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COMPLETE SPECIFICATION.

Polymers.

We, CELANESE CORPORATION OF AMERICA, of 180 Madison Avenue, New York 16, 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 polymers and is more particularly concerned with the production of polyoxymethylene mouldable under heat and pressure.

Polyoxymethylenes are polymers of formaldehyde having recurring $\text{—CH}_2\text{O—}$ units and have been known for many years. These polymers vary in thermal stability and in molecular weight, depending on the method of preparation used, those of high molecular weight sometimes being of sufficient stability to be mouldable by the action of heat and pressure. They may be prepared by spontaneous polymerisation of liquid formaldehyde at low temperatures, higher temperatures sometimes resulting in polymerisation with explosive speed. They may also be prepared from formaldehyde with the aid of catalysts such as aliphatic or primary amines and organic amines, stillbenes and phosphines. Formaldehyde is, however, not easily or cheaply produced in a form sufficiently pure for satisfactory production of these polymers and is utilisable as a liquid only at such low temperatures that the polymerisation is rapid and difficult to control.

Trioxane can also be used as a source of polymers of the type referred to. Trioxane is a cyclic trimer of formaldehyde having a six-membered heterocyclic ring

consisting of alternating oxygen atoms and methylene groups. It melts at about 64°C , boils without decomposition at about 115°C and is soluble in water from which it can be crystallised. This compound is thus easily and cheaply obtained in a state of reasonably high purity and can, if necessary, be obtained in very highly purified form without great expense. Trioxane analysing:—iron 1 part per million, acidity (as formic acid) 0.002%, water 0.02% and formaldehyde 0.00%, and having a freezing point of 60°C is readily obtainable and has given excellent results in the process of the invention.

It has been stated that certain inorganic fluorides can be used as catalysts to convert trioxane into a thermoplastic polyoxymethylene, but that the nature of the inorganic fluoride is quite critical and that many such fluorides, e.g. sodium fluoride, calcium fluoride, lead fluoride and ferric fluoride, show no catalytic activity in the process, while those fluorides said to be active as catalysts needed polymerisation times ranging from 1 to 7 days to give satisfactory results.

According to the present invention, tough polymers of high molecular weight and suitable for shaping under heat and pressure are formed by polymerising trioxane in presence of certain catalysts consisting of or containing boron fluoride, employing relatively short polymerisation times which may, if desired, be no longer than a few minutes.

The catalyst used may be boron fluoride itself or may be a co-ordination complex of boron fluoride with water or with an organic compound in which the donor atom is oxygen or sulphur. The co-ordination complex may be one between a molecule of boron fluoride and one, two or three

molecules of water, while complexes with organic compounds which may be used are ones with an alcohol, a phenol, an acid, an ether, an acid anhydride, an ester, a ketone, an aldehyde, a dialkyl sulphide or a mercaptan. Specific complexes with organic compounds which are suitable are those with ethanol, methanol, propanol, butanol, methyl acetate, butyl acetate, phenyl acetate, benzoic acid, acetic acid, acetic anhydride, acetone, methyl ethyl ketone, dimethyl ether, diethyl ether, methyl phenyl ether, phenol, acetaldehyde, chloral, dimethyl sulphide and ethyl mercaptan; of these, the diethyl ether complex is preferred, while the complexes with phenol and with acetic acid are also very effective, the boron fluoride-phenol complex giving rather low polymerisation rates at temperatures below about 50° C.

The novel catalysts are so effective that with their aid substantially instantaneous polymerisation of trioxane can, if desired, be effected although, as will be described later, under suitable conditions longer polymerisation times can be used and better control thereby achieved. Not more than 3% of boron trifluoride (as such or combined in a complex) based on the weight of trioxane is desirable to obtain a polymer of high molecular weight and, indeed, it is preferred not to exceed 1%; at least .001% seems necessary and usually excellent results are obtained by introducing into the reaction zone between about .003 and about .1% by weight.

The catalyst may be used in solid, liquid or vapour form, according to its physical properties, and the method chosen for effecting the polymerisation. Generally excellent results are achieved when the trioxane is polymerised while it is molten, the temperature used at normal atmospheric pressure thus being from, say, 65 to 114° C., the preferred temperatures being from 70 to 100° C. Temperatures obtaining in different parts of the reaction system may, however, be outside this range and so likewise may the temperature at which the trioxane is supplied. Thus, quite low temperatures may be used in the process, although generally it is preferred not to use temperatures below -10 or -20° C., while, for instance when the trioxane is supplied in vapour form, fairly high temperatures, e.g. up to 180° C. may be used.

The trioxane employed is preferably anhydrous or substantially anhydrous. Traces of moisture, such as may be present in commercial grade trioxane or may be introduced by contact with atmospheric air, do not prevent polymerisation but should be removed for best results. On the other hand, the bound water in boron fluoride co-ordination complexes with water appears to have no

adverse effect on the polymerisation.

One method of carrying out the polymerisation consists in simply adding a measured quantity of the chosen catalyst to a molten body of trioxane maintained at the chosen temperature. Boron trifluoride vapour may be sparged into the molten trioxane at a constant predetermined rate over a period of from about one to five seconds, by which time polymerisation will be substantially complete at temperatures of 70 to 90° C. The co-ordination complexes may be added in measured amount to the molten trioxane and distributed evenly by vigorous stirring.

The polymer produced is freed from monomer, if any, and catalyst by one or more water washes before being used.

The following examples illustrate the invention:—

EXAMPLE I.

150 parts by weight of commercial trioxane was heated to 90° C. in a vessel equipped with a condenser. About 0.1 part by weight of gaseous boron trifluoride was added over a period of 3 seconds. Polymerisation was almost instantaneous.

The polymer was broken up into small particles and washed three times with hot water. The polymer was dried overnight at 60 to 65° C. at atmospheric pressure. The dried polymer had no odour of formaldehyde.

When stabilized with 5% by weight of diphenylamine a white, translucent disc was formed by compression at 180° C. for 2 minutes.

EXAMPLE II.

150 parts by weight of commercial trioxane (melting point 60 to 62° C.) was heated to 90° C. in an open vessel, resulting in a fluid melt. There was then added 0.05 part by weight of boron fluoride etherate. The melt solidified almost immediately as a result of the formation of polyoxymethylene. After cooling to room temperature the mass was broken up into small particles and refluxed with water for 1 hour. A second hot water wash was carried out for a half hour and the polymer was filtered off. The polymer was dried overnight at 60° C. at atmospheric pressure. The dried polymer had no odour of formaldehyde.

On 2 parts by weight of polymer, a solution of 0.2 part by weight of diphenylamine in 3.6 parts by weight of diethyl ether was sprayed. The ether was evaporated off the polymer by drying at 90° C. for 30 minutes. A disc was moulded from the polymer at 180° C. for 2 minutes. The disc was tough, strong and translucent.

The stabilized polymer did not decompose when maintained at 105° C. for more

than 7 days. A moulded sheet, 5 mils in thickness, could be creased back and forth along a line 100 times without cracking.

Other properties of the diphenylamine-stabilized polymer are shown in the table below:—

	Property	Value	Units	Test
	Flexural strength	12,000	p.s.i.	ASTM D790
	Flexural modulus	300,000	p.s.i.	" D790
10	Tensile strength	7,000	p.s.i.	" D638
	Izod impact strength	1.4—2.1	foot lb./in.	" D256
	Rockwell Hardness	M73	—	" D785
	Deformation 200 p.s.i. at 122° F.	1.5	%	" D621
15	Heat Distortion at 264 p.s.i.	80	°C.	" D648
	Inherent Viscosity	1.37	—	At 0.5% by weight in <i>p</i> -chlorophenol containing 2% alpha pinene at 60° C.
20				

EXAMPLE III.

3,373 parts by weight of dried commercial trioxane was heated to 70° C. in an open vessel, resulting in a fluid melt. There was then added 0.34 part by weight of boron trifluoride phenol complex with thorough agitation. Polymerisation was not quite as rapid as in the case of boron trifluoride etherate but was essentially complete in 5 minutes. After cooling to room temperature the polymer was purified, stabilized and moulded as above to produce a tough, strong and translucent disc.

EXAMPLE IV.

150 parts by weight of commercial trioxane was heated to 70° C. in an open vessel. About 0.1 part by weight of boron trifluoride acetic acid complex was added with thorough agitation. Polymerisation was almost instantaneous, and produced a polyoxymethylene product similar to that described above.

Although some polyoxymethylenes of the type with which the present invention is concerned are more stable than others, according to the method of preparation used, it is desirable for many uses that even in these cases the thermal stability should be increased. It will be noted that in each of the above cases a small quantity of diphenylamine was added to the polymer before moulding at 180° C. for 2 minutes; these moulding conditions are generally applicable to the stabilized products of the invention. Quantities of diphenylamine of between 1 and 10% based on the weight of the polymer can be used satisfactorily and so likewise can similar quantities of certain other amines, particularly secondary and tertiary monomeric amines, hydrazines, phenols and ureas. A novel class of stabilizer has been found

which is more effective than those previously known when used in equal concentrations or equally effective when used in smaller concentrations. These novel stabilizers are N,N,N',N' tetra(hydroxyalkyl)alkylene diamines, particularly those having from 1 to 5 carbon atoms and only one hydroxy group in each of their hydroxyalkyl radicals and from 1 to 6 carbon atoms in their alkylene groups. The hydroxyalkyl radicals in any particular diamine need not be identical. Specific compounds of this class which have been found to be very effective are N,N,N',N' tetrakis (2-hydroxypropyl)-1,2 ethylene diamine and N,N,N',N' tetrakis (2-hydroxyethyl)-1,2 ethylene diamine. These novel stabilizers are generally not needed in amounts exceeding 15% based on the weight of the polymer and preferably amounts between about 0.5 and about 10% by weight are used.

In order to incorporate the stabilizers into the polymer they may be applied in solution, for example in diethyl ether, to the finely divided polymer followed by evaporation of the solvent. Alternatively, the stabilizer and polymer may be milled together as dry solids or both stabilizer and polymer may be dissolved in a common solvent which can then be evaporated.

Although these novel stabilizers improve the thermal stability of even polyoxymethylenes of relatively low molecular weight, they are of particular importance in connection with polymers which are of high molecular weight and relatively stable in the raw state against thermal degradation. It is preferred to use polymers having an inherent viscosity of at least 1.0 measured at 60° C. as a 0.5% solution in *p*-chlorophenol containing 2% alpha-pinene; it is also preferred that the polymers, in the raw state, should be such that they lose less than

50% in weight in three-quarters of an hour when maintained at 222° C. in a vessel under nitrogen but open to the atmosphere through a capillary tube. Polymers having the properties referred to are obtainable by the processes herein described.

The following example illustrates the effectiveness of the novel stabilizers:—

EXAMPLE V.

Polyoxymethylene, prepared by polymerising molten trioxane at a temperature of 90 to 100° C. in the presence of 0.033% by weight of boron fluoride etherate, was ground and screened to pass through a U.S. No. 40 screen. To a portion of the polymer, sufficient N,N,N',N' tetrakis (2-hydroxypropyl)-1,2 ethylene diamine, in 5% solution by weight in diethyl ether, was applied to yield upon drying a composition containing 1% by weight of the diamine. A 2 gram sample of the composition was compression moulded at 200° C. for 3 minutes to produce a disc of 20 mil thickness. The disc could be bent through 180° and back through 360° without breaking.

A comparative experiment was carried out with a further portion of the ground and screened polymer used in the above example in which, instead of N,N,N',N' tetrakis (2-hydroxypropyl)-1,2 ethylene diamine, there was applied to the polymer sufficient diphenylamine in 5% solution by weight in diethyl ether to yield upon drying a composition containing 1% by weight of diphenylamine. A 2 gram sample of this composition was likewise compression moulded at 200° C. for 3 minutes to produce a disc of 20 mil thickness. This disc broke when it was bent through 180°.

As already shown, the catalysts of the invention result in very rapid and even instantaneous polymerisation. This makes it difficult to secure uniform blending of the catalyst with the trioxane before substantial polymerisation has occurred; this has been found liable to lead to lack of uniformity in the polymer produced. The presence of a solvent for the catalyst, for the trioxane or for both catalyst and trioxane has been found to be of value in reducing this effect. If substantial quantities of solvent are present the polymerisation is slowed down. When molten trioxane is polymerised with the aid of one of the catalysts of the invention, the polymerisation may be so rapid and complete that the solid polymer fills the entire volume of the reaction mass and must be broken up mechanically to effect satisfactory washing or other purification. With the aid of suitable quantities of solvent the polymer can be produced as a slurry of particles while still not increasing the polymerisation time to an uneconomic extent.

The catalyst alone may be dissolved and the solution blended with the molten trioxane. In this case, in view of the small quantity of catalyst used, the amount of solvent, even with 20 or more parts by weight of solvent per part of catalyst as is preferred, introduces insufficient solvent to affect materially the melting point of the trioxane and it is necessary to maintain the mixture at a temperature not lower than the melting point of trioxane. If desired, sufficient solvent may be used for it to predominate so that the solution remains liquid at temperatures well below the normal melting point of trioxane. This method of operation is especially suitable where the trioxane is dissolved and the catalyst or catalyst solution then added. For example, 1 part of trioxane may be dissolved in from $\frac{1}{2}$ to 20 parts by weight of solvent, e.g. benzene, to produce a solution in which polymerisation can be effected at room temperature or even below, e.g. down to -10° C., or at a higher temperature if a shorter reaction time is desired, and from which the polymer precipitates in particle form.

Preferably a mutual solvent for the catalyst and trioxane is used. Specific solvents which have been found satisfactory, for example with boron fluoride as catalyst, are benzene, cyclohexane, ethylene dichloride, pentane, trichlorethylene, ligroin (90 to 100° C. boiling point), carbon tetrachloride, symmetrical tetrachlorethane, nitromethane, nitroethane, 1,1,1-trichlorethane, diethyl ether, petroleum ether (30 to 60° C. boiling point), methylene chloride and a mixture of tetrahydrofurane and methyl cyclohexane.

The following examples illustrate the use of solvents in the process of the invention:

EXAMPLE VI.

3,000 grams trioxane was heated to 90° C. in a flask and a solution of 0.33 gram BF₃ etherate in 25 ml. benzene was added (in about 30 seconds) to the well stirred molten trioxane. The trioxane went solid almost immediately and the temperature rose to 113° C. within 1 minute. After standing overnight the polymer was pulverised and washed three times with water at 90 to 95° C. After drying overnight at 60 to 65° C. the polymer weighed 2,156 grams (72% yield). A portion of this polymer was tested and found to have a weight loss when maintained at 222° C. of 1.0% per minute. Two grams of the polymer were stabilized with 2.5% diphenylamine and compression moulded at 180° C. for 2 minutes. The disc thus formed was quite tough, white and translucent.

2,000 grams of the polymer was stabilized with 5% diphenylamine and converted by extrusion at about 380° F. into $\frac{1}{4}$ inch rod which was then chip ground and injection

moulded into test bars. These bars were white, translucent and very tough. Conditions for injection moulding were as follows:

	Nozzle temperature ...	420° F.
5	Front cylinder temperature	430° F.
	Back cylinder temperature	410° F.
	Die temperature ...	140° F.
	Cycle time ...	45 seconds
	Dwell time ...	15 seconds
10	Cylinder pressure ...	20,000 p.s.i.

Physical properties were found to be as follows:—

	Heat distortion temperature, 264 p.s.i. ...	80° C.
15	Deformation under load, 2,000 p.s.i. ...	1.5%
	Impact strength, Izod 73° F. ...	1.7 ft. lb./in.
	Rockwell Hardness ...	M73
20	Flexural strength ...	12,000 p.s.i.
	Flexural modulus, 73° F. ...	300,000 p.s.i.
	Tensile strength, 73° F. ...	7,000 p.s.i.

The injection moulded polymer had an inherent viscosity of 1.37 as measured in *p*-chlorophenol (with 2% alpha pinene) at 60° C. at 0.5% concentration.

EXAMPLE VII.

A solution of 100 grams trioxane and 400 ml. of benzene was heated to boiling and a small amount of water removed by the use of a Dean-Stark trap. Then approximately 75 ml. was distilled off. The solution was cooled to 25° C. and 0.1 gram BF_3 -etherate was added with stirring. After about 15 minutes the solution began to turn cloudy. Stirring was continued for about 24 hours. The slurry was filtered and the polymer refluxed twice with 500 ml. water, filtered and dried overnight at 60 to 65° C. A yield of 27.6 grams of polyoxymethylene was obtained. A white translucent disc was compression moulded at 180° C. for 2 minutes by using 10% diphenylamine as stabilizer for the polymer. The unstabilized polymer showed an inherent viscosity of 0.65 when measured in *p*-chlorophenol (containing 2% alpha pinene) at 60° C. at 0.5% concentration.

EXAMPLE VIII.

A solution of 100 grams trioxane and 100 grams benzene was heated to 35° C. and 0.2 gram BF_3 -etherate added. Polymer began forming almost immediately. Heating was continued and the temperature rose to 60° C. in 2 minutes. Heating was stopped but the temperature continued to rise until it reached 80° C. Heating was started again and a temperature of 79 to 80° C. was maintained for 4½ hours, after

which 100 ml. benzene was added to help slurry the reaction mixture. The polymer was filtered off, refluxed twice with water, filtered and dried at 60 to 65° C. overnight. The polymer weighed 92.4 grams. The polymer was stabilized with 5% diphenylamine and compression moulded into discs at 180° C. in 2 minutes.

EXAMPLE IX.

A solution of 150 grams trioxane in 185 grams of ethylene dichloride was stirred with 3.35 grams calcium hydride for 1 hour at 70° C. under a nitrogen atmosphere. The solution was then filtered under a nitrogen atmosphere into a reaction flask. The temperature was allowed to drop to 36° C. and 0.036 gram BF_3 -etherate was added. The temperature rose to 85° C. in 5 minutes. After stirring for 2 hours and 40 minutes at 70° C. the reaction mixture was cooled to room temperature.

200 millilitres ethyl ether was added and the mixture was stirred for 10 minutes and filtered. This was repeated with 300 ml. ether and filtered. The polymer thus obtained was washed 3 times with water at 90° C., filtered and dried at 60° C. overnight. The yield of polymer was 77%.

The polymer had an inherent viscosity of 1.04 when measured at 60° C. in 0.5% concentration in *p*-chlorophenol containing 2% alpha pinene. When the polymer was stabilized with 5% diphenylamine and compression moulded at 190° C. for 4 minutes a tough white translucent disc was produced.

EXAMPLE X.

1,500 grams of trioxane and 1,500 grams of cyclohexane were heated at 75° C. to form a homogeneous solution. There was then added 0.35 ml. BF_3 -dihydrate catalyst. Polymer began to precipitate in 7 minutes. After 3 hours' heating and stirring at 75° C. a heavy polymer slurry was obtained.

A 2,500 gram portion of the polymer slurry was stirred for half an hour with 8.6 ml. tributyl amine at 75° C. The portion was filtered and washed twice with 200 ml. water at 90 to 95° C. for 15 minutes, after which it was dried overnight at 60° C. The inherent viscosity in *p*-chlorophenol (containing 2% alpha pinene) at 0.5% concentration at 60° C. was 1.20. The polymer formed very tough discs on compression moulding at 190° C. for 4 minutes.

The production of the polymer in particle form by the use of a substantial amount of inert liquid diluent during the polymerisation without slowing down the rate of polymerisation to the degree obtaining when the diluent is a solvent for trioxane can be obtained by effecting the polymerisation in a suspension comprising a continuous phase containing an inert, non-aqueous



liquid which is at least partially a non-solvent for trioxane and a disperse phase containing trioxane. The catalyst may be added to the suspension or it may be added to the suspension medium prior to the introduction of the trioxane. For best results the catalyst should be soluble in the suspension medium, although polymerisation will take place even when the catalyst is not soluble.

When operating in this manner, the liquid diluent is preferably a normal paraffin hydrocarbon having from 7 to 20 carbon atoms in the molecule. Mixtures of such hydrocarbons can be used, including suitable petroleum hydrocarbon fractions. The amount of diluent may, in general, be between 0.5 and 10 parts by weight per part of trioxane. It is desirable that the suspended trioxane should be molten, the temperatures used under normal atmospheric pressure thus being about 64° C. or higher, temperatures of 64 to 75° C. being preferred. Higher temperatures can, however, be employed, if necessary with the use of super-atmospheric pressure.

The suspension is maintained during polymerisation by vigorous stirring and, if desired, a surface active agent, e.g. sodium lauryl sulphate, can be used to assist the production and maintenance of a fine dispersion.

The following example illustrates this form of the invention:—

EXAMPLE XI.

100 parts by weight of trioxane was mixed with 73 parts by weight of normal decane and heated to 70° C. with rapid stirring to form a suspension of the molten trioxane in decane. Then 0.07 part by weight of BF_3 -etherate was added. Polymer began to form in a few minutes. The temperature rose to 73° C. The reaction mixture was held at 68° C. and stirred overnight. The reaction product was filtered off and washed twice with ether. The polymer was then washed 3 times with water at 90 to 95° C. and dried overnight at 60 to 65° C. in an air-circulating oven. 56.3 parts by weight of polymer was recovered. The polymer had an inherent viscosity of 0.86 when measured in *p*-chlorophenol (containing 2% alpha pinene) at 60° C. at 0.5% weight concentration.

On stabilizing the polymer with 5% diphenylamine, it was moulded at 180° C. for 2 minutes to produce white translucent discs.

Another method of producing the polymer in particle form comprises continuously introducing vapour phase trioxane into a confined reaction zone having a cooled surface, continuously introducing a vapour phase catalyst into said zone and continuously withdrawing the polymer particles.

This method can be operated so that the polymer particles are swept out of the reaction zone by a stream of gas or so that they are removed as a dense fluid suspension. The following example illustrates this method of operation:—

EXAMPLE XII.

Trioxane vapour at a temperature of 120° C. is introduced into a cylindrical jacketed reactor, provided with two inlets at one end and an outlet at the other, at the rate of 31 reactor volumes per minute. A stream of boron fluoride vapour diluted with 14,000 times its volume of nitrogen is simultaneously fed in at a boron fluoride rate of 0.08 volume per cent of the trioxane vapour feed. By circulating cooling water through its jacket, the wall of the reactor is maintained at 25° C.

Polyoxymethylene having an intrinsic viscosity of 3.69 (measured after washing with water in 0.5% solution at 60° C. in *p*-chlorophenol containing 2% alpha pinene) forms on the reactor wall upon which unreacted trioxane also collects. A rotatable scraper blade acting on the wall of the reactor is rotated intermittently or continuously to dislodge polymer and condensed trioxane which are thus blown out of the reactor by the effluent nitrogen. The solid particles of polymer and trioxane are recovered from the nitrogen stream by means of a cyclone separator, nitrogen and uncondensed materials being recycled to the reactor.

Instead of cooling the wall of the reactor other cooled surfaces may be provided, for instance cooling coils may be provided within the reaction zone and are generally more convenient when using the "fluid bed" principle. A cooling surface, which may satisfactorily be at a temperature between -20 and 50° C., must always be used since, in its absence, the trioxane vapour passes through the reactor without polymerising.

The diluent gas, which can, if desired, be introduced together with the trioxane, may usually be employed in quantities up to 50 times the volume of trioxane vapour fed, but is preferably not more than 20 times the volume of the trioxane vapour. The total gas feed rate should be between 10 and 1,000 reactor volumes per minute but is preferably not more than 500 reactor volumes per minute. When using the fluid bed principle a linear gas velocity of about 0.2 feet per second is satisfactory.

As is illustrated in Example XII, an important feature of this method of operation is that it enables polymers of exceptionally high molecular weight (as shown by their high intrinsic viscosities) to be obtained.

When using the fluid bed technique the





trioxane introduced as vapour possibly condenses to molten particles in the cooler part of the suspended bed of polymer particles. It is indeed likely that the trioxane passes through a similar stage when operating in the manner illustrated in Example XII. In any case, a very effective method of operation is one in which the trioxane is supplied to the reaction zone where it comes into contact with a gasiform catalyst as small droplets having a high surface to volume ratio. Preferably the surface of the trioxane is at least 0.8 square feet per pound weight, e.g. between 0.8 and 35 square feet per pound weight. For example, trioxane may be sprayed into the reaction zone as droplets having an average diameter of between 10 and 400 microns, e.g. about 200 microns, while at the same time gaseous boron fluoride diluted with a substantial quantity of nitrogen, e.g. 100 times its volume, is introduced. Solid polymer collects as a layer of powder at the bottom of the reaction vessel while nitrogen can be recycled after addition of boron fluoride to make up for that carried away by the product. The production of a sufficiently finely divided spray of trioxane may be assisted by feeding an inert gas to the spray nozzle or by injecting into the reaction zone trioxane dissolved in an aerosol propellant, e.g. the easily liquefiable halogenated hydrocarbons sold under the Registered Trade Mark "Freon", held liquid under pressure. The catalyst, where it is not gaseous, can likewise be introduced in dispersed form with the aid of an inert gas or an aerosol propellant.

Another method of achieving a high surface: volume ratio is to employ trioxane during at least part of the polymerisation as a liquid film. Thus a body of molten trioxane can be maintained in a hopper or other suitable supply source from which it is fed on to the moving surface of a casting wheel, an endless belt, a rotating disc or other convenient member or on to the surface of a current of mercury or molten alloy of low melting point. By bringing vapour-phase catalyst into contact with the molten film while maintaining the latter at a suitable temperature, e.g. 65° to 110° C., rapid production of polymer in a form convenient for after-treatment can be achieved. By providing sealing means between the surface of the film and the source of supply of molten trioxane, a confined reaction zone can be formed and thus control over catalyst utilization achieved. The residence time in the confined zone may vary from about 15 seconds to an hour, depending on the activity of the catalyst used at the operating temperature. The film thickness may vary between 5 and 200 mils to give an exposed area of between about 0.8 and about 35

square feet per pound of trioxane.

A modification of this method of operation which enables the operation to be carried out continuously, while taking advantage of the rapidity with which the novel catalysts enable the polymerisation to be effected, comprises effecting the intimate admixture of catalyst with a body of liquid-phase trioxane in a reaction zone and, after partial polymerisation has occurred, distributing the mixture containing trioxane, polymer and catalyst as a layer on a solid surface in a second reaction zone in which the polymerisation is continued. To avoid too rapid polymerisation it is desirable to have present a quantity of inert diluent and preferably the catalyst is dissolved in a suitable solvent, e.g. benzene. The following example illustrates this form of the invention:

EXAMPLE XIII.

Molten trioxane is continuously introduced into a reaction vessel provided with a high speed stirrer. Boron fluoride etherate, as a 1% solution in benzene, is simultaneously introduced at a rate which is 0.02% by weight of the trioxane introduction rate. The vessel and its contents are maintained at about 75° C. while stirring vigorously by operation of the stirrer at about 10,000 r.p.m.

The mixture in the reaction vessel is continuously withdrawn, the rate of withdrawal and the rate of feed of fresh materials being such that the volume remaining in the vessel stays constant and so that, if the feed were discontinued the vessel would empty in about 10 seconds.

The withdrawn material is dropped on to a moving conveyor belt enclosed in a chamber maintained at about 100° C. by the passage of hot nitrogen therethrough. The hot nitrogen vaporises most of the benzene and catalyst and a portion of the unreacted trioxane so that these materials can all be readily recovered.

The polymer formed is removed from the belt by a scraper blade placed at a suitable point in the path of the belt which is driven at such a rate that the layer of material deposited on it is about half an inch thick and the time occupied from deposition to polymer removal is about 5 seconds.

The conditions employed in the above Example XIII may be varied considerably while still giving excellent results. Generally the temperature in the reaction vessel may be between 65° and 114° C., temperatures between 70° and 110° C. being preferred. The average reaction time in the vessel may be between 1 and 60 seconds and is preferably between 5 and 10 seconds. The temperature maintained on the belt may be between 80° and 114° C., the thickness of the layer on the belt from one eighth to one

70
polymerisation

75

80

85

90

95

100

105

110

115

120

125

inch, and the reaction time in layer form between 3 seconds and 10 minutes.

The crude polymer produced by the process of the invention generally contains unreacted trioxane and catalyst. These substances can be removed by one or more washing operations with water, preferably hot, although, where an organic diluent has been used, a preliminary wash with a volatile solvent for the diluent, e.g. ether or acetone, is desirable. Even after washing the polymer normally contains traces of boron.

During the removal of the unreacted trioxane it has been found that degradation of the polymer is liable to occur, especially when the polymer is left in contact with substances such as the catalysts used in the polymerisation after removal of the trioxane.

It has been discovered that such degradation can be substantially avoided by treating the mixture of polymer, trioxane and catalyst with certain catalyst neutralising agents before removing the trioxane.

Treatment of the crude polymer with an aqueous washing liquid, e.g. water itself or, preferably, an aqueous solution of a basic salt such as sodium carbonate or an aqueous mixture with a water-soluble organic solvent such as a lower aliphatic alcohol or ketone, is effective in removing the catalyst. Indeed, by the use of sufficient washing liquid the trioxane can be removed as well. However, the use of water makes it necessary to dry the trioxane recovered, or even to separate it, e.g. by solvent extraction, from the washing liquor before drying it, before it is suitable for return to the polymerisation process.

The preferred catalyst neutralising agents are aliphatic primary, secondary and tertiary amines and heterocyclic amines, e.g. *n*-butylamine, di-*n*-butylamine, tri-*n*-butylamine and pyridine. Preferably slightly more amine is used than is needed to neutralise the catalyst and is applied to the crude polymer in organic liquid solution.

The following example further illustrates the use of a catalyst neutralising agent which has already been shown in Example X:—

EXAMPLE XIV.

1,500 grams of trioxane and 1,500 grams of cyclohexane were heated at 75° C. to form a homogeneous solution. There was then added 0.33 ml. BF₃·dihydrate catalyst. Polymer began to precipitate in 7 minutes. After 3 hours' heating and stirring at 75° C. about 2,500 grams of polymer slurry was stirred for half an hour with 8.6 ml. tributylamine at 75° C. The product was filtered and washed twice with cyclohexane at 75° C. and then twice with 2,000 ml. water at 90 to 95° C. for 15 minutes, after which it was dried overnight at 60° C. The inherent viscosity in *p*-chlorophenol (containing 2%

alpha pinene) at 0.5% concentration at 60° C. was 1.20. The polymer formed very tough discs on compression moulding at 190° C. for 4 minutes.

The effectiveness of the neutralising treatment described in the above Example XIV can be demonstrated by taking a further portion of 2,500 grams of the polymer slurry, filtering it, washing the recovered crude polymer twice with hot cyclohexane at 75° C. by re-slurrying and filtering, and then twice with water at 90 to 95° C. and drying overnight. The polymer thus obtained had an intrinsic viscosity (measured as in the example) of only 0.36 and produced a very brittle disc on compression moulding at 190° C. for 4 minutes. That the increased stability obtained when working according to the example was not due to the presence of tributylamine is clear from the fact that this amine is soluble in cyclohexane and would therefore be completely removed by the two washings with cyclohexane.

Apart from their use in purifying crude polymer, the catalyst neutralising amines can sometimes be used to advantage during the polymerisation process as a means of stopping further polymerisation. Thus, when carrying out the polymerisation so as to recover the polymer as particles suspended in a gaseous medium, the introduction of such an amine at the outlet from the reaction zone prevents further polymerisation and consequent danger of plugging of downstream lines.

The polymers made by the process of the invention can be compression moulded, satisfactory results usually being obtained at about 180° to 200° C. using moulding times of up to 4 or 5 minutes. The polymers, before moulding, may be blended with plasticisers, fillers, pigments, anti-oxidants and other stabilizers, such as stabilizers against degradation by ultra-violet light.

WHAT WE CLAIM IS:—

1. Process for the production of tough polymers of high molecular weight suitable for shaping under heat and pressure, which comprises polymerising trioxane in presence of free boron fluoride or a co-ordination complex of boron fluoride with water or with an organic compound in which the donor atom is oxygen or sulphur.

2. Process according to Claim 1, wherein the catalyst consists of a co-ordination complex of boron fluoride with diethyl ether, with phenol or with acetic acid.

3. Process according to either of the preceding claims, wherein the catalyst is present in the polymerisation zone in quantity equal to between .003 and .1% by weight based on the weight of the trioxane.

4. Process according to any of the pre-





inch, and the reaction time in layer form between 3 seconds and 10 minutes.

The crude polymer produced by the process of the invention generally contains unreacted trioxane and catalyst. These substances can be removed by one or more washing operations with water, preferably hot, although, where an organic diluent has been used, a preliminary wash with a volatile solvent for the diluent, e.g. ether or acetone, is desirable. Even after washing the polymer normally contains traces of boron.

During the removal of the unreacted trioxane it has been found that degradation of the polymer is liable to occur, especially when the polymer is left in contact with substances such as the catalysts used in the polymerisation after removal of the trioxane.

It has been discovered that such degradation can be substantially avoided by treating the mixture of polymer, trioxane and catalyst with certain catalyst neutralising agents before removing the trioxane.

Treatment of the crude polymer with an aqueous washing liquid, e.g. water itself or, preferably, an aqueous solution of a basic salt such as sodium carbonate or an aqueous mixture with a water-soluble organic solvent such as a lower aliphatic alcohol or ketone, is effective in removing the catalyst. Indeed, by the use of sufficient washing liquid the trioxane can be removed as well. However, the use of water makes it necessary to dry the trioxane recovered, or even to separate it, e.g. by solvent extraction, from the washing liquor before drying it, before it is suitable for return to the polymerisation process.

The preferred catalyst neutralising agents are aliphatic primary, secondary and tertiary amines and heterocyclic amines, e.g. *n*-butylamine, di-*n*-butylamine, tri-*n*-butylamine and pyridine. Preferably slightly more amine is used than is needed to neutralise the catalyst and is applied to the crude polymer in organic liquid solution.

The following example further illustrates the use of a catalyst neutralising agent which has already been shown in Example X:—

EXAMPLE XIV.

1,500 grams of trioxane and 1,500 grams of cyclohexane were heated at 75° C. to form a homogeneous solution. There was then added 0.33 ml. BF₃-dihydrate catalyst. Polymer began to precipitate in 7 minutes. After 3 hours' heating and stirring at 75° C. about 2,500 grams of polymer slurry was stirred for half an hour with 8.6 ml. tributylamine at 75° C. The product was filtered and washed twice with cyclohexane at 75° C. and then twice with 2,000 ml. water at 90 to 95° C. for 15 minutes, after which it was dried overnight at 60° C. The inherent viscosity in *p*-chlorophenol (containing 2%

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The polymers made by the process of the invention can be compression moulded, satisfactory results usually being obtained at about 180° to 200° C. using moulding times of up to 4 or 5 minutes. The polymers, before moulding, may be blended with plasticisers, fillers, pigments, anti-oxidants and other stabilizers, such as stabilizers against degradation by ultra-violet light.

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2. Process according to Claim 1, wherein the catalyst consists of a co-ordination complex of boron fluoride with diethyl ether, with phenol or with acetic acid.

3. Process according to either of the preceding claims, wherein the catalyst is present in the polymerisation zone in quantity equal to between .003 and .1% by weight based on the weight of the trioxane.

4. Process according to any of the pre-





ceding claims, wherein the trioxane employed is substantially anhydrous.

5 5. Process according to any of the preceding claims, wherein the trioxane is subjected to polymerisation while it is in liquid form.

10 6. Process according to any of the preceding claims, wherein the polymerisation is carried out in presence of a solvent for the catalyst, for the trioxane or for both catalyst and trioxane.

15 7. Process according to Claim 6, wherein the polymerisation is carried out in presence of such a quantity of solvent that the polymer is produced as a slurry of particles.

20 8. Process according to any of Claims 1 to 5, wherein the polymerisation is effected in a suspension comprising a continuous phase containing an inert non-aqueous liquid which is at least partially a non-solvent for trioxane and a disperse phase containing trioxane.

25 9. Process according to Claim 8, wherein the catalyst is soluble in said non-aqueous liquid.

30 10. Process according to Claim 9, wherein said non-aqueous liquid is a normal paraffin hydrocarbon having from 7 to 20 carbon atoms in the molecule.

35 11. Process according to any of Claims 1 to 4, wherein the polymer is produced in particle form by a process which comprises continuously introducing vapour phase trioxane into a confined reaction zone having a cooled surface, continuously introducing a vapour phase catalyst into said zone, and continuously withdrawing the polymer particles.

40 12. Process according to any of Claims 1 to 5, wherein the trioxane is supplied to the reaction zone as small droplets having a high surface to volume ratio, the catalyst within the reaction zone being in the gas phase.

45 13. Process according to any of Claims 1 to 5, wherein the trioxane during at least part of the polymerisation process is in the form of a liquid film.

50 14. Process according to Claim 13, wherein said film is supported on a moving surface.

55 15. Process according to Claim 12, 13 or 14, wherein the form of the trioxane in the polymerisation zone is such that its surface amounts to between 0.8 and 35 square feet per pound weight.

16. Process according to any of Claims 1 to 5, wherein the catalyst is mixed with a

body of liquid phase trioxane in a reaction zone and, after partial polymerisation has occurred, the mixture obtained containing trioxane, polymer and catalyst is distributed as a layer on a moving solid surface upon which further polymerisation occurs.

60 17. Process according to any of the preceding claims, wherein the crude polymer is subjected to treatment with a catalyst neutralising agent before removing any unpolymerised trioxane therefrom.

70 18. Process according to Claim 17, wherein the catalyst neutralising agent is an aliphatic primary, secondary or tertiary amine or a heterocyclic amine.

75 19. Process according to any of the preceding claims, wherein the thermal stability of the polymer is improved by incorporating therein an N,N,N^1,N^1 tetra(hydroxyalkyl) alkylene diamine.

80 20. Process according to Claim 19, wherein the said diamine contains from 1 to 5 carbon atoms and only 1 hydroxy group in each hydroxyalkyl radical and from 1 to 6 carbon atoms in its alkylene group.

85 21. Process according to Claim 20, wherein the diamine is N,N,N^1,N^1 tetrakis (2-hydroxypropyl)-1,2 ethylene diamine or N,N,N^1,N^1 tetrakis (2-hydroxyethyl)-1,2 ethylene diamine.

90 22. Process according to Claim 19, 20 or 21, wherein the diamine is added in quantity equal to between 0.5 and 10% by weight on the polymer.

95 23. Process for the production of tough polymers of high molecular weight and suitable for shaping under heat and pressure, substantially as hereinbefore described.

24. Tough polymers of high molecular weight and suitable for shaping under heat and pressure, whenever produced by any of the processes claimed in the preceding 100 claims.

25. Tough polyoxymethylene of high molecular weight and suitable for shaping under heat and pressure and stabilized with an N,N,N^1,N^1 tetra(hydroxyalkyl) alkylene 105 diamine.

26. Polymers according to Claim 25, wherein the polymer is stabilized with from 0.5 to 10% by weight of the N,N,N^1,N^1 tetrakis (2-hydroxypropyl)-1,2 ethylene di- 110 amine or the N,N,N^1,N^1 tetrakis (2-hydroxyethyl)-1,2 ethylene diamine.

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