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(54) **Production of linear aromatic polyester**

(57) A problem associated with known techniques of preparing a polyester by transesterification polymerisation from a hydroxylic reactant and a diaryl ester of a dicarboxylic acid using either a stoichiometric equivalent proportion of hydroxylic and diaryl ester reactants or a large excess of diaryl ester is the tendency of the polyester to develop an undesirable yellow color. This can be overcome by effecting trans-esterification polymerization of a diaryl ester of a dicarboxylic acid and a hydroxylic reactant comprising a major proportion of a bisphenol employing an excess of from 0.05 to less than 1.8 mole percent of said diaryl ester over the stoichiometric equivalent proportion of said diaryl ester with respect to

said hydroxylic reactant. The resulting polyesters can be moulded to produce shaped articles.

## SPECIFICATION

**Production of linear aromatic polyester**

5 This invention relates to an improvement for preparing polyesters which achieves low product color. The invention is more particularly directed to an improvement in the preparation of linear aromatic polyesters by transesterification of a hydroxylic reactant comprising a bisphenol and a diaryl ester of a dicarboxylic acid. 5

10 Linear aromatic polyesters of a hydroxylic component comprising a bisphenol (and, optionally, a minor proportion of a difunctional aliphatic glycol modifier and/or a long chain monofunctional aliphatic alcohol) and a dicarboxylic acid are a commercially important type of engineering thermoplastic since they possess in combination the desirable properties of high impact resistance, heat distortion temperature and clarity. 10

15 The polyesters can be produced by the known transesterification mode of polymerization which is generally carried out in the melt. In accordance with one well known transesterification process for preparing these polyesters, a difunctional hydroxylic reactant comprising bisphenol (and, optionally, also a minor molar proportion of an aliphatic glycol and/or a monofunctional hydroxy aliphatic compound) is reacted with a diaryl ester of a dicarboxylic acid, e.g. a diphenyl ester of the dicarboxylic acid, to prepare a polyester containing as end groups a hydroxy end 20 group derived from the difunctional hydroxylic reactant and a carboxylate, ester end group corresponding to the ester group of the diaryl ester. When the aforementioned monofunctional alcohol reactant is employed, some of the ester end groups of the polyester are modified to alkyl carboxylate ester end groups wherein the alkyl group is derived from the alcohol. 20

25 Although prior workers in preparing the present polyester have employed about a stoichiometric equivalent proportion of the diaryl ester and hydroxylic reactants or taught use of a large molar excess, e.g. of 5 mole percent or larger, of one or the other of these reactants, use of the presently described small excess of the diaryl ester has not been described in the prior art. 25

30 A persistent problem in the transesterification preparation of linear polyesters of bisphenol and dicarboxylic acids containing the aforementioned aryl ester end groups has been the undesirable high color in the product, i.e. the tendency of the polyester to develop an undesirable yellow color during the polyesterification. The color is attributed to thermal decomposition of the product polyester and/or the reactants in the reaction which is carried out at high temperatures ranging up to 400°C, or higher, and generally in the melt, i.e. without the use of a diluent. 30

35 Another aspect of this problem associated with production of these polyesters prepared by transesterification is obtaining a product of satisfactory high molecular weight while maintaining a satisfactory low color in the polyester. Thus, it is found by the present workers that use of a substantial molar excess, e.g. an excess of 1.8% or greater, of the diaryl ester reactant over the aforementioned stoichiometric equivalent proportion of diaryl ester reactant inhibits the transesterification reaction. As a result, use of said diaryl ester in such substantial molar excess requires 40 an undesirably extended reaction time to reach a given, e.g. a satisfactory, product molecular weight. Because of the extension of the reaction time incurred with the use of said substantial molar excess of the diaryl ester reactant, under the aforementioned severe conditions of elevated temperature and melt reaction condition, the product is found to be more highly colored than is the case when a stoichiometric equivalent proportion of the reactants is employed. 40

45 The aforementioned problems associated with preparation of a linear aromatic polyester of low color and satisfactory high molecular weight are overcome by the improvement of the present invention. 45

50 The invention is directed to an improvement in the preparation of a linear aromatic polyester by transesterification polymerization of reactants comprising a diaryl ester of a dicarboxylic acid and a hydroxylic reactant comprising a major molar proportion of a bisphenol. 50

55 According to this improvement, the preparation of the polyester by transesterification polymerization is carried out employing about 0.05 to less than 1.8 mole percent excess, of said aryl ester reactant over the stoichiometric proportion of said diaryl ester reactant with respect to said hydroxylic reactant, to obtain a product of improved low color and satisfactory high molecular weight. 55

60 The use of the present excess of diaryl ester is found to provide, unexpectedly, a product of low coloration compared to the product obtained with a stoichiometric molar proportion of the ester monomer without entailing an undesirably extended reaction time to reach a given product molecular weight (e.g. a satisfactory high molecular weight) as is the case when an excess of diaryl ester larger than that of the invention is employed to prepare a polyester of given molecular weight. The present products contain a molar excess of carboxylate ester end groups (and carboxylic acid end groups, if present), over the hydroxy end groups with aryl carboxylate ester end groups comprising a major molar proportion of the total molar amount of end groups derived from the carboxylic acid function, including any free carboxylic acid end groups, 60 aliphatic carboxylate ester end groups, and the aryl carboxylate ester end groups. By major 65

proportion is meant a proportion of above 50 percent.

Preferably, the polyester of the invention is prepared from reactants consisting of the diaryl ester and difunctional hydroxylic reactants, i.e. the bisphenol reactant or bisphenol and aliphatic glycol reactants, or especially the bisphenol alone. In accord with the latter preferred embodiment, the end groups of the polyester are hydroxy and carboxylate ester end groups, the latter consisting of aryl carboxylate ester end groups.

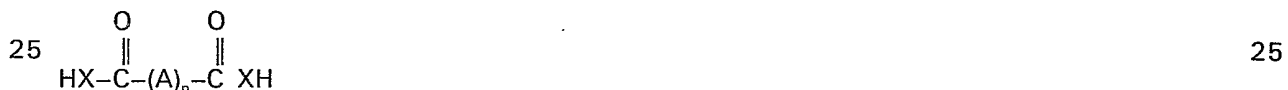
#### REACTANTS

The reactants of the process of the invention employs a diester of a dicarboxylic acid and monohydroxy aromatic compound of the benzene or naphthalene series of 6 to 20 carbon atoms.

Examples of monohydroxy aromatic compounds are disclosed in copending European Patent Application No. 80301867.0, published as EP-A-0021654 and corresponding to United States Application Serial No. 45,461 of G. Salee and J. C. Rosenfeld filed June 4, 1979, and European Patent Application No. 80301865.4, published as EP-A-0021652 and corresponding to United States Application Serial No. 45,464 of J. C. Rosenfeld filed June 4, 1979, the disclosures of which are incorporated herein by reference. Preferred is a monohydroxy compound of the benzene series especially phenol.

#### 20 DICARBOXYLIC ACIDS

The dicarboxylic acids which are useful in the process are also well known and can be represented by the formula:



in which X is oxygen or sulfur, A is alkylene, -Ar- or -Ar-Y-Ar where Ar has the same definition as given with respect to the bisphenols, Y is alkylene of 1 to 10 carbons, haloalkylene, -O-, -S-, -SO-, -SO<sub>2</sub>-, -SO<sub>3</sub>-, -CO-,



n is 0 or 1, and G is alkyl, haloalkyl, aryl, haloaryl, alkylaryl, haloalkylaryl, arylalkyl, haloarylalkyl, cycloalkyl, and halocycloalkyl. Illustrative aromatic and aliphatic dicarboxylic acids are disclosed in G. Salee, US Patent 4,126,602, the disclosure of which is incorporated herein by reference. Diesters of an aromatic dicarboxylic acid which, in general, are normally solids, i.e. solids at ambient temperature, are preferably employed, especially diesters of isophthalic acid and/or terephthalic acid, typically a mixture of about 60 to about 100 mole percent isophthalic acid and about 40 to 0 mole percent terephthalic acid.

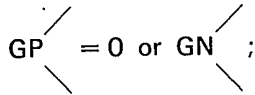
In carrying out the present process in a series of batch reaction vessels, i.e. batch reaction zone, or by a semi- or fully continuous production mode wherein liquid reaction mass is conducted or piped from one reaction vessel to another, it is much preferred to employ a dicarboxylic acid component comprising a mixture of iso- and terephthalic acids containing greater than about 15 to less than about 85 mole percent isophthalic acid and greater than about 15 to less than about 85 mole percent terephthalic acid. Use of said proportion inhibits or prevents precipitation, or crystallization from the molten transesterification reaction mass of low molecular weight polyester, i.e. polyester oligomers, which precipitated oligomers can clog the piping or conduits between the reaction vessels through which the molten reaction mass flows.

#### THE BISPHENOL

The bisphenols useful in the invention are disclosed in aforementioned US Patent 4,126,602. Generally, the bisphenols which can be used in this process are known in the art and correspond to the general formula:



wherein Ar is aromatic, preferably containing 6-18 carbon atoms (including phenyl, biphenyl and naphthyl); G is alkyl, haloalkyl, aryl, haloaryl, alkylaryl, haloalkylaryl, arylalkyl, haloarylalkyl, cycloalkyl, and halocycloalkyl; E is a divalent (or di-substituted) alkylene, haloalkylene, cycloalkylene, halocycloalkylene, arylene, or haloarylene, -O-, -S-, -SO-, -SO<sub>2</sub>-, -SO<sub>3</sub>-, -CO-,

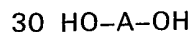


5 T and T' are independently selected from the group consisting of halogen, such as chlorine or bromine, G and OG; m is an integer from 0 to the number of replaceable hydrogen atoms on Ar; b is an integer from 0 to the number of replaceable hydrogen atoms on Ar, and x is 0 or 1. When there is a plurality of G substituents in the bisphenols, such substituents may be the same  
10 or different. The T and T' substituents may occur in the ortho, meta or para-positions with respect to the hydroxyl radical. The foregoing hydrocarbon radicals preferably have carbon atoms as follows: alkyl, haloalkyl, alkylene and haloalkylene of 1 to 14 carbons; aryl, haloaryl, arylene and haloarylene of 6 to 14 carbons; alkylaryl, haloalkylaryl, arylalkyl and haloarylalkyl of  
15 7 to 14 carbons; and cycloalkyl, halocycloalkyl, cycloalkylene and halocycloalkylene of 4 to 14 carbons. Additionally, mixtures of the above described bisphenols may be employed to obtain a polymer with especially desired properties. The bisphenols generally contain 12 to about 30 carbon atoms, and preferably 12 to about 25 carbon atoms. The bisphenols are in general normally solids. The preferred bisphenol is commonly called bisphenol-A.

## 20 THE OPTIONAL GLYCOL MODIFIER COMPONENT 20

The present invention is most preferably directed to the preparation of polyesters derived exclusively from a dicarboxylic acid and a bisphenol. However, it is also within the scope of the invention to prepare polyesters containing the residue of an aliphatic glycol difunctional  
25 dicarboxylic acid residues. Such modified polyesters possess excellent engineering properties such as high impact strength and high modulus.

The aliphatic glycol modifier is a reactive difunctional component which may be represented by the formula:



wherein A is a bivalent or disubstituted aliphatic radical, free of tertiary carbon atoms, selected from the group consisting of alkylene, cycloalkylene, arylalkylene, alkyleneoxyalkyl, poly(alkyleneoxy)alkyl, alkylene-carboxyalkylene-carboxyalkyl, and poly(alkylene carboxyalkylene-carboxy)al-  
35 kyl. Typical examples of aliphatic glycol modifiers having the foregoing formula include ethylene glycol, and other glycol modifiers illustrated in the aforementioned US Patent 4,126,602 at Column 4, lines 55-66. Combinations of the above-described aliphatic glycol modifiers can also be employed, usually to obtain special properties.

The glycol modifier may contain 2 to 100 carbon atoms. Polyesters of bisphenol and a  
40 dicarboxylic acid which contain residues of such aliphatic glycol modifiers, and which are prepared by a transesterification polymerization reaction technique are described in British Patent 924,697 to Imperial Chemicals Industries, issued April 24, 1963 (see page 3, lines 12-26), F. Blascke et al., US Patent 3,339,170 issued August 27, 1968 (see Column 2, lines 14-16) and A. L. Lemper et al., US Patent 4,137,278 issued January 30, 1979, the subject  
45 matter of these patents being incorporated herein by reference.

## OPTIONAL LONG CHAIN ALCOHOL COMPONENT

The present invention is preferably directed to a polyester prepared from difunctional reactants. However, if desired, a long chain ( $C_8-C_{45}$ ) monofunctional, i.e. monohydroxy alcohol,  
50 reactant may also be employed in the present transesterification process to convert some of the aryl carboxylate ester end groups of the polyester to alkyl carboxylate ester end groups (wherein the alkyl substituent is the  $C_8-C_{45}$  residue of the long chain alcohol) according to the techniques described in aforementioned European Applications Nos. 80301865.4 and 80301867.0 and US Applications Serial Nos. 45,461 and 45,464. However, use of said monofunctional long  
55 chain alcohol is a less preferred embodiment of the invention, since, as described in these European and US Applications, some of the aforementioned alkyl ester end groups decompose in the transesterification reaction to free carboxylic acid end groups and an aliphatic mono-olefin by-product.

Since one or more of the aforementioned transesterification reactants is normally a solid, it is  
60 generally necessary to melt the reactants prior to introduction of the reactants to the polymerization reaction which is carried out in molten state. Normally solid reactants can be individually melted and subsequently mixed together prior to their addition to the polymerization but it is preferred to mix the reactants together and subsequently melt the reactants since the mixture of solid reactants generally melts at a temperature lower than the melting point of many  
65 individual solid reactants. Use of the latter preferred embodiment generally conserves energy

employed to melt the normally solid reactants.

In accordance with copending European Patent Application No. 81300961.0, published as EP-A-0035897 and corresponding to United States Application Serial No. 128,743 filed March 10, 1980 of J. C. Rosenfeld, (the disclosure of which is incorporated herein by reference), the bisphenol reactant and the diaryl ester reactant are preferably substantially free of impurities, for example, those arising from oxidation of the reactants via contact of the reactants with oxygen-containing gas, e.g. air. Preferably, reactants are maintained under nitrogen prior to and during the reaction to provide monomer reactants substantially free of the aforementioned impurities.

## 10 CATALYST

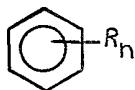
The present transesterification process is carried out in the presence of an ester-interchange or transesterification catalyst of the type conventionally employed in preparing linear aromatic polyesters from diaryl esters of dicarboxylic acid and bisphenols. Preferably, the catalyst present in the transesterification reaction of the invention is an acidic, neutral or basic catalyst, such classifications being based on the reaction of a conventional acid-base indicator and the catalyst when the latter is dissolved in a polar ionizing solvent such as water.

More preferably, a basic catalyst is employed, such as disclosed in the aforementioned copending European Application No. 81300961.0 and US Application Serial No. 128,743. Prior to its introduction into the reaction mass, the preferred basic catalyst is preferably converted to liquid form, e.g. by melting or by dissolution in a liquid or normally solid, low melting solvent as described in the aforesaid copending US Application Serial No. 128,743 and European Application No. 81300961.0.

Suitable basic catalysts include the alkali metals, such as lithium, sodium, potassium, rubidium, cesium and francium; and the carbonates, hydroxides, hydrides, borohydrides, phenates, bisphenates, (i.e. salt of a bisphenol or bisphenol), carboxylates such as acetate or benzoate, oxides of the foregoing alkali metals. Group II and III elements can also be used in place of the alkali metals of the foregoing classes of compounds such as metals and compounds of calcium, magnesium and aluminum. Other bases include trialkyl or triaryl tin hydroxides, acetates, phenates, and the like.

Examples of catalysts are lithium, sodium, potassium, rubidium, cesium and francium metals, potassium or rubidium carbonate, potassium hydroxide, lithium hydride, sodium borohydride, potassium borohydride, calcium acetate, magnesium acetate, aluminum triisopropoxide and triphenyl tin hydroxide.

Phenol is the preferred solvent for the normally solid catalysts. Substituted phenols which can be used include those having the formula



wherein R is alkyl of 1 to 10 carbon atoms, alkoxy of 1 to 10 carbon atoms, aryl of 6 to 10 carbon atoms, chloro, bromo or mixtures thereof, and wherein n is 1 or 2.

Typical solvents include o-benzyl phenol, o-bromo phenol, m-bromo phenol, m-chloro phenol, p-chloro phenol, 2,4 dibromo phenol, 2,6 dichloro phenol, 3,5 dimethoxy phenol, o-ethoxy phenol, m-ethyl phenol, p-ethyl-phenol, o-isopropyl phenol, m-methoxy phenol, m-propyl phenol, p-propyl phenol, and the like.

Other solvents which are particularly useful are of the ether type, for example, tetrahydrofuran and the various glymes, for examples, ethylene glycol dimethylether and the like.

Combinations of catalysts and combinations of phenols or phenols and solvents may also be used.

Especially preferred liquid basic catalysts are charged dissolved in molten normal solid-low melting organic solvent such as phenol. Especially preferred catalysts providing excellent results are the basic catalysts, rubidium phenoxide, potassium phenoxide, and potassium borophenoxide, each dissolved in molten phenol as described in the aforementioned copending US Application Serial No. 128,743 and European Application No. 81300961.0.

Preferably, also when a basic catalyst is employed, the catalyst is introduced concurrently with the aforementioned molten reactants to the polymerization to avoid heating the reactants in the presence of the catalyst prior to onset of the transesterification also as described in copending Application Serial No. 128,743 and European Application No. 81300961.0.

Less preferred catalysts include the metal oxides, metal acetates, titanium and tin compounds. Suitable metal oxides include antimony trioxide, germanium oxide, arsenic trioxide, lead oxide, magnesium oxide, and zinc oxide. Suitable metal acetates include cobalt acetate, zinc acetate, cadmium acetate and manganese acetate. Suitable titanium compounds include the organic titanates such as tetrabutyl titanate and tetrakispropyl titanate. Suitable tin compounds include dibutyltin oxide, dibutyl tin methoxide and dibutyl tin dilaurate.

In accord with conventional transesterification reaction practice, a catalytically effective amount of the catalyst is employed, for example, about 0.005 to about 2 mol percent or more, preferably about 0.01 to 1 mole percent of the bisphenol in accordance with known techniques of transesterification.

#### 5 THE CONDITIONS OF THE CONVENTIONAL TRANSESTERIFICATION PROCESS 5

The present process can be carried out employing in general conditions which are conventional in this art.

10 According to the conventional practice, the solid reactant are heated above about 100°C., preferably above about 160°C. to melt the reactants. Onset of reaction in the presence of catalyst is generally at a temperature ranging from above about 100°C. to about 275°C., for example, above about 160°C. for reaction of bisphenol A, diphenyl terephthalate and diphenyl isophthalate. The reaction temperature employed is generally above about 100°C. to about 400°C. or higher, preferably above about 175°C. to about 350°C., more preferably about 15 175°C. to about 330°C. with the reaction temperature being raised gradually during the polymerization. 15

In the transesterification reaction, the aryl group of the diester is displaced as the corresponding relatively volatile monohydroxy aromatic compound, e.g. phenol, for which provision is made for removal e.g. by distillation from the reaction mixture during the transesterification.

20 Reaction pressure is generally diminished during the reaction, e.g. from atmospheric pressure to a subatmospheric pressure, e.g. of about 0.1 mm. of mercury or lower, to aid in the aforementioned removal of the monohydroxy aromatic compound. 20

Generally, it is preferable in accord with the prior art to carry out reaction in two stages. The first or prepolymerization stage is carried out at above about 100°C. to about 350°C. preferably about 160°C. to about 330°C., especially about 180°C. to about 300°C. to prepare a low 25 molecular weight polyester or prepolymer of relatively low intrinsic viscosity, e.g. of less than about 0.1 to about 0.3 dl./g. A subsequent polymerization stage in which the prepolymer is heated at a somewhat higher temperature namely, at above about 200°C. to about 400°C. or higher, preferably of about 225°C. to about 350°C., especially at about 275°C. to about 30 330°C. 30

Conveniently, the polymerization stage is carried out in a different reaction vessel from that employed in the prepolymerization reaction stage with effective agitation of reaction mixture in both stages with generally more extreme agitation being used in the polymerization. When a polyester of a bisphenol and a dicarboxylic acid is prepared employing a glycol with a portion of 35 the dicarboxylic acid to prepare a glycol-dicarboxylic acid ester oligomer, such an oligomer can be used to prepare the polyester by transesterification of the oligomer with the bisphenol and the diaryl reactants as described in aforementioned US Patent 4,137,278. 35

Conventional processes of the transesterification are described in aforementioned copending European Patent Applications Nos. 80301865.4 and 80301867.0 and United States Applica- 40 tions SN 45,461 and SN 45,464, British Patent 924,607 and US Patents 3,399,170 and 4,137,278, K. Eise et al., German Preliminary Appl. 2,232,877 published January 16, 1974, and G. Bier, *Polymer* 15 527-535 (1974), the disclosures of which are incorporated herein by reference. 40

In carrying out the present invention, it is preferred prior to catalyst addition to melt the 45 normally solid reactants to provide molten reactants and then heat the reactants if necessary to a temperature sufficient for onset of transesterification. According to this embodiment, a basic catalyst for the polymerization that is normally solid at 30°C is then introduced in the liquid form (as described above) to the polymerization concurrent with the molten reactants. This technique is more particularly described in the aforementioned copending European Application 50 No. 81300961.0 and US Application Serial No. 128,743. 50

According to another preferred embodiment of the invention, there is contemplated a semi-continuous process for transesterification polymerization wherein the prepolymerization stage of the process is carried out batchwise and the subsequent polymerization stage is carried out substantially continuously in one or more counter-current flow mechanically agitated thin film or 55 wiped film reactors as is described in copending European Application No. 81300958.6, corresponding to US Application Serial No. 128,742 of G. M. Kosanovich and G. Salee filed March 10, 1980, the disclosure of which is incorporated herein by reference. 55

As an alternative to the aforementioned semi-continuous mode of operation, another preferred embodiment of the invention contemplates a fully continuous transesterification polymerization 60 wherein, the prepolymerization is carried out in one or more stirred tank reactors, and preferably, the polymerization stage is carried out in one or more of the aforementioned wiped film reactors or thin film reactors as is also described in the aforementioned copending European Application No. 81300958.6 and US Application Serial No. 128,742. 60

It is especially preferred in carrying out semi- or fully continuous polymerization according to 65 the aforementioned preferred modes of operation to complete polymerization in a polymerisation 65

reaction zone wherein the aforementioned wiped film reactor is followed by a multi-screw extrusion reaction vessel as described in the copending US Application Serial No. 198979 of G. M. Kosanovich and G. Salee filed October 21 1980, of which copending US Application Serial No. 232929, filed February 9, 1981 and corresponding to European Application No.

5 81300958.6, is a continuation-in-part, the disclosure of which is incorporated herein by reference. 5

#### PROPORTION OF THE DIARYL ESTER REACTANT

In carrying out the present invention, the minimum molar excess of the diaryl ester monomer which is useful in providing a polyester product of diminished color may vary somewhat depending upon the particular constituents of the polyester. 10 10

In general, at least about 0.05% molar excess provides a perceptible improvement in product color, i.e. a perceptibly diminished color compared to the corresponding reactions using a stoichiometric equivalent proportion of the diaryl ester or the corresponding reaction using an excess of diaryl ester greater than the present excess, for a product of a given molecular weight. 15 15  
Preferably, at least about 0.1 mole percent excess of diaryl ester monomer is employed.

Use of 1.8% mol percent or greater excess of the diaryl ester reactant is generally undesirable since such excess entails an undesirable long reaction time in the polymerization reaction as well as concomitant undesirable product discoloration.

20 Preferably, the molar excess of diaryl ester employed in the invention is about 0.1 mole percent to about 1.5 mole percent. 20

More preferably employed in the invention is a mole percent excess of diaryl ester reactant of from about 0.5 to about 1.0 mol percent.

An especially preferred range for the mole percent excess of diaryl ester reactant is about 25 0.75 to less than about 1.0 mole percent. 25

In computing the mole percent excess of the diaryl ester monomer over the stoichiometric proportion of said ester monomer equivalent to a hydroxylic reactant consisting of difunctional hydroxylic reactants, said stoichiometric proportion is taken in accordance with conventional practice as the moles of diaryl ester equivalent to the moles of the hydroxylic reactants, 30 employed. When a monofunctional aliphatic alcohol reagent is employed in preparation of the polyester, the stoichiometric equivalent proportion of diaryl ester is the molar amount of said ester equivalent to the total equivalents of hydroxylic reactants inclusive of said alcohol. 30

The present polyester products especially the polyester products from difunctional reactants, i.e. a dicarboxylic acid diaryl ester reactant and a hydroxylic reactant comprising a bisphenol and, optionally, an aliphatic glycol modifier, have substantially improved color, i.e. low color, at 35 a satisfactory polyester molecular weight, i.e. a number average molecular weight corresponding to an intrinsic viscosity above about 0.5 at 30°C. as measured as described herein below. 35

The improved color of the present product polyester renders the present polyester product especially suitable for engineering thermoplastic applications where low color of the thermoplastic is desirable or essential. For example, the present products are eminently suitable for use as 40 molded decorative articles without incorporation of excessive amounts of pigment in the polyester to mask objectionable polyester color. 40

In order to further illustrate the invention but without being limited thereto, the following examples are given. In this specification and claims, unless otherwise indicated, parts, 45 percentages and proportions are by weight, and temperatures are in degrees centigrade. 45

#### EXAMPLES

##### Testing Procedures for Polyester Intrinsic Viscosity and Color in the Examples.

##### A. Intrinsic Viscosity (I.V.)

50 A 0.50 gm/100 cc solution of polymer in 1,1,2,2,tetrachloroethane is prepared in a volumetric flask. The solution is filtered into a Cannon Ubelhole #75 viscometer maintained in a water bath at 30°C. Solution flow times are measured and the I.V. is calculated (using  $K' = 0.43$  determined separately for the polymer) according to F. W. Billmeyer, Testbook of Polymer Science, 1964, page 80. 50

##### B. Color

55 APHA polymer color in Examples 1-4 below is measured by comparison of a 1% solution of polymer in  $\text{CH}_2\text{Cl}_2$  with APHA standard color solution in 50 ml Nessler tubes. 55

Yellowness Index of the polymer in Examples 5-7 below is measured on a Hunterlab Spectrophotometer and is described in ASTM D 1924-70.

60 In determination of Yellowness Index color, as the molten polymer is being removed from the two-gallon reactor, a small portion of the polymer is placed between the preheated (600°F) plates of a Carver Press with two sheets of heavy aluminum foil and 1/8 inch shims and pressed for several minutes. The molded polymer is removed and allowed to cool. Then the aluminum foil is removed and the molded polymer is employed in the color test. 60

*EXAMPLES 1-4**A. Prepolymer Preparation*

Bisphenol-A (4.61 moles), diphenyl terephthalate (1.15 moles), and a diphenyl isophthalate (molar proportions described in Table I below) are dried in glass trays in a vacuum oven for about 16 hours at about 75°, and charged to a 5-liter resin kettle equipped with gas inlet, mechanical stirrer and a combination vigreux column-distillation head having a thermometer immersed in the reaction mixture and curved glass tube attached to a 3-necked flask receiver with a stopper and outlet tube. The system is put under a blanket of dry nitrogen. 5

The reactants are heated to about 200°C with a heating mantle and the catalyst is added to the reaction mass under the dry nitrogen blanket. Vacuum is applied gradually to the reaction mass and temperature is raised gradually and the phenol by-product is distilled off and collected in the 3-necked flask receiver which is cooled by ice. After about two hours, most of the phenol has been removed. The temperature of the reaction mass is about 280° and the pressure is about 7 mm Hg. The vacuum is released under dry nitrogen and the polyester prepolymer obtained is poured into a teflon-lined tray to cool to ambient temperature. The prepolymer is light yellow, clear and brittle. The intrinsic viscosity of the prepolymer is determined. 10 15

*B. Polymer Preparation*

The above prepolymer is crushed and a 1500 gm portion thereof is charged to a two-gallon stainless steel reactor with a helical stirrer driven by an electric motor, a hot oil circulating jacket, and a small column and receiver connected to a vacuum pump. The reaction mixture is maintained under a blanket of dry nitrogen overnight. Vacuum is applied (about 1 mm Hg) and the reactor is heated to 290-295°C over about 2.5 hours. The reaction is continued under these conditions with stirring, generally until the desired intrinsic viscosity is reached (as indicated by stirrer motor current draw). Then the vacuum is released under dry nitrogen, the reactor head is removed, and the polymer is scraped from the reactor. The intrinsic viscosity and color of the polymer product is determined. The polymer is clear and very tough. 20 25



TABLE I

	Example 1 (Control)	Example 2 (Comparative)	Example 3 (Control)	Example 4
Bisphenol-A (BPA) moles Charged	4.80	4.71	4.61	4.56
Diphenyl Isophthalate (DPI) moles Charged	3.60	3.60	3.46	3.46
Diphenyl Terephthalate (DPT) moles Charged	1.20	1.20	1.15	1.15
Excess of Diphenyl Ester (mole-%) Used	None	1.8	None	1.0
Catalyst (mole-% based on BPA)	LiOØ (0.05) <sup>1</sup>	LiOØ (0.05) <sup>1</sup>	KOØ (0.05) <sup>2</sup>	KOØ (0.05) <sup>2</sup>
Prepolymer I.V. (dl/g)	0.14	0.12	0.17	0.17
Reaction Time (Duration) at 290-295 °C.	4.4 hr.	6.9 hr.	5.0 hr.	4.2 hr.
Polymer I.V. (dl/g) <sup>3</sup>	0.55	0.54	0.63	0.66
Polymer Color (APHA, 1% CH <sub>2</sub> Cl <sub>2</sub> Solution)	20	30-40	20	17

<sup>1</sup>Catalyst is lithium phenate dissolved at a concentration of 0.5M in a mixture of about 16% anhydrous phenol and 84% anhydrous tetrahydrofuran prepared by dissolving and reacting lithium wire in the solvent mixture.

<sup>2</sup>Catalyst is potassium phenate dissolved at a concentration of 0.5M in distilled phenol prepared by dissolving potassium carbonate in the phenol solvent.

<sup>3</sup>A known measure of polymer number average molecular weight.

Comparison of the data comparable Examples 1 and 2 in Table 1 demonstrates that with 1.8 mole percent excess diphenyl ester over the stoichiometric proportion required with the amount of bisphenol-A used, a longer reaction time is required in Example 2 in order to reach the same product intrinsic viscosity, i.e. molecular weight, compared to use of a stoichiometric proportion of diaryl ester in Example 1. The longer reaction time required in Example 2 to reach about the same product molecular weight as in Example 1 causes the polymer color to be darker in Example 2 compared to that in Example 1 which employs a stoichiometric equivalent proportion of the diaryl ester.

Comparison of the data of comparable Examples 3 and 4 in Table 1 demonstrates that when a molar excess of diphenyl ester in accordance with the invention is used in Example 4, the reaction time is shorter and the polymer color is improved compared to the corresponding polymerization in Example 3 which is carried out with a molar proportion of the diaryl ester which is stoichiometrically equivalent to the amount of bisphenol used.

The following Examples 5, 6 and 7 illustrate preparation of the polyester according to the invention employing a semi-continuous reaction mode illustrated in the aforementioned US Application Serial No. 198979 of G. M. Kosanovich and G. Salee of which United States Application Serial No. 232929, corresponding to European Application No. 81300958.6, is a continuation-in-part.

#### EXAMPLES 5, 6 and 7

Mixtures of 75:25 diphenyl isophthalate:diphenyl terephthalate and bisphenol-A were vacuum oven dried for about 3 hours at 20 mm Hg in large flat trays then weighed into polyethylene-lined 5-gallon pails and sealed until used. The diphenyl isophthalate, diphenyl terephthalate, and bisphenol-A are charged to a stainless steel melt tank and melted at about 100°C under a blanket of dry nitrogen. The molten monomer mixture is transferred via heated lines to a continuously stirred oil heated reactor. Catalyst (potassium phenoxide; 0.041 mole solution in phenol; 0.0081 moles; i.e. 0.05 mole percent based on bisphenol-A) is added. Vacuum is applied and the temperature (which is initially 220°) is raised gradually. After about 2.5 hours, the pressure is about 70 mm and the temperature is 280°C. Intrinsic viscosity of the polyester prepolymer at this point is about 0.17 dl/g.

The prepolymer is transferred via heated lines to a second stirred reactor and another prepolymer is prepared similarly in the first stirred reactor.

The prepolymer in the second stirred reactor is fed continuously at about 20–25 lbs/hour to a vertical wiped thin film reactor which is maintained at an internal temperature of 300°C. and a pressure of 1.50 mm Hg (abs.). The reaction mass fed to the top of the wiped thin film reactor flows down through the reactor propelled by gravity and by the downward thrust of the pitched rotor blades. These blades also agitate and renew the polymer on the heated reaction surface of the thin film reactor. The material leaving the thin film reactor has an intrinsic viscosity of about 0.4 dl/g.

The polymer is pumped out from the bottom of the thin film reactor and fed to a 5-stage twin screw horizontal extruder having five vacuum vents (one from each stage). The extruder is operated at about 0.8 mm Hg (abs.) pressure, 330°C. melt temperature and a screw speed of 125 rpm. The pressure and temperature are maintained uniformly throughout the barrel, i.e. through the extruder stages. Under these operating conditions, light yellow, clear, tough polymer is produced at a rate of 20 lbs/hour. The product is essentially free of black char and brown polyester gel particles in accordance with the teaching of the aforementioned copending US Application Serial No. 198979 of G. M. Kosanovich and G. Salee of which US Application Serial No. 232929, corresponding to European Application No. 81300958.6, is a continuation-in-part.

The foregoing semi-continuous polyester preparatory process is initially run with a 0.5 mole percent excess of the diaryl ester reactant over the stoichiometric proportion corresponding to the molar amount of the bisphenol used. After a steady reaction state is reached, samples of polyester product are removed at two-hour intervals and tested for polyester intrinsic viscosity and Yellowness Index color. The statistical deviation in results for the Intrinsic Viscosity and Yellowness Index color of the samples is also determined. This data is reported as Example 5 in Table II below.

The proportion of the diaryl ester reactant charged to the process is then adjusted to provide a mole percent excess of 0.75 of the diaryl ester. After the reaction has reached a steady state, the foregoing product sampling and testing procedures are repeated substantially as described. The resultant intrinsic viscosity and yellowness index color data are reported as Example 6 in Table II below.

The proportion of the diaryl ester reactant charged to the process is then adjusted to provide a 1.0 mole percent excess of the diaryl ester monomer. After the semi-continuous reaction has reached a steady operating state, the foregoing product sampling and testing procedure is repeated substantially as described. The resultant data is reported in Table II below as Example 7.

TABLE II

Part A: Amounts of Reactants Used (moles, weight (Kg))		Example 5	Example 6	Example 7	
Bisphenol-A		16.25 (3.710)	16.25 (3.710)	16.25 (3.710)	
Mixture of 75% Diphenyl Isophthalate and 25% Diphenyl Terephthalate Charged		16.33 (5.199)	16.37 (5.211)	16.41 (5.224)	
Mole-% Excess Diphenyl Isophthalate and Diphenyl Terephthalate Employed		0.50	0.75	1.0	
Part B: Intrinsic Viscosity and Yellowness Index Color of Product					
Sample	Example 5		Example 6		Example 7
	I.V. (dl/g) <sup>1</sup>	Color (Y.I.) <sup>2</sup>	I.V. (dl/g)	Color (Y.I.)	I.V. (dl/g) Color (Y.I.)
1	0.56	37	0.49	26	0.45 19
2	0.56	38	0.50	28	0.50 22
3	0.58	35	0.54	34	0.50 22
4	0.58	38	0.52	35	0.50 30
5	0.58	37	0.53	27	0.50 30
6	—	—	—	—	0.49 28
Average	0.57	37	0.52	30	0.49 25
Standard Deviation of Average Result	±0.01	±1	±0.02	±4	±0.02 ±5

<sup>1</sup>Intrinsic viscosity determined at 30°C. in 1,1,2,2-tetrachloroethane.

<sup>2</sup>Yellowness Index of a compression molded 1/8" plate (Hunterlab Spectrophotometer)

## CLAIMS

1. A process for the preparation of a linear aromatic polyester, which process comprises effecting trans-esterification polymerization of a diaryl ester of a dicarboxylic acid and a hydroxylic reactant comprising a major molar proportion of a bisphenol employing an excess of from 0.05 to less than 1.8 mole percent of said diaryl ester over the stoichiometric equivalent proportion of said diaryl ester with respect to said hydroxylic reactant. 5
2. A process according to claim 1 wherein the hydroxylic reactant is a difunctional hydroxylic reactant.
3. A process according to claim 1 or 2 wherein the mole percent excess of said diaryl ester is from 0.1 to 1.5. 10
4. A process according to claim 3 wherein the mole percent excess of said diaryl ester is from 0.5 to 1.0.
5. A process according to any one of the preceding claims wherein a minor molar proportion of an aliphatic glycol reactant based on said hydroxylic reactant is employed.
6. A process according to any one of the preceding claims wherein an aliphatic monofunctional alcohol is employed, the organic residue of said alcohol being a saturated alkyl group containing only carbon-to-hydrogen bonds. 15
7. A process according to any one of claims 1 to 4 wherein the reactants consist essentially of a bisphenol and the diaryl ester of dicarboxylic acid.
8. A process according to any one of the preceding claims wherein said dicarboxylic acid has the formula: 20



wherein Z is alkylene, -Ar- or -Ar-Y-Ar- where Ar is aromatic Y is alkylene, haloalkylene, -O-, -S-, -SO<sub>2</sub>-, -SO<sub>3</sub>-, -CO-, -SO-,



wherein G is alkyl, haloalkyl, aryl, haloaryl, alkylaryl, haloalkylaryl, arylalkyl, haloarylalkyl, cycloalkyl, or cyclohaloalkyl; and n is 0 or 1. 35

9. A process according to claim 8 wherein said dicarboxylic acid is an aromatic dicarboxylic acid.
10. A process of claim 8 wherein the dicarboxylic acid is isophthalic acid, terephthalic acid or a mixture thereof.
11. A process according to claim 10 wherein said mixture consists of from greater than 15 to less than 85 molar percent of isophthalic acid and from greater than 15 to less than 85 molar percent of terephthalic acid. 40
12. A process according to any one of the preceding claims wherein said bisphenol has the formula: 45



wherein Ar is aromatic, G is alkyl, haloalkyl, aryl, haloaryl, alkylaryl, haloalkylaryl, arylalkyl, haloarylalkyl, cycloalkyl, or cyclohaloalkyl; E is divalent alkylene, haloalkylene, cycloalkylene, halocycloalkylene, arylene, or haloarylene, -O-, -S-, -SO-, -SO<sub>2</sub>-, -SO<sub>3</sub>-, -CO-, 50



T and T' are independently selected from halogen, G and OG; m is 0 or an integer up to the number of replaceable hydrogen atoms on E; b is 0 or an integer up to the number of replaceable hydrogen atoms on Ar, and x is 0 or 1. 60

13. A process according to claim 12 wherein the bisphenol is bisphenol-A.
14. A process according to any one of the preceding claims wherein the diaryl ester is a diphenyl ester.
15. A process according to any one of the preceding claims wherein the reactants are introduced into the polymerization reaction in the liquid state and polymerization is carried out in 65

the presence of a basic catalyst which is normally solid at 30°C. and which is introduced in liquid form into the polymerization zone.

16. A process according to any one of the preceding claims wherein the reactants are introduced into the polymerization reaction in the liquid state and polymerization is carried out in the presence of a basic catalyst, said catalyst and said liquid state reactants being introduced substantially concurrently into the polymerization reaction. 5
17. A process according to any one of the preceding claims which is effected in a series of batch reaction zones. \*
18. A process according to any one of claims 1 to 16 wherein reaction is conducted in a first stage to prepare a polyester oligomer and is continued in a second stage to produce the polyester product, said polymerization being carried out batchwise or substantially continuously in said first stage and continued substantially continuously in said second stage. 10
19. A process according to claim 18 wherein polymerization in the first stage is carried out batchwise.
20. A process according to claim 18 wherein polymerization in said first stage is substantially continuous. 15
21. A process according to any one of claims 18 to 20 wherein polymerization in the second stage is carried out in a wiped film reaction zone.
22. A process according to claim 21 wherein polymerization in the second stage comprises polymerization in a wiped film reaction zone followed by polymerization in a vented extrusion reaction zone. 20
23. A process for preparing a linear aromatic polyester, which process comprises effecting trans-esterification polymerization of a diaryl ester of a dicarboxylic acid and hydroxylic reactant comprising a major molar proportion of a bisphenol in the presence of a basic catalyst that is normally solid at 30°C and employing an excess of from 0.05 to less than 1.8 mole percent of said diaryl ester over the stoichiometric equivalent proportion of said diaryl ester with respect of said hydroxylic reactant, the reactants and the catalyst being introduced into the polymerization reaction in the liquid state substantially concurrently and the polymerization being carried out in a polymerization zone which comprises a series of at least two reaction stages wherein the polymerization reaction in the final stage of the series is carried out continuously in a wiped film reaction zone. 25 30
24. A process according to claim 23 wherein the polymerization zone consists of two stages and the reaction in the first stage is carried out batchwise.
25. A process according to claim 23 wherein the reactants and catalyst are introduced to the polymerization zone substantially continuously and the polyester product is withdrawn from the polymerization zone substantially continuously. 35
26. A process according to any one of claims 23 to 25 wherein polymerization in the final stage of the series is carried out continuously in a wiped film reaction zone followed by polymerization carried out continuously in a vented extrusion reaction zone.
27. A process for the preparation of a linear aromatic polyester, which process comprises effecting transesterification polymerization of monomer reactants consisting essentially of a bisphenol and a diaryl ester of a dicarboxylic acid employing an excess of from 0.75 to 1.0 mole percent of said diaryl ester over the stoichiometric equivalent proportion of said diaryl ester with respect to said hydroxylic reactant. 40
28. A process for the preparation of a linear aromatic polyester substantially as hereinbefore described in any one of Examples 4 to 7. 45
29. Shaped articles prepared from a linear aromatic polyester produced by a process as claimed in any one of the preceding claims. 5