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Musser et al.

[11] **3,875,257**

[45] **Apr. 1, 1975**

[54] **BROMINATED BISPHENOL A DIETHANOL POLYFORMAL**

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[22] Filed: **Nov. 30, 1973**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 281,259, and a continuation-in-part of Ser. No. 365,773.

[52] **U.S. Cl.**..... **260/860,** 8/DIG. 4, 260/DIG. 24

[51] **Int. Cl.**..... **C08g 39/10**

[58] **Field of Search**..... 260/52, 860, 51 R; 8/21 C, 8/179, DIG. 4

[56] **References Cited**

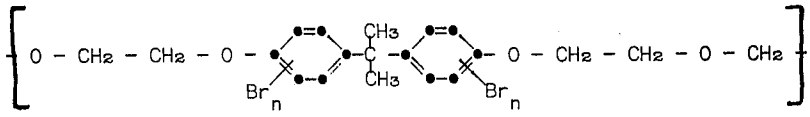
UNITED STATES PATENTS

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Primary Examiner—Harold D. Anderson
Assistant Examiner—Edward Woodberry

[57] **ABSTRACT**

Disclosed is a brominated bisphenol A diethanol polyformal comprised of recurring units of the structure



where *n* is 1 or 2. This polyformal can be formed into a moldable or fiber-forming composition comprising an admixture of from 75 to 98 weight percent polyester and from 25 to 2 weight percent of the polyformal. The admixture of the polyester and the polyformal can, depending on the precise conditions of time, temperature and pressure, form, in whole or in part, a copolymer of blocks of polyester and blocks of polyformal. The admixture, the block copolymer or a combination of the two can be formed into useful articles.

16 Claims, No Drawings

BROMINATED BISPHENOL A DIETHANOL POLYFORMAL

This application is a continuation-in-part of our copending application Ser. No. 281,259, filed Aug. 16, 1972, entitled BROMINATED BISPHENOL A DIETHANOL POLYFORMAL, now U.S. Pat. No. 3,809,681 and our copending application Ser. No. 365,773, filed May 31, 1973, and now abandoned, entitled BROMINATED BISPHENOL A DIETHANOL POLYFORMAL COPOLYMER.

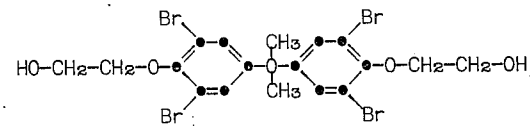
This invention broadly relates to a polyformal of brominated bisphenol A diethanol and formaldehyde. In a first embodiment, this invention relates to the brominated bisphenol A diethanol polyformal itself. In a second embodiment, this invention relates to a composition formed by admixing the brominated bisphenol A diethanol polyformal with a polyester. In a third embodiment, this invention relates to a composition of a block copolymer formed from the admixture.

The use of textile fibers and molded objects of synthetic polymers has increased tremendously over the last several decades. The increase in the use of synthetic polymers for preparing synthetic fibers has resulted in large part from the desirable combination of properties that can be achieved in a textile article by using synthetic fibers or blends of natural and synthetic fibers.

Although synthetic fibers exhibit many desirable properties, one undesirable property of many synthetic fibers is a lack of flame retardancy. Several years ago the desirability of flame retardant fabrics began to be recognized. At this time, synthetic fibers were regarded as satisfactory from the flame retardancy standpoint if they exhibited even a moderate degree of flame retardancy. Later, higher standards of flame retardancy for certain finished goods became desirable. These standards required more than a moderate degree of flame retardancy. Still later, federal legislation created the current standards of flame retardancy. These standards require a great deal of flame retardancy for certain types of finished goods, such as children's sleepwear. Pursuant to this legislation a test was established, often called "the Children's Sleepwear Test," to determine the acceptability of fabrics for children's sleepware. Thus, the current standard of flame retardancy has now caused many textile fibers to be regarded as commercially unsatisfactory for children's sleepwear because, even though the fabric exhibits a substantial degree of flame retardency, the fabric will not pass the Children's Sleepwear Test. Consequently, because of the present flame retardancy standards, a fabric which exhibits additional flame retardancy often means the difference between being passing and failing the Children's Sleepwear Test and consequently the difference between the fiber being commercially acceptable and commercially unacceptable.

The published prior art that applicants are aware of is German Pat. No. 1,252,413, Polish Pat. No. 48,893, German Pat. No. 1,149,899, German Pat. No. 1,001,819, Japanese Pat. No. 71/3174, Japanese Pat. No. 71/10101, Dutch Pat. No. 70/15991, British Pat. No. 1,115,611, British Pat. No. 1,206,171, U.S. Pat. No. 2,968,646, U.S. Pat. No. 2,568,658, U.S. Pat. No. 2,587,442, U.S. Pat. No. 3,234,167, U.S. Pat. No. 3,234,168, U.S. Pat. No. 3,294,742, U.S. Pat. No. 3,334,152, U.S. Pat. No. 3,367,990, U.S. Pat. No. 3,395,118 and U.S. Pat. No. 3,524,901.

The unpublished prior art that applicants are aware of is the knowledge by others in this country, before the invention thereof by the applicants, of a textile fiber, hereinafter called the diethanol fiber, formed from a polymer of terephthalic acid, ethylene glycol and tetrabromobisphenol A diethanol having the formula

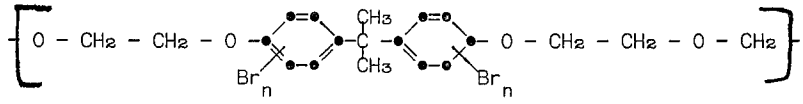


The tetrabromobisphenol A diethanol polyformal containing fibers of this invention, hereinafter called the polyformal fibers, are patentably distinguishable over the diethanol fibers of the prior art because the polyformal fibers exhibit an unobviously high degree of flame retardancy over the diethanol fibers.

The tetrabromobisphenol A diethanol polyformal copolymer, hereinafter called the polyformal copolymer, is thought to be patentable over the polymer of terephthalic acid, ethylene glycol and tetrabromobisphenol A diethanol, hereinafter called the diethanol polymer, because the amorphous polyformal copolymer exhibits an unobviously low crystallization temperature upon heating and an unobviously high crystallization temperature upon cooling from the melt.

The tetrabromobisphenol A diethanol polyformal is thought to be patentable because of the unobviously high flame retardancy of the polyformal fibers and because of the unobvious crystallization temperature properties of the polyformal copolymers.

Broadly speaking, the brominated bisphenol A diethanol polyformal of the first embodiment of this invention, hereinafter called the polyformal, can be described as a polymeric composition having repeating units of the structure



wherein n is 1 or 2. Broadly, the inherent viscosity of the polyformal can be in the range of 0.03 to 1.0. In another aspect of this invention the inherent viscosity of the polyformal can be in the range of 0.05 to 0.30.

In a preferred aspect n is 2 and both bromine atoms are in the ortho position with regard to the oxygen atom. Both bromine atoms can be in the meta position with regard to the oxygen atom.

Broadly speaking, the admixture of the brominated bisphenol A diethanol polyformal and polyester of the second embodiment of this invention can be described as a moldable or fiber-forming composition comprising an admixture of

A. based on the weight of the composition, from 75 to 98 weight percent polyester, and

B. based on the weight of the composition, from 25 to 2 weight percent of the brominated bisphenol A diethanol polyformal described above.

In a preferred aspect of this embodiment, (A) is from 80 to 92 weight percent and (B) is from 20 to 8 weight percent.

In another preferred aspect of this embodiment the polyester is poly(ethylene terephthalate), poly(tetramethylene terephthalate) or poly(1,4-cyclohexylenedimethylene terephthalate). Poly(tetramethylene terephthalate) is an especially preferred polyester.

Textile fibers can be formed from the admixture of the second embodiment. Broadly speaking, the polyformal copolymer of the third embodiment can be described as a moldable or fiber-forming copolymer having an inherent viscosity in the range of 0.30 to 1.0 comprised of

A. based on the weight of the composition, from 75 to 98 weight percent blocks of a polyester, and

B. based on the weight of the composition, from 25 to 2 weight percent blocks of the polyformal described above having an inherent viscosity of 0.03 to 1.0.

In a preferred aspect of this embodiment, (A) is from 80 to 92 weight percent and (B) is from 20 to 8 weight percent.

In still another preferred aspect of this embodiment the polyester is poly(ethylene terephthalate) or poly(tetramethylene terephthalate). Poly(ethylene terephthalate) is an especially preferred polyester.

Textile fibers can be formed from the copolymers of the third embodiment. In a preferred aspect the polyester is poly(ethylene terephthalate).

In this invention the admixture or copolymer can contain minor amounts of other materials which alter selected properties of the polymer. These materials can be introduced into the polyesters either as a comonomer or a physical blend. Specifically the polyester can be modified with a comonomer that imparts basic dyeability to textile fibers.

The usefulness of the polyformal is that the polyformal can be admixed or copolymerized with a polyester to form the admixture or polyformal copolymer and useful flame retardant articles, such as molded objects and fibers, can be prepared from the admixture or polyformal copolymer.

The polyformal can be admixed with the polyester by several methods well known in the art. One suitable method includes mixing together pellets of each polymer. The polyformal can be copolymerized with the polyester by several methods well known in the art. One suitable method includes melt extruding or melt spinning an admixture of pellets of the polyformal and the polyester.

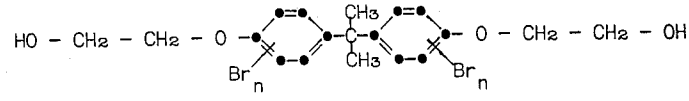
The usefulness of the admixture of the polyformal and the polyester is that the admixture can be prepared into useful flame retardant articles, such as molded objects and fibers.

The admixture can be used to prepare useful flame retardant articles by techniques well known in the art. For example, the admixture can be melt spun, drawn, heatset and processed into textile fibers according to conventional methods well known in the art. Additionally, the admixture can be injection molded into useful molded objects using conventional processes and apparatus.

The usefulness of the polyformal copolymer is that the copolymer can be prepared into useful flame retardant articles, such as molded objects and fibers.

The polyformal copolymer can be used to prepare useful flame retardant articles by techniques well known in the art. For example, the polyformal copolymer can be melt spun, drawn, heatset and processed into textile fibers according to conventional methods well known in the art. Additionally, the polyformal copolymer can be injection molded into useful molded objects using conventional processes and apparatus.

The polyformal of this invention can be prepared by a process comprising contacting in a solvent, under polymerization conditions and in the presence of a suitable acid catalyst, formaldehyde and brominated bisphenol A diethanol corresponding to the structure



where *n* is 1 or 2.

The solvent useful in this process can comprise a solvent that is inert with regard to the reactants. Although many conventional solvents can be used, benzene, toluene and hexane are preferred because of their cost and availability.

The pressure used for the polymerization reaction can vary widely. Pressures higher than atmospheric can be used but water removal is, of course, more difficult at elevated pressures. Pressures lower than atmospheric can be used, but low pressures are to some extent undesirable because low pressures will tend to allow the formaldehyde to escape from the inert solvent. Atmospheric pressure is preferred because of the ease of creation as well as the minimization of undesirable side effects.

The temperature used for the polymerization reation can also vary widely. Temperatures above about 100°C. can be used but are to some extent undesirable because the formaldehyde will tend to escape from the polymerization solvent. In a preferred embodiment the temperature is about 100°–110°C. In this embodiment the reaction mixture can be heated at reflux to azeotropically remove the water created by condensation of the formaldehyde and the brominated bisphenol A diethanol.

The acid catalyst of this invention can be a variety of catalysts that function as proton donors to catalyze the polymerization reaction. Examples of acids that could be used include p-toluenesulfonic acid, sulfuric acid, trifluoromethanesulfonic acid, methanedisulfonic acid, camphorsulfonic acid, perchloric acid, and sulfonated resins.

In this invention the formaldehyde can be in various forms such as paraformaldehyde or gaseous formaldehyde. Paraformaldehyde is preferably used because of its ease in handling, lack of color forming impurities, and its ability to form high molecular weight polyformals. When paraformaldehyde is used the acid catalyst not only functions as a proton donor to catalyze the polymerization reaction, but, in addition, functions to depolymerize the paraformaldehyde.

The contact between the brominated bisphenol A diethanol and formaldehyde can be preferably effected by merely stirring a solution of the formaldehyde and brominated bisphenol A diethanol in the solvent. If desired, other contacting procedures well known in the art could be used, such as packed towers, bubble towers and the like.

After polymerization is complete, isolation of the polyformal can be accomplished by techniques well known in the art such as removal of the solvent or precipitation in a nonsolvent, such as methanol.

The brominated bisphenol A diethanol that is condensed with formaldehyde can be prepared by condensing one mole of brominated bisphenol A with 2 moles of ethylene oxide to form one mole of brominated bisphenol A diethanol. This reaction is well known in the art and is disclosed in Canadian Pat. No. 663,542.

The thermal stability of the polyformal may be increased by acetylation of hydroxy end groups, if desired.

Other methods for preparing the polyformal are disclosed in U.S. Pat. No. 2,968,646.

The polyesters useful in this invention can be derived from aliphatic or alicyclic diols containing 2 to 40 carbon atoms. Examples of such diols include ethylene glycol; diethylene glycol; 1,2-propylene glycol; 2,4-dimethyl-2-ethylhexane-1,3-diol; 2-ethyl-2-butyl-1,3-propanediol; 1,4-butanediol; 1,5-pentanediol 1,6-hexanediol; 1,10-decanediol; 1,4-cyclohexanediol; 1,4-cyclohexanedimethanol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol. Ethylene glycol, 1,4-butanediol and 1,4-cyclohexanedimethanol are preferred diols. Copolyesters may be prepared using two or more of the above diols. Two or more dicarboxylic acids or diols may be used to give copolyesters or block polymers.

The polyesters useful in this invention can be derived from aliphatic, alicyclic, or aromatic dicarboxylic acids having 3 to 40 carbon atoms. Examples of such acids include adipic; azelaic; sebacic; 1,4-cyclohexanedicarboxylic; terephthalic; isophthalic and 1,4-naphthalic. Terephthalic acid is preferred. It will be understood that the corresponding esters of these acids are included in the term "dicarboxylic acid." Copolyesters may be prepared using two or more of the above dicarboxylic acids or esters thereof.

The polyformal copolymer can optionally contain other materials such as phosphorus and/or antimony to improve the flame retardance of articles prepared from the polyformal copolymer.

In addition, the polyformal copolymer can contain antioxidants, ultraviolet stabilizers, thermal stabilizers, nucleating agents, plasticizers, fillers, glass fibers, pigments lubricants and other additives.

To reduce the spinning temperature of the admixture of the polyformal and the polyester, a processing aid also may be blended with the polyformal and polyester.

The presence of synergists, such as phosphorus and/or antimony, further improves the flame resistance of articles prepared from the admixture of the polyformal and the polyester.

In addition to antimony compounds and brominated additives, the articles prepared from the admixture of the polyformal and the polyester can contain antioxidants, ultraviolet stabilizers, thermal stabilizers, nucleating agents, plasticizers, fillers, glass fibers, pigments, lubricants and other additives.

In one particularly preferred embodiment of the invention the polyformal is blended with poly(tetramethylene terephthalate). In this embodiment, other additives can be added to the poly(tetramethylene terephthalate) such as antioxidants, pigments, fillers, plasticizers, and reinforcing agents such as glass fibers or asbestos. A composition of about 16 weight percent polyformal, about 5 weight percent antimony trioxide and about 20 weight percent glass fiber gives especially desirable results because objects molded of the composition are quite strong and pass even the most stringent flammability tests.

The polyformal copolymer of this invention can be prepared in accordance with several methods.

According to one method, the polyformal may be dry blended with the polyester and the blend subjected to melt extrusion and/or melt spinning. During either of these operations, the hydroxyl-terminated polyformal can be caused to react with the polyester by glycolysis, thus producing the polyformal copolymer. If the inherent viscosity of the polyformal is lower than that of the initial polyester, the inherent viscosity of the polyformal copolymer will be less than that of the initial polyester. Although the precise conditions of time, temperature and pressure necessary to form the polyformal copolymer vary depending on the particular polyester, poly(ethylene terephthalate) and the polyformal will react to form the polyformal copolymer when held within a temperature range of 260° to 300°C. for from 2 to 5 minutes at a pressure of 0.1 to 760 mm. Some polyesters such as poly(1,4-cyclohexylenedimethylene terephthalate) will react very little or not at all with the polyformal and remain essentially as an admixture with the polyester.

According to another method, the hydroxyl-terminated polyformal may be melt blended with polyester polymer or prepolymer and allowed to equilibrate at a temperature which is in the range of about 240°–300°C. and above the melting point of the polyester. The subsequent application of reduced pressure permits removal of glycol and formation of a higher molecular weight block polymer.

According to still another method, the polyformal may be charged to a reaction vessel containing the dialkyl ester of a dibasic acid, glycol, and conventional polyester catalyst and built into the polyester as it is being formed. The application of reduced pressure and elevated temperatures with subsequent removal of excess glycol gives high molecular weight block polymers of polyester and polyformal according to techniques well known in the art.

The following examples are intended to illustrate but not limit the invention.

In this disclosure, the inherent viscosities are determined at 25°C. in 60/40 phenol/tetrachloroethane at a concentration of 0.50 g./100 ml. All samples are vacuum dried at 90°–100°C. overnight prior to spinning or molding.

The oxygen index test is described in MODERN PLASTICS, March 1970, p. 124.

EXAMPLE 1

This example describes the preparation of the brominated bisphenol A diethanol polyformal.

In a 1,000-ml., three-neck flask fitted with a mechanical stirrer, Dean-Stark trap, and condenser are placed 400 g. (0.633 mole) of tetrabromobisphenol A diethanol and 460 ml. of benzene. The reaction mixture is heated at reflux for 2 hours during which time the tetrabromobisphenol A diethanol dissolves. The solution temperature is then decreased to 65°C. and 20.6 g. (0.650 mole) of 95 percent paraformaldehyde and 2.0 g. of p-toluenesulfonic acid are added. After the reaction mixture is allowed to stir at 65°C. for 90 minutes, the temperature is increased to reflux and the water (11.4 ml., 0.633 mole) is azeotropically removed. This

requires approximately 3½ hours. After the mixture is cooled to room temperature, 0.5 ml. of 15 M ammonium hydroxide is added with vigorous stirring to neutralize the catalyst. The slightly viscous benzene solution is then coagulated by slow addition to 8 liters of methanol. The resultant white powder is washed with 500 ml. of methanol and dried overnight at 50°C. under a nitrogen sweep and a vacuum of 17 in. of mercury. The polymer has an inherent viscosity of 0.12 and a softening point of 80°C.

EXAMPLE 2

This example describes the preparation of a fiber of a copolymer of a polyester and the brominated bisphenol A diethanol polyformal.

Granules of poly(ethylene terephthalate) having an inherent viscosity of 0.60 are dry blended with granules of tetrabromobisphenol A diethanol polyformal having an inherent viscosity of 0.15 to give a mixture containing 8 percent by weight of polyformal. Fibers are spun at 270°C. The fibers are drawn in water at 68°C. and then in superheated steam for an overall draw factor of 4.0. After being heatset in a relaxed state for 5 minutes at 145°C., the fibers have the following properties: 2.5 den./fil., 3.6 g./den. tenacity, 33 percent elongation, 44 g./den. elastic modulus, and a 234°C. flow point at 0.2 g./den. load. A tube knitted from these fibers shows no yellowing after 40 hours exposure in a carbon-arc Fade-Ometer. The knit fiber also passes the Children's Sleepwear Test (DOC FF 3-71). The fibers in the knitted sample show no loss in bromine content after 10 laundry cycles in accordance with AATCC Text Method 61-1969, Number IIIA. Another sample shows no loss in bromine content after 15 dry cleaning cycles in accordance with AATCC Test Method 132-1969. The knitted samples dye well and exhibit desirable light fastness.

Analysis of the polymer of the fiber shows the polyester and polyformal have reacted to form a polyformal copolymer under the particular conditions of melt spinning. Under other conditions of time, temperature, and pressure the polyester and polyformal might not form the polyformal copolymer or only a portion of the polyester and polyformal might combine to form the polyformal copolymer. Long times and high temperatures tend to favor the formation of the polyformal copolymer.

EXAMPLE 3

This example describes the preparation of a molded object of an admixture of a polyester and the brominated bisphenol A diethanol polyformal.

Poly(tetramethylene terephthalate) having an inherent viscosity of 1.5 is placed in a large evaporating dish, and a solution of methylene chloride containing two antioxidants, Goodrite 3114 and dilauryl thiodipropionate (DLTDP), is added to the polyester. The mixture is slurried and the methylene chloride allowed to evaporate. the antioxidants are present to the extent of 0.1 percent by weight for the Goodrite 3114 and 0.3 percent by weight for the DLTDP. The polyester containing the antioxidants is then dry blended with 15 percent tetrabromobisphenol A diethanol polyformal (inherent viscosity 0.15) and 2.5 percent antimony oxide. The blend is extruded at 280°C. with a Brabender Plasticorder extruder. The resultant white pellets are then injection molded at 280°C. to give ⅛- × ½- × 5-inch bars. The bars have an oxygen index of 27 as compared to 21 for the control poly(tetramethylene terephthalate). The bromine content of the bars does not decrease during aging for 1 month in an oven at 155°C. The bars exhibit no discoloration during molding or during exposure to ultraviolet light in a carbon-arc Fade-Ometer for 40 hours.

EXAMPLE 4

This example describes the preparation of a fiber of an admixture of a polyester and the brominated bisphenol A diethanol polyformal.

Poly(1,4-cyclohexylenedimethylene terephalate) having an inherent viscosity of 0.86 is dry blended with tetrabromobisphenol A diethanol polyformal (inherent viscosity 0.12) to give a mixture containing 10 percent by weight of polyformal. The blend is spun at 290°C. to give white fibers. The fibers are drawn in water at 68°C. and then in superheated steam for an overall draw factor of 3.8. After being heatset in a relaxed state at 175°C. for 5 minutes, the fibers have the following properties: 3.2 den./fil., 2.7 g./den. tenacity, 21 percent elongation, 33 g./den. elastic modulus, and a 260°C. flow point at 0.2 g./den. load. The fibers exhibit improved resistance to burning, resistance to yellowing during 40 hours in a carbon-arc Fade-Ometer, and no significant loss of bromine during 15 dry cleaning treatments.

EXAMPLE 5

This example describes the preparation of fibers of a copolymer of a polyester and the brominated bisphenol A diethanol polyformal.

A blend of the poly(ethylene terephthalate) used in Example 2 and 20 percent tetrabromobisphenol A diethanol polyformal is melt spun at 260°C. into nondiscolored fibers. The drafted, heat-set fibers have the following properties: 2.4 den./fil., 3.4 g./den. tenacity, 21 percent elongation, 42 g./den. elastic modulus, 240°C. flow point at 0.2 g./den. load. The fibers show further improved resistance to burning compared to the fibers in Example 2, no yellowing during 40 hours in a carbon-arc Fade-Ometer, and no significant loss of bromine during 15 dry cleaning treatments.

EXAMPLE 6

This example illustrates preparation of the polyformal copolymer.

Poly(ethylene terephthalate) powder with an inherent viscosity of 0.66 and tetrabromobisphenol A diethanol polyformal with an inherent viscosity of 0.09 (number average molecular weight 3800) are dried under vacuum at 100°C. overnight. The dry polymers are mechanically blended together to give 12 percent by weight polyformal and extruded at 265°C. with a 1½ inch Modern Plastics Machinery single screw extruder. The resultant white poly(ethylene terephthalate)/polyformal pellets have an inherent viscosity of 0.53. Gel permeation chromatography indicates equilibration of the polyester and polyformal to give the polyformal copolymer.

EXAMPLE 7

This example illustrates that the polyformal retains its integrity and is present as a block after the polyformal is melt extruded.

29 grams of the copolymer from Example 6 are placed in 100 ml. of 1N KOH in ethanol and the mixture allowed to stir for 30 minutes at reflux. The resultant hydrolyzed polymer is then subjected to extraction in the following manner: The solution is filtered through a 350-ml. "medium" fritted glass funnel and the white residue air dried overnight. The residue is then added to 300 ml. of distilled water and stirred for 30 minutes during which time most of the residue dissolves. The aqueous solution containing small amounts of white solid is then extracted with 300 ml. of benzene. The benzene solution is washed once with distilled water, dried, and the benzene removed by evaporation. The clear, glassy residue is then analyzed by nuclear magnetic resonance spectroscopy and shown to be tetrabromobisphenol A diethanol polyformal. The polymer has an inherent viscosity of 0.09, which is identical to that of the polyformal initially blended with poly(ethylene terephthalate).

EXAMPLE 8

This example illustrates that the polyformal copolymer retains its integrity and is present as a block under polycondensation reaction conditions.

Ninety-seven grams of dimethyl terephthalate, 62 g. of ethylene glycol, and 8 g. of tetrabromobisphenol A diethanol polyformal (I.V. 0.09) are heated with continuous stirring under a nitrogen atmosphere for 1 hour at 200°C. in the presence of a polyester catalyst mixture consisting of 14 ppm. Mg, 49 ppm. Mn, 20 ppm. Ti, and 247 ppm. Sb salts. The temperature is raised to 225°C. for an additional hour. The temperature is then increased to 270°C., and 88 ppm. phosphorus as the acid phosphate is added. A vacuum is gradually applied to the reaction mixture and held for 1 hour at 0.1 mm. Hg. The inherent viscosity of the resultant polymer is 0.60. The polymer is hydrolyzed and analyzed in a manner identical to Example 7. The yield of polyformal is 70 percent with an inherent viscosity of 0.07.

EXAMPLE 9

This example describes the unobviously low crystallization temperature upon heating and the unobviously high crystallization temperature upon cooling for the polyformal copolymer as compared to the diethanol polymer.

Using procedures similar to those of Examples 6 and 13 a polyformal copolymer and a diethanol polymer are prepared using dimethyl terephthalate and ethylene glycol to form the polyester component.

The samples were heated under nitrogen to about 275°C. to melt them and remove previous thermal history, quenched by rapidly cooling, then heated back to 275°C. at 20°C./min., then cooled at a rate of 20°C./min.

Listed below are different scanning calorimetry (DSC) results for these polymers.

Sample	Tg(°C.)	Heating Tc'(°C.)	Tm(°C.)	Cooling Tc(°C.)
Polyformal copolymer (4% Br)	81	139	253	221
Diethanol copolymer (4% Br)	84	165	247	180

-Continued

Tm = Crystalline melting point
Tg = Glass transition temperature
Tc' = Crystallization temperature on heating
Tc = Crystallization temperature on cooling

From the above data it can be observed that the polyformal copolymer has an appreciably lower Tc' on heating (crystallizes more readily) and a higher Tc on cooling (crystallizes sooner) than the diethanol polymer. Because the diethanol polymer crystallizes more slowly than the polyformal copolymer, longer heat-setting times will be required in processing. Also, because of the slower crystallization rate of the diethanol copolymer, more shrinkage is produced during heat-setting of fibers; and consequently, orientation of the fiber is lower, giving lower tenacity.

EXAMPLE 10

This example describes the high crystallization temperature upon cooling for a polyformal admixture as compared to the diethanol polymer.

Using procedures similar to those of Examples 6 and 13, a polyformal copolymer and a diethanol polymer are prepared using dimethyl terephthalate and 1,4-butanediol to form the polyester component.

The polymers are heated under nitrogen about 20°C. above their melting points to remove previous thermal history, rapidly cooled, then heated back to 245°C. at 20°C./min., then cooled at a rate of 20°C./min. DSC results for these polymers are presented below.

Sample	Heating Tc'(°C.)	Tm(°C.)	Cooling Tc(°C.)
Polyformal admixture (6.8% Br)	—	222	187
Diethanol copolymer (6.8% Br)	68	212	166

Tm = Crystalline melting point
Tc' = Crystallization temperature on heating
Tc = Crystallization temperature on cooling

In spite of the quenching treatments, advantageously the polyformal admixture apparently had crystallized completely since it did not crystallize further (no Ic') on the subsequent heating step as did the copolyester. Also, on the following cooling step, the diethanol polymer did not crystallize until an appreciable lower temperature had been reached.

EXAMPLE 11

This example described the low crystallization temperature upon heating and the high crystallization temperature upon cooling for a polyformal admixture as compared to the diethanol copolymer.

Using procedures similar to those of Examples 6 and 13 a polyformal admixture and a diethanol polymer are prepared using 90 mole percent dimethyl terphthalate, 10 mole percent dimethyl isophthalate and 1,4-cyclohexanedimethanol to form the polyester component.

The samples are heated above their melting points to about 290°C. and treated in a manner similar to those described in Examples 9 and 10.

Sample	Heating Tg(°C.)	Heating Tc' (°C.)	Heating Tm(°C.)	Cooling TC(°C.)
Polyformal admixture (5% Br)	85	145	270	206
Diethanol copolymer (5% Br)	91	162	269	190

Tm = Crystalline melting point
Tg = Glass transition temperature
Tc' = Crystallization temperature on heating
Tc = Crystallization temperature on cooling

EXAMPLE 12

This example illustrates the preparation of fibers from the diethanol polymer and the comparative flammability of fibers from the polyformal copolymer fibers from a diethanol polymer.

242 grams of dimethyl terephthalate, 155 g.of ethylene glycol and 40.7 g. of tetrabromobisphenol A diethanol are stirred, under nitrogen, with 65 ppm. zinc and 230 ppm. antimony acetate catalysts for 90 minutes at 180°C. The temperature is then increased to 230°C. and a vacuum of 0.5 mm. applied for 45 minutes. The temperature is again increased to 275°C. for an additional 5 minutes. The resulting low melt viscosity polymer has an inherent viscosity of 0.17. After grinding to pass a 3-mm. screen, the prepolymer is subjected to solid phase polymerization under 0.1 mm. vacuum for 1 hour at 180°C., 1 hour at 210°C. and 14 hours at 230°C. The resultant off-white diethanol polymer has an inherent viscosity of 0.51.

The diethanol polymer is then spun into fiber, drafted, and heatset as in Example 2. Knit fabrics of this fiber contain 7.7 weight percent bromine by analysis and failed the Children's Sleepwear Test (DOC FF 3-71) three out of six times when a flat-lock seam is sewed with a silicon-lubricated thread.

A knit fabric of the polyformal copolymer of this invention prepared as described in Example 2 and containing only 4.0 percent bromine passes the above Children's Sleepwear Test 10 out of 10 times.

Fibers spun from the diethanol polymer and fibers spun from the polyformal copolymer are drafted, heatset, processed according to conventional techniques, and knit into test samples. These samples are tested in accordance with the so-called "Children's Sleepwear Test."

Children's Sleepwear Test
(Federal Government Standard DOC FF 3-71)

Fiber composition	I.V.	Children's Sleepwear Test[a] Failures/Samples Tested	Children's Sleepwear Test[a] Avg. RFT[b], Sec.
Diethanol polymer (4% Br)	.47	3/8	10.4
Polyformal copolymer (4% Br)	.44	0/10	4.8

[a]Samples (5–6 oz./yd.²) were seamed (flat-lock seams) with silicone lubricated thread.
[b]Average residual flame time.

As noted above, the samples of the polyformal copolymer fiber pass the test 10 out of 10 times while the samples of the diethanol polymer fiber pass the test only 5 out of 8 times.

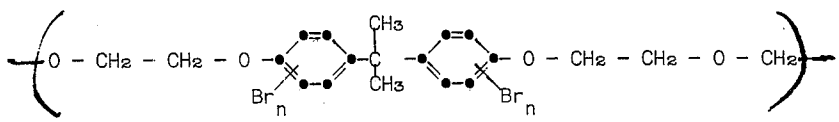
The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A moldable or fiber-forming composition consisting essentially of an admixture of

A. based on the weight of the composition, from 75 to 98 weight percent polyester, said polyester being the condensation product of at least one aliphatic or alicyclic diol containing 2 to 40 carbon atoms and at least one aliphatic, alicyclic or aromatic dicarboxylic acid or ester thereof having 3 to 40 carbon atoms and

B. based on the weight of the composition, from 25 to 2 weight percent of a polymer having an inherent viscosity in the range of 0.03 to 1.0 consisting essentially of recurring units of the structure



where *n* is 1 or 2, said inherent viscosity being determined at 25°C in 60/40 phenol/tetra chloro ethane at a concentration of 0.50 g./100 ml.

2. The composition of claim **1** wherein (A) is from 80 to 92 weight percent and (B) is from 20 to 8 weight percent.

3. The composition of claim **2** wherein n is 2 and both bromine atoms are in the ortho position with regard to the oxygen atoms.

4. The composition of claim **3** wherein the polyester is poly(ethylene terephthalate), poly(tetramethylene terephthalate) or poly(1,4-cyclohexylenedimethylene terephthalate).

5. The composition of claim **4** wherein the polyester is poly(tetramethylene terephthalate).

6. A textile fiber consisting essentially of an admixture of

4. based on the weight of the admixture, from 75 to 98 weight percent polyester, said polyester being

EXAMPLE 13

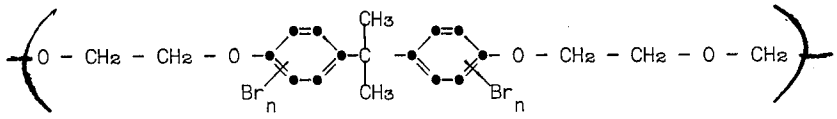
This example illustrates the preparation of fibers from the diethanol polymer and the comparative flammability of fibers from a polyformal copolymer and fibers from the diethanol polymer.

259 g. (1.35 moles) dimethyl terephthalate
167 g. (2.70 moles) ethylene glycol
22.1 g. (0.035 mole) tetrabromobisphenol A diethanol

The above ingredients and a standard Ti, Sb, Mn poly(ethylene terephthalate) catalyst system are placed in a 1,000-ml. flask equipped with a stirrer, a short distillation column and an inlet for nitrogen. The mixture is stirred at 195°C. in a nitrogen atmosphere until the ester interchange is completed (90 minutes). The temperature is then increased to 230°C. and held for 15 minutes. The temperature is again increased to 275°C. and a vacuum of 0.5 mm. is applied for 45 minutes. A pale yellow polymer with an inherent viscosity of 0.51 is obtained.

the condensation product of at least one aliphatic or alicyclic diol containing 2 to 40 carbon atoms and at least one aliphatic, alicyclic or aromatic dicarboxylic acid or ester thereof having 3 to 40 carbom atoms and

B. based on the weight of the admixture, from 25 to 2 weight percent of a polymer having an inherent viscosity in the range of 0.03 to 1.0 consisting essentially of recurring units of the structure



where *n* is 1 or 2, said inherent viscosity being determined at 25°C in 60/40 phenol/tetra chloro ethane at a concentration of 0.50 g./100 ml.

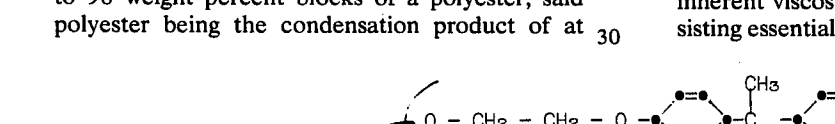
7. The fiber of claim **6** wherein (A) is from 80 to 92 weight percent and (B) is from 20 to 8 weight percent.

8. The fiber of claim **7** wherein *n* is 2 and both bromine atoms are in the othro position with regard to the oxygen atom.

9. A copolymer having an inherent viscosity of at least 0.35 consisting essentially of

A. based on the weight of the composition, from 75 to 98 weight percent blocks of a polyester, said polyester being the condensation product of at least one aliphatic or alicyclic diol containing 2 to 40 carbon atoms and at least one aliphatic, alicyclic or aromatic dicarboxylic acid or ester thereof having 3 to 40 carbon atoms, and

B. based on the weight of the composition, from 25 to 2 weight percent blocks of a polyformal having an inherent viscosity in the range of 0.03 to 1.0 consisting essentially of recurring units of the structure



where *n* is 1 or 2, said inherent viscosity being determined at 25°C in 60/40 phenol/tetra chloro ethane at a concentration of 0.50 g./100 ml.

10. The copolymer of claim **9** wherein (A) is from 80 to 92 weight percent and (B) is from 20 to 8 weight percent.

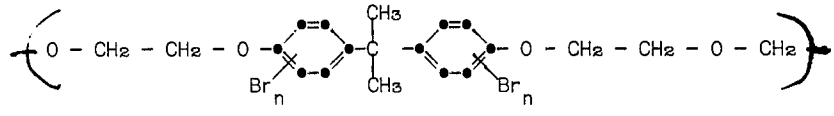
11. The copolymer of claim **10** wherein n is 2 and both bromine atoms are in the ortho position with regard to the oxygen atom.

12. The copolymer of claim **11** wherein the polyester is poly(ethylene terephthalate) or poly(tetramethylene terephthalate).

13. A textile fiber formed from a copolymer having an inherent viscosity of at least 0.35, the copolymer consisting essentially of

A. based on the weight of the copolymer, from 75 to 98 weight percent blocks of a polyester, said polyester being the condensation product of at least one aliphatic or alicyclic diol containing 2 to 40 carbon atoms and at least one aliphatic, alicyclic or aromatic dicarboxylic acid or ester thereof having 3 to 40 carbon atoms, and

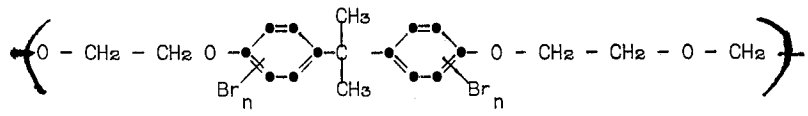
B. based on the weight of the copolymer, from 25 to 2 weight percent blocks of a polyformal having an inherent viscosity in the range of 0.03 to 1.0 consisting essentially of recurring units of the structure



where *n* is 1 or 2, said inherent viscosity being determined at 25°C in 60/40 phenol/ tetra chloro ethane at a concentration of 0.50 g./100 ml.

14. The textile fiber of claim **13** wherein (A) is from 80 to 92 weight percent and (B) is from 20 to 8 weight percent.

15. The textile fiber of claim **14** wherein *n* is 2 and both bromine atoms are in the ortho position with regard to the oxygen atom.



where *n* is 1 or 2, said inherent viscosity being determined at 25°C in 60/40 phenol/tetra chloro ethane at a concentration of 0.50 g./100 ml.

16. The textile fiber of claim **15** wherein the polyester is poly(ethylene terephthalate).

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