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NO DRAWINGS

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COMPLETE SPECIFICATION

Stabilising Oxymethylene Polymers

We, CELANESE CORPORATION OF AMERICA, of 180 Madison Avenue, New York 16, 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 the stabilisation of oxymethylene polymers against thermal degradation.

Oxymethylene polymers, i.e. polymers having recurring $\text{—CH}_2\text{O—}$ units directly attached to each other, may be prepared by the polymerisation of anhydrous formaldehyde or of trioxane, the cyclic trimer of formaldehyde. Oxymethylene polymers vary in thermal stability and in molecular weight, depending on their method of preparation.

Oxymethylene polymers which consist mainly of oxymethylene groups but contain also oxyalkylene groups having two or more adjacent carbon atoms are of improved thermal stability; such polymers can be prepared by copolymerising trioxane with from 0.1 to 15 mole percent of a cyclic ether having at least two adjacent carbon atoms, as described in British Patent No. 903668. The preferred polymers are those made up of oxymethylene and oxyethylene groups, such as may be obtained by copolymerising trioxane with dioxolane or with ethylene oxide. By incorporation of chemical stabilisers it has been possible to stabilise these oxymethylene polymers further so that their degradation rate is less than 0.1 weight percent per minute for most of the polymer mass. (Throughout this specification "thermal degradation rate" of a polymer means the rate at which the polymer loses weight when it is maintained in an open vessel in a circulating air oven at $222^\circ\text{C}.$). However, despite this high stability for most of the polymer mass, it has

been difficult to reduce the initial thermal degradation rate of the polymer to a satisfactory level. It has been found that a polymer may be reduced to a thermal degradation rate for most of its mass of less than 0.1 weight percent per minute while the initial 0.5 to 20 weight percent of the polymer has a higher thermal degradation rate of the order of between 1 and 0.5 weight percent per minute. For the purpose of convenience the thermal degradation rate for most of the polymer mass is hereinafter designated as the "base" degradation rate.

During moulding processes, oxymethylene polymers are generally heated to temperatures between 180° and $230^\circ\text{C}.$ for relatively short periods of time between 5 seconds and 5 minutes. Even where the base thermal degradation rate has been reduced to below 0.1 weight percent per minute, it has been found that moulded products have uneven surface characteristics, due to gas formation, unless the initial thermal degradation rate is also reduced to below 0.1 weight percent per minute.

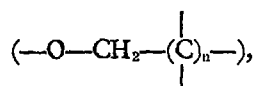
According to the present invention, an oxymethylene polymer containing in the polymer molecule oxyalkylene units having two or more adjacent carbon atoms is heated under non-acidic conditions with water, an organic hydroxy compound or a mixture thereof to remove formaldehyde or the elements thereof from the polymer until the polymer weight loss per minute falls below 5% of the weight loss during the first minute of heating. The organic hydroxy compound may be, for instance, a primary, secondary or tertiary alcohol. A most important method of carrying out the process involves the use of an aqueous mixture which is a solvent for the polymer at elevated temperatures. Preferably the polymer is subjected to the degradation treatment until substantially constant weight is achieved.

Formaldehyde is the principal hydrolysis degradation product of oxymethylene polymers and it is believed to be formed by the succes-

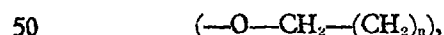
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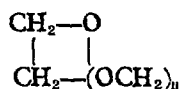
- sive detachment of terminal $-\text{CH}_2\text{OH}$ units from the end of the polymer chain, a hydrogen atom of each such terminal group removed passing to the oxygen atom of the neighbouring group. When oxyethylene units, for example, are present in the polymer chain, as described above, it would appear that the successive detachment of $-\text{CH}_2\text{OH}$ units takes place until an oxyethylene unit is reached, but that the $-\text{CH}_2\text{CH}_2\text{OH}$ group then formed is resistant to such detachment and remains attached to the polymeric chain and protects the polymer from further hydrolysis. The thus degraded polymer has been found to have a better initial thermal stability than the original polymer from which it was derived. Moreover, it has been found that the product, after substantially constant weight is achieved, is also extremely stable against attack by the basic reactants even at concentrations and conditions more severe than those employed in the degradation treatment despite the fact that the polymer still has a high content of oxymethylene units. By means of the invention oxymethylene polymers can be obtained which may be subjected (as a disc of 50 mils thickness) to the action of 50 weight percent sodium hydroxide at 145°C . with the loss of no more than 1% of its weight in $\frac{1}{2}$ hour.
- The invention is of especial importance in connection with normally solid, water-insoluble polymers containing recurring oxymethylene groups and from 0.5 to 25 higher oxyalkylene groups per 100 oxymethylene groups, and especially from 0.7 to 4 higher oxyalkylene groups having up to 5 carbon atoms per 100 oxymethylene groups. In the preferred polymers the higher oxyalkylene groups are oxyethylene groups.
- Among the polymers which may, with advantage, be subjected to the process of the invention are those having a structure comprising recurring units having the formula



- wherein n is an integer from zero to 4 and wherein n is zero in from 99.5 to 75% of the recurring units. Preferred polymers are those having a structure comprising recurring units having the formula



- wherein n is an integer from zero to 2 and wherein n is zero in from 95.5 to 75% of the recurring units. These polymers can be prepared by copolymerising trioxane with a cyclic ether having the structure



where n is an integer from zero to two. 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 - butylene oxide, neopentyl formal, pentaerythritol diformal, paraldehyde, tetrahydrofuran and butadiene monoxide.

Preferably the catalyst used in the preparation of the desired polymers is a boron fluoride co-ordination complex with organic compounds in which oxygen or sulphur is the donor atom, especially boron fluoride dibutyl etherate, the co-ordination complex of boron fluoride with dibutyl ether. The reaction mixture used in making the polymer may contain the cyclic ether in amounts between about 0.5 and 30 mole percent, and preferably between about 0.7 and about 4 mole percent, based on the total moles of monomer. The polymers and their production are described in detail in our British Patent No. 903,668.

The polymer may be subjected to the degradation treatment immediately after completion of the polymerisation reaction or, if desired, it may first be subjected to washing and drying to remove unreacted monomers, solvent and catalyst residues. The polymer may be subjected to the degradation treatment as a finely divided solid material, as in a slurry, but, preferably, is subjected to the treatment while in solution.

Suitable solvents or solvent ingredients for the polymer include dimethyl formamide, benzyl alcohol, methanol, ethylene glycol and anisole. A solvent or solvent ingredient which contains a hydroxyl group, such as benzyl alcohol, methanol or ethylene glycol, may also function as the hydroxy-compound above described as part of the agent for effecting degradation. Some solvents, such as aqueous dimethyl formamide, do not have any solvent action on the polymer until temperatures of the order of 130°C . are reached. The amount of solvent will naturally depend on the nature of the solvent, the polymer and the basic material. Generally, amounts between 200 and 3 cc. of solvent per gram of polymer are suitable and preferably between 20 and 7 cc. are used.

As already indicated, a most important method of carrying out the degradation treatment involves the use of an aqueous mixture which is a solvent for the polymer at elevated temperatures, for instance a mixture of water and a water-soluble, normally liquid, non-acidic organic compound containing an ether oxygen atom or an oxygen atom in a hydroxy group or a non-terminal carbonyl group directly bonded to a carbon atom.

The solvent mixture may comprise from 10 to 90 weight percent of water. Among the organic compounds which may thus be used are alcohols such as methanol, ethanol, propanol, isopropyl alcohol, tertiary butyl alcohol

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pentacerythritol

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- and allyl alcohol; glycols such as ethylene glycol; ketones such as acetone and methyl ethyl ketone; alkanolamines such as mono-, di- and triethanolamine; esters such as methyl acetate and methyl formate; and ethers such as methyl isopropyl ether, methylal, m-dioxane and p-dioxane. The preferred organic compounds are the water-soluble, normally liquid alkanols and the invention is described below primarily in terms of such alkanols. The water-solubility of the organic compound must be at least such as to permit the formation of a single phase mixture of the desired proportions at the treatment temperature.
- It has been found that the aqueous mixtures described permit complete solution of the polymer at lower temperatures than either the water or the organic compound alone and permit the hydrolysis to proceed more rapidly and at lower temperatures than are otherwise possible except when expensive and exotic solvents are used.
- The degradation treatment of oxymethylene polymers may take from less than 15 seconds to 10 hours, depending on the ingredients of the degradation medium, the severity of the conditions used and the physical state of the polymer. Under the preferred conditions the treatment can usually be completed in from 15 seconds to 2 minutes. The degradation treatment can be carried out very satisfactorily between 90° and 200°C. and is preferably effected between 130° and 180°C.
- The preferred basic materials are water-soluble, or soluble in the organic hydroxy-compound or aqueous solvent mixture employed. There may be used a strongly basic hydroxide, such as the hydroxide of an alkali metal or of an alkaline earth metal, or a salt of a strong base with weak acid, or ammonia, or an organic base such as an amine or an amidine.
- Among the specific basic materials which are satisfactory are sodium hydroxide, potassium hydroxide, sodium carbonate, sodium acetate, ammonium hydroxide, triethanolamine, tripropylamine, tetramethylguanidine, trimethylamine and tributylamine.
- The amount of basic material used may be varied widely, according to the particular polymer, basic material and hydrolysis conditions used.
- Preferably at least 0.1% by weight of basic material is used based on the weight of polymer. More may be employed, e.g. up to ten times the weight of polymer, while the degradation treatment can, if desired, consist of hydrolysis in the absence of any basic material. When no basic material is used, it is desirable to hydrolyse in a buffered system since the products of hydrolysis would otherwise cause the system to become acidic. Acidic degradation is not selective and does not produce the stable polymer formed by the process of the invention. Alkaline hydrolysis is preferable to neutral hydrolysis since it is more rapid and since the alkaline material neutralises any polymerisation catalyst present which would otherwise tend to degrade the polymer during the hydrolysis step. The preferred proportion of basic material is generally from 0.1 to 20% by weight of basic material, based on the weight of polymer; however, where ammonia is used as the basic material, it is preferred to use between 0.1 and 5% by weight to avoid the formation of odour-containing by-products.
- The water, organic hydroxy-compound or aqueous solvent mixture is preferably present in amounts between 5 and 10 times the weight of polymer. Smaller quantities, e.g. down to 0.1% of the weight of polymer, may however be used and, of course, much more may be used if desired, e.g. up to 100 times the weight of polymer. At the higher temperatures indicated for the degradation treatment, water may be present in the reaction zone as steam. However, it is preferred to conduct the treatment under sufficient pressure to maintain the water present in liquid phase.
- In one advantageous method of operation, crude oxymethylene polymer taken from the polymerisation zone may be quenched with a medium which is suitable for effecting the degradation treatment. For example, a product removed from a polymerisation zone at a temperature between 60° and 116°C. may be quenched with from 5 to 50 times its weight of a water-methanol mixture containing from 30 to 90 weight percent of methanol, based on the weight of the mixture. The mixture of polymerisation product and quench medium is wet ground to break up the larger particles of polymer and form a slurry containing from 2 to 20 weight percent of solids. From 10 to 1000 ppm of ammonia (based on the weight of solid polymer) is added and the slurry is passed through a double pipe exchanger wherein it reaches a temperature between 150° and 180°C. and a pressure between 230 and 300 pounds per square inch gauge. Under these conditions, the polymer dissolves in the slurry medium. The dwell time in the pipe exchanger is between 30 and 60 seconds. Water is then added in a mix tee to reduce the temperature to between 30° and 95°C. to precipitate the polymer.
- Isopropyl alcohol-water mixtures are particularly desirable as solvent media since the polymers precipitate therefrom in granular form.
- During the degradation treatment a portion of the polymer is decomposed resulting in a weight loss of polymer. The treatment is complete when the weight loss substantially ceases. Between 5 and 40 weight percent of polymer may be lost before the rate of weight loss drops to between 0.1% and 5% of its original value, indicating substantial completion of the treatment. At this stage at

least 95% of the oxymethylene polymer molecules appear to have both ends terminated by higher oxyalkylene units. The weight loss suffered by an oxymethylene polymer during treatment is dependent on the particular polymer treated and particularly on the number of higher oxyalkylene groups per 100 oxymethylene groups in the polymer.

After completion of the treatment, the polymer may be precipitated from solution by cooling as described above, or by adding a large amount of a non-solvent, and may then be washed with water and dried.

It is generally desirable to incorporate one or more thermal stabilisers into the polymer in order to bring its thermal degradation level even lower. While the proportion of stabiliser incorporated depends upon the specific stabiliser used, a proportion between 0.05 and 10 weight percent (based on the weight of polymer) has been found to be suitable for most stabilisers.

One suitable stabiliser system is a combination of an anti-oxidant ingredient, such as phenolic anti-oxidant and most suitably a substituted bisphenol, and an ingredient to inhibit chain scission, generally a compound or a polymer containing trivalent nitrogen atoms. Suitable stabiliser systems of this type, and methods of incorporating the stabilisers, are

described in our British Patent No. 964,004.

The following examples illustrate the invention:—

EXAMPLE 1

500 parts by weight of an oxymethylene polymer containing 3.1 weight percent of monomeric units derived from dioxolane, 1000 parts of water and 150 parts of triethanolamine were heated at 140 to 150°C. for 2½ hours in a sealed pressurized vessel. At the end of this period the vessel was cooled to room temperature and opened. The polymer was washed successively with acetone and hot water and then dried.

Samples of the product and of the original polymer were each milled with 0.1% by weight of cyanoguanidine and 0.5% by weight of 2,2' - methylenebis - (4 - methyl - 6 - tertiarybutyl phenol). The milling operation was carried out in a heated chamber with sigma blade mixers over a period of 45 minutes and the temperature during milling was 200 to 202°C. The amount of material lost during milling and the thermal degradation rates of both original and treated polymer, both before and after incorporation of the stabilisers, is shown in Table 1 below. The thermal degradation rate in this and subsequent Examples is reported as weight percent loss/minute.

TABLE 1

Polymer	Degradation Rate		Weight Loss During Milling
	Without Stabilisers	With Stabilisers	
Original	0.88	0.018	5%
After treatment	0.50	0.015	0.2%

EXAMPLE 2

A mixture of 100 grams of an oxymethylene polymer made by copolymerising trioxane and dioxolane, and having an oxyethylene content equivalent to 3.9 weight percent of dioxolane, 1000 cc. of water and 67 cc. of ammonium hydroxide (28% NH₃) was heated 17½ hours at 95 to 98°C. in a glass flask under reflux. At the end of this period the reaction mixture was cooled. The polymer was separated by filtration and afterwards was washed with water to neutrality and dried. The weight loss

was 9% based on the weight of original polymer.

Samples of the original polymer and the treated polymer were each milled for 45 minutes as in Example 1 with 0.1 weight percent of nitrilotripropionamide and 0.5 weight percent of 2,2' - methylene bis - (5 - methyl - 6 - tertiary butyl phenol). The amount of material lost during milling and the degradation rates of both original and treated polymer, after incorporation of the stabilisers, is shown in Table 2 below:—

TABLE 2

Polymer	Degradation Rate	Weight Loss During Milling
Original	0.06	16.4%
After treatment	0.02	7.4%

EXAMPLE 3

5 A mixture of 120 grams of an oxymethylene polymer made by copolymerising trioxane and dioxolane and having an oxyethylene content equivalent to 3.1 weight percent of dioxolane, 600 cc. of water, 600 cc. of dimethyl - formamide and 37 grams of tripropylamine was heated to 148 to 152°C. in a pressure vessel for 21 minutes. The polymer was in solution.

After cooling to precipitate the polymer, the precipitated material was separated by filtration, washed with acetone and dried. The weight loss was 8.4% of the original polymer.

Samples of the original polymer and the treated polymer were milled with the stabilisers used in Example 1. The results after stabilisation are shown in Table 3.

TABLE 3

Polymer	Degradation Rate	Weight Loss During Milling
Original	0.016	6%
After treatment	0.010	2%

20 When the treated polymer was milled with the stabilisers for only 7 minutes, the weight loss was 1.7% and the degradation rate was 0.009.

EXAMPLE 4

25 A mixture of 120 grams of the polymer used in Example 3, 600 cc. of dimethyl-formamide, 590 cc. of water and 20 grams of concentrated ammonium hydroxide (28% NH_3) was heated to 148 to 152°C. for 10 minutes in a pressure vessel. The polymer was in solution. After cooling to precipitate the polymer, washing with water and drying, 10.3 weight percent of the original polymer had been lost.

30 When the polymer was milled for 7 minutes, as in Example 3, it lost 1.8% of its weight and its degradation rate was 0.007.

EXAMPLE 5

40 A mixture of 100 grams of the polymer used in Example 3, 1000 cc. of methanol and 20 grams of tetramethylguanidine was heated to 158 to 165°C. for 15 minutes in a pressure vessel. After cooling to precipitate the polymer, washing with water and drying, 12.1 weight percent of the original polymer had been lost. When the polymer was milled for 7 minutes, as in Example 3, it lost 1.4% of its weight and its thermal degradation rate was 0.009.

EXAMPLE 6

50 (a) A mixture of 100 parts by weight of trioxane, 2.4 parts of ethylene oxide, 1.1 parts of cyclohexane, 340 ppm of methylal and 70 ppm of boron trifluoride (as the dibutyl etherate complex) was fed to one end of a continuous mixer having an interrupted thread screw placed in a cylindrical barrel. The mixer barrel had rows of teeth on its inner surface and the screw was both rotated and reciprocated in such a manner that the teeth on the barrel passed through the interruptions in the thread of the screw. The reaction mass

advanced in a generally helical path with alternate advance and retraction as is progressed to the discharge point.

The temperature in the mixer rose to a maximum of 105° to 115°C. at the discharge point. Dwell time in the mixer was about 1 minute.

(b) The discharged product was mixed in a wet grinder with 1250 parts of a solution of 59.9 weight percent of methanol, 40 weight percent of water and 0.1 weight percent of ammonia and ground to produce a slurry of 8% solids content. The slurry was passed into a double-pipe heat exchanger wherein it was heated to 160°C. at 240 pounds per square inch gauge. The polymer dissolved. After 45 seconds in the exchanger, water was added in a mixing tee to reduce the temperature and precipitate the polymer.

EXAMPLE 7

80 A sample of a polymer prepared in the manner as described in Example 6(a) was quenched in an ammonia-free methanol-water solution (60—40 ratio by weight), removed and dried. A mixture of 130 parts by weight of the dry polymer and 867 parts by weight of a solution containing 59.9 weight percent of isopropyl alcohol, 40.0 weight percent of water and 0.1 weight percent of ammonia was heated rapidly to 160°C. and 150 pounds per square inch gauge in a 3 litre rocking autoclave. As soon as the temperature reached 160°C. the autoclave was immersed in a water bath to reduce the temperature rapidly and precipitate the polymer. The polymer precipitated as a uniform granular mass containing approximately 95% of the mother liquor.

EXAMPLE 8

100 A mixture of 130 parts by weight of a polymer prepared as described in Example 6(a) and 867 parts by weight of a solution

containing 58 weight percent acetone, 41.9 weight percent water and 0.1 weight percent sodium acetate was treated in a 3 litre autoclave as described in Example 7. The polymer

5 precipitated as a uniform granular mass containing approximately 95% of the mother liquor.

The advantage achieved by using a water-containing solvent mixture as in Examples 7 and 8 is seen from the fact that if in Example 7, 867 parts of either water or isopropyl alcohol alone are used instead of the mixture, the polymer is obtained as a hard non-friable lump instead of a uniform granular mass.

15 WHAT WE CLAIM IS:—

1. Process for improving the thermal stability under moulding conditions of a solid oxymethylene polymer containing in the polymer molecule oxyalkylene units having two or more adjacent carbon atoms, which comprises heating the polymer under non-acidic conditions with water, an organic hydroxy compound or a mixture thereof to remove form-
20 aldehyde or its elements from the polymer until the polymer weight loss per minute falls below 5% of the weight loss during the first minute of heating.

2. Process according to Claim 1, wherein maintenance of non-acidic conditions is ensured by the presence of a basic substance.

3. Process according to Claim 2, wherein the polymer is heated with at least 0.1% of its weight of ammonia.

4. Process according to Claim 1, 2 or 3,

wherein the polymer is heated in solution in a medium containing a water-soluble, normally liquid, non-acidic organic compound containing an ether oxygen atom or an oxygen atom in a hydroxy group or a non-terminal carbonyl group directly bonded to a carbon atom.

5. Process according to Claim 4, wherein said organic compound is an alkanol.

6. Process according to Claim 5, wherein said alkanol is isopropanol.

7. Process according to any of Claims 1 to 5, wherein the degradation treatment is effected at a temperature between 90 and 200°C.

8. Process according to any of Claims 1 to 7, wherein the polymer treated is made up of oxymethylene and oxyethylene groups.

9. Process according to any of the preceding claims, wherein the degradation treatment is continued until substantially constant weight is achieved.

10. Process for the treatment of oxymethylene polymers, substantially as hereinbefore described.

11. Process for the treatment of oxymethylene polymers containing oxyethylene groups, substantially as described in each of the Examples.

12. Stabilised polymers whenever produced by any of the processes claimed in the preceding claims.

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containing 58 weight percent acetone, 41.9 weight percent water and 0.1 weight percent sodium acetate was treated in a 3 litre autoclave as described in Example 7. The polymer

5 precipitated as a uniform granular mass containing approximately 95% of the mother liquor.

The advantage achieved by using a water-containing solvent mixture as in Examples 7 and 8 is seen from the fact that if in Example

10 7, 867 parts of either water or isopropyl alcohol alone are used instead of the mixture, the polymer is obtained as a hard non-friable lump instead of a uniform granular mass.

15 WHAT WE CLAIM IS:—

1. Process for improving the thermal stability under moulding conditions of a solid oxymethylene polymer containing in the polymer molecule oxyalkylene units having two or

20 more adjacent carbon atoms, which comprises heating the polymer under non-acidic conditions with water, an organic hydroxy compound or a mixture thereof to remove formaldehyde or its elements from the polymer

25 until the polymer weight loss per minute falls below 5% of the weight loss during the first minute of heating.

2. Process according to Claim 1, wherein maintenance of non-acidic conditions is ensured by the presence of a basic substance.

30 3. Process according to Claim 2, wherein the polymer is heated with at least 0.1% of its weight of ammonia.

4. Process according to Claim 1, 2 or 3,

wherein the polymer is heated in solution in a medium containing a water-soluble, normally liquid, non-acidic organic compound containing an ether oxygen atom or an oxygen atom in a hydroxy group or a non-terminal carbonyl group directly bonded to a carbon atom.

5. Process according to Claim 4, wherein said organic compound is an alkanol.

6. Process according to Claim 5, wherein said alkanol is isopropanol.

7. Process according to any of Claims 1 to 5, wherein the degradation treatment is effected at a temperature between 90 and 200°C.

8. Process according to any of Claims 1 to 7, wherein the polymer treated is made up of oxymethylene and oxyethylene groups.

9. Process according to any of the preceding claims, wherein the degradation treatment is continued until substantially constant weight is achieved.

10. Process for the treatment of oxymethylene polymers, substantially as hereinbefore described.

11. Process for the treatment of oxymethylene polymers containing oxyethylene groups, substantially as described in each of the Examples.

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