, based on its boron fluoride content, amounts between 0.0005 and 0.025 weight per cent preferably being used.

Trioxane may be the sole monomeric constituent, or it may be blended with a co-monomer and particularly with a cyclic ether having adjacent carbon atoms. A preferred class of co-monomer consists of cyclic ethers having from 2 to 4 adjacent carbon atoms. Among the specific cyclic ethers which may be used are ethylene oxide, 1,3-dioxolane, 1,3,5-trioxepane, 1,3-dioxane, trimethylene oxide, pentamethylene oxide, 1,2-propylene oxide, 1,2-butylen oxide, neopentyl formal, pentaerythritol diformal, paraldehyde, tetrahydrofuran and butadiene monoxide.

The co-monomer is preferably used in amounts between 0.1 and 10 weight per cent, based on the weight of trioxane, but more may be used, e.g. up to 20 weight per cent.

A small amount of an inert solvent may be present, e.g. cyclohexane, benzene, ethylene dichloride, pentane, trichloroethylene, ligroin (90 to 100° C. boiling point), carbon tetrachloride, octane, symmetrical tetrachloroethane, diethyl ether, petroleum ether 30 to 60° C. boiling point) and methylene chloride.

The polymerisation mixture is preferably maintained at a temperature between 0° and 116° C. after initiation of polymerisation at temperatures above approximately 60° C.

In the process of the invention, carried out as above described, the polymerisation mixture changes from a free flowing clear liquid to a slurry which progressively thickens and finally becomes a dry granular powder which consists largely of polymer in a form which is easy to wash and process. Under the preferred conditions the time occupied by the mixture in travelling through the barrel is generally between 0.5 and 2 minutes, although a longer polymerisation time, e.g. up to 10 minutes, may be used if desired. It has been found possible, by means of the invention, not only to produce the polymer directly in powder form but also to obtain polymer of considerably higher molecular weight, using the continuous mixer

described, than is obtained from the same polymerisation mixture in a batch polymerisation.

The following example illustrates the invention:—

#### EXAMPLE.

A mixture of 100 parts by weight of trioxane, 2.4 parts by weight of ethylene oxide and 1.1 parts by weight of cyclohexane, together with, for each million parts by weight of mixture, 840 parts by weight of methylal and 70 parts by weight of boron trifluoride dibutyl etherate, was fed to one end of a continuous mixer of the type described above and comprising an interrupted-thread screw arranged to be rotated and reciprocated in a cylindrical barrel.

The temperature in the mixer rose to a maximum of 105° to 115° C. at the discharge point. Residence time in the mixer was about one minute. The reaction product was a fine powder.

#### WHAT WE CLAIM IS:—

1. Process for the production of an oxymethylene polymer directly in powder form, which comprises carrying out the polymerisation of trioxane, or its co-polymerisation with another monomer, in a liquid mixture containing at least 50 weight per cent of trioxane while subjecting the polymerising material simultaneously to shearing and blending, the blending causing admixture of the polymerising material at various stages of polymerisation with material in which the polymerisation has not yet progressed to the same degree, and continuing the shearing and blending until a product is obtained in which at least 65 weight per cent of the trioxane present is in polymer form.

2. Process according to Claim 1, wherein the polymerisation mixture is fed into a continuous mixer, comprising a barrel provided with rows of teeth along its inner surface and an interrupted-thread screw fitting in the barrel, and said screw is both rotated and reciprocated so that the polymerisation mixture travels through the barrel while the mixture at any point is blended with mixture immediately behind it.

3. Process according to Claim 2, wherein the polymerisation mixture is maintained at a temperature between 0° C. and 116° C. during passage through the mixer.

4. Process according to Claim 3, wherein the mixture taken from 0.5 to 2.0 minutes to travel through the mixer.

5. Process according to any of the preceding claims, wherein a boron trifluoride etherate is used as catalyst.

6. Process according to any of the preceding claims, wherein trioxane is co-polymerised with between 0.1 and 10 per cent of its weight of a cyclic ether containing 2 to 4 adjacent carbon atoms.

7. Process for the production of a co-



about to enter the barrel or the catalyst may be introduced into the barrel through a separate feed line.

5 The preferred polymerisation catalysts are boron fluoride and boron fluoride co-ordination complexes with organic compounds in which oxygen or sulphur is the donor atom, with water or with basic tri-  
10 valent nitrogen or phosphorus compounds having ionization constants in water at 25° C. not higher than about  $1 \times 10^{-9}$ . Boron fluoride ether complexes, such as boron fluoride dibutyl etherate, give especially satisfactory results.

15 The catalyst is usually mixed with the trioxane in amounts between 0.0001 and 0.10 weight per cent, based on its boron fluoride content, amounts between 0.0005 and 0.025 weight per cent preferably being used.

20 Trioxane may be the sole monomeric constituent, or it may be blended with a co-monomer and particularly with a cyclic ether having adjacent carbon atoms. A preferred class of co-monomer consists of cyclic ethers  
25 having from 2 to 4 adjacent carbon atoms. Among the specific cyclic ethers which may be used are ethylene oxide, 1,3-dioxolane, 1,3,5-trioxepane, 1,3-dioxane, trimethylene oxide, pentamethylene oxide, 1,2-propylene  
30 oxide, 1,2-butylene oxide, neopentyl formal, pentaerythritol diformal, paraldehyde, tetrahydrofuran and butadiene monoxide.

The co-monomer is preferably used in amounts between 0.1 and 10 weight per cent,  
35 based on the weight of trioxane, but more may be used, e.g. up to 20 weight per cent.

A small amount of an inert solvent may be present, e.g. cyclohexane, benzene, ethylene dichloride, pentane, trichloroethylene,  
40 ligroin (90 to 100° C. boiling point), carbon tetrachloride, octane, symmetrical tetrachloroethane, diethyl ether, petroleum ether 30 to 60° C. boiling point) and methylene chloride.

45 The polymerisation mixture is preferably maintained at a temperature between 0° and 116° C. after initiation of polymerisation at temperatures above approximately 60° C.

In the process of the invention, carried  
50 out as above described, the polymerisation mixture changes from a free flowing clear liquid to a slurry which progressively thickens and finally becomes a dry granular powder which consists largely of polymer in  
55 a form which is easy to wash and process. Under the preferred conditions the time occupied by the mixture in travelling through the barrel is generally between 0.5 and 2 minutes, although a longer polymerisation  
60 time, e.g. up to 10 minutes, may be used if desired. It has been found possible, by means of the invention, not only to produce the polymer directly in powder form but also  
65 to obtain polymer of considerably higher molecular weight, using the continuous mixer

described, than is obtained from the same polymerisation mixture in a batch polymerisation.

The following example illustrates the invention:—

#### EXAMPLE.

A mixture of 100 parts by weight of trioxane, 2.4 parts by weight of ethylene oxide and 1.1 parts by weight of cyclohexane, together with, for each million parts by  
75 weight of mixture, 840 parts by weight of methylal and 70 parts by weight of boron trifluoride dibutyl etherate, was fed to one end of a continuous mixer of the type described above and comprising an interrupted-  
80 thread screw arranged to be rotated and reciprocated in a cylindrical barrel.

The temperature in the mixer rose to a maximum of 105° to 115° C. at the discharge  
85 point. Residence time in the mixer was about one minute. The reaction product was a fine powder.

#### WHAT WE CLAIM IS:—

1. Process for the production of an oxy-methylene polymer directly in powder form,  
90 which comprises carrying out the polymerisation of trioxane, or its co-polymerisation with another monomer, in a liquid mixture containing at least 50 weight per cent of trioxane while subjecting the polymerising material simultaneously to shearing and blending,  
95 the blending causing admixture of the polymerising material at various stages of polymerisation with material in which the polymerisation has not yet progressed to the  
100 same degree, and continuing the shearing and blending until a product is obtained in which at least 65 weight per cent of the trioxane present is in polymer form.

2. Process according to Claim 1, wherein  
105 the polymerisation mixture is fed into a continuous mixer, comprising a barrel provided with rows of teeth along its inner surface and an interrupted-thread screw fitting in the barrel, and said screw is both rotated and  
110 reciprocated so that the polymerisation mixture travels through the barrel while the mixture at any point is blended with mixture immediately behind it.

3. Process according to Claim 2, wherein  
115 the polymerisation mixture is maintained at a temperature between 0° C. and 116° C. during passage through the mixer.

4. Process according to Claim 3, wherein  
120 the mixture taken from 0.5 to 2.0 minutes to travel through the mixer.

5. Process according to any of the preceding claims, wherein a boron trifluoride etherate is used as catalyst.

6. Process according to any of the pre-  
125 ceding claims, wherein trioxane is co-polymerised with between 0.1 and 10 per cent of its weight of a cyclic ether containing 2 to 4 adjacent carbon atoms.

7. Process for the production of a co- 130

polymer of trioxane and ethylene oxide, substantially as described in the example.

8. Oxymethylene polymers whenever produced by any of the processes claimed in the preceding claims.
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