

PATENT SPECIFICATION

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- (32) Filed 22 Dec. 1975 in
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C3R 3D13 3D2A 3D2E 3D6 3N1



(54) POLYESTERS AND CONTAINERS MADE THEREFROM

(71) We, OWENS-ILLINOIS INC., a Corporation organised under the laws of the State of Ohio, of Toledo, Ohio, 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:—

The present invention relates to copolyesters, to a method for the production thereof, and to containers made therefrom.

Packages, such as bottles, made of polyethylene terephthalate, and their method of manufacture, are disclosed in U.S. Patent No. 3,733,309. These packages are biaxially oriented bottles and are manufactured from a homopolymer of ethylene glycol and terephthalic acid or copolymers of ethylene terephthalate wherein up to 10 mole percent consists of the monomer units of for example diethylene glycol, propane - 1,3 - diol, butane 1,4 - diol, 1,4 - hydroxymethylcyclohexane or isophthalic acid. While bottles made from polyethylene terephthalate have quite satisfactory permeability characteristics which allow them to be used for packaging various products of commerce especially comestible items including foodstuffs, or medicines, they need improvement in order to allow them to satisfactory withstand higher temperatures. Generally, as indicated above, the permeability characteristics of polyethylene terephthalate are satisfactory and typically an unoriented polyethylene terephthalate will have an oxygen permeability of 8—10 cc · mil/100 in.² · day · atm. and a CO₂ permeability of 48 to 50. The glass transition temperature of polyethylene terephthalate, however, is of the order of 72°C. and, whether a container made therefrom is unoriented or biaxially oriented, it will be realized that a higher glass transition temperature is needed in order to allow a container thereof to withstand higher temperatures. Thus a need exists for a polyester container which is capable of withstanding higher temperatures, for example those encountered in an autoclaving procedure and even the temperatures quite frequently existing in warehouses.

As will be subsequently seen, the present invention provides copolyesters which have glass transition temperatures in excess of 72°C. and which have satisfactory oxygen permeability characteristics thus making them ideally suited for forming oriented or un-oriented containers or bottles and for the packaging of various products of commerce; additionally these polyesters have the needed balance of properties to allow them to be melted and expediently formed into containers and the present copolyesters have decomposition points which are above normal processing temperatures so as not to cause any significant discoloration problems when synthesizing the copolyesters and manufacturing bottles and packages therefrom. The invention also includes containers made from such copolyesters.

While not directed to bottles, U.S. Patent No. 3,862,084 mentions the homopolymer of ethylene glycol and terephthalic acid, as well as copolyesters formed from terephthalic acid and/or one or more different acids, e.g. isophthalic acid, and from ethylene glycol and/or one or more different alcohols, such as neopentyl glycol, that is, 2,2-dimethyl-1,3-propane diol.

A wide variety of copolyesters are known in the prior art. U.S. Patent No. 3,522,215 discloses a copolyester formed from terephthalic acid, 1,4 - cyclohexane dimethanol and a third, broadly disclosed, dicarboxylic acid (or ester) component which may, for example, be p,p'-sulfonyldibenzoic acid or p,p'-isopropylidenedibenzoic acid; as a fourth component, another acid or glycol can be used; the glycols disclosed include ethylene glycol, ether glycols, and branched glycols and carbocyclic glycols with neopentyl glycol (i.e., 2,2 - dimethyl 1,3 - propane diol) being set forth as a branched chain glycol. U.S. Patent No. 3,547,888 discloses compounds formed from terephthalic acid (or its ester), 1,4 - cyclohexane dimethanol and, for example, p,p'-isopropylidenedibenzoic acid (or esters); reference may also be had to 78 *Chemical Abstracts* 160332y and German Offenlegungsschrift 2,146,055.

U.S. Patent No. 2,744,094 discloses polyesters formed from p,p' - sulfonyldibenzoic acid (or its esters or acid chloride) plus an aromatic dibasic acid diester, and a polymethylene glycol, and/or an aliphatic ether glycol, and indicates that mixtures of straight chain alkane diols or ether glycols may be employed. U.S. Patent No. 2,744,097 discloses polyesters from beta-hydroxyalkyl diesters of p,p' - sulfonyldibenzoic acid and dihydroxy compounds, for example, aliphatic ether glycols, and polymethylene glycols. U.S. Patent No. 2,744,088 discloses polyesters of p,p' - sulfonyldibenzoic acid (or esters or acid chlorides), an aliphatic straight-chain dibasic acid, or ester thereof, and an alkylene glycol and/or aliphatic ether glycol; branched chain glycols are mentioned and ethylene glycol and neopentyl glycol (2,2 dimethyl-propane diol-1,3) are specifically set forth. The foregoing patents are discussed in Vol. 50, *Chemical Abstracts*, col 16183 and other polyesters from p,p' - sulfonyldibenzoic acid are discussed in cols. 16180-16182.

U.S. Patent No. 2,901,466, somewhat similar to some of the above patents, discloses linear polyesters formed from 1,4-cyclohexanedimethanol and one or more hexacarboxylic dicarboxylic acids (or its ester or halide), e.g. p,p' - sulfonyldibenzoic acid, isophthalic acid, terephthalic acid; modifying glycols, e.g., ethylene glycol, ether glycols, neopentyl glycol (2,2' - dimethyl - 1,3 - propanediol), and carbocyclic glycols are also indicated.

German Offenlegungsschrift 2,140,615 and *Chemical Abstracts*, Vol. 78 148445e describe a linear polyester having a glass transition temperature of about 145°C. to about 163°C. which is made from ethylene glycol, neopentyl glycol (2,2' - dimethyl 1,3 - propanediol) and bis(4 - butoxycarbonylphenyl) sulfone (butyl ester of p,p' - sulfonyldibenzoic acid).

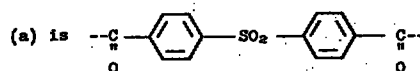
Recently issued U.S. Patent No. 3,890,256 discloses polyesters formed from neopentyl glycol but indicates that, for its purposes of producing high impact and high tensile strength, such a glycol is unsatisfactory.

British Specification 962,913, and its addition Patent 1,044,015, and French Brevet 1,456,345 disclose linear polyesters, formed from 2,2,4,4 - tetramethyl 1,3 - cyclobutane diol, optionally with another glycol. Polyester-forming acid reactants include terephthalic acid, isophthalic acid, and p,p' - sulfonyldibenzoic acid. Ethylene glycol and neopentyl glycol, as possible modifying alcohols, are indicated in all three documents.

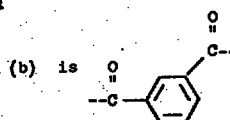
Thus, as will be seen from the foregoing, an extensive amount of work has been done with polyesters but little has been done to satisfy the needs of the packaging industry for an improved polyester container suitable for the packaging of various products, especially comestibles like foodstuffs and medicines. That is, no one has focused their attention on

satisfying the need for providing a packaging container of a linear polyester having satisfactory oxygen permeability characteristics and a glass transition temperature higher than polyethylene terephthalate.

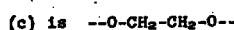
Thus in accordance with the present invention there is provided an improved copolyester which can be melted and molded to a clear container for use in the packaging industry wherein the repeating units of the copolyester, i.e. the radicals remaining after transesterification, or esterification, and polycondensation consist essentially of (a), (b), (c), and (d) wherein



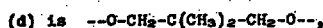
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said polyesters having an oxygen permeability as measured by ASTM D-1434-66 of less than 15 cc · mil/100 in.² · day · atm. and a glass transition temperature in excess of 72°C. The mole ratio, based on the amounts of the reactants, i.e., the polyester-forming precursor, used in the reaction, of the (b) units above to the (a) units above is between 80:20 and 20:80 and the ratio of the (c) units above to (d) units above is about 80:20.

The copolyesters herein are those wherein units (a), indicated above, are obtained from a polyester-forming precursor which is p,p' - sulfonyldibenzoic acid, an ester thereof, or an acid halide thereof, and wherein the (b) units indicated above are obtained from isophthalic acid, an ester or acid halide thereof. Units (c) and (d) above are respectively obtained from polyester-forming precursors which are ethylene glycol and neopentyl glycol (2,2-dimethyl 1,3-propanediol).

In an especially desirable embodiment the ratio of (b) units to (a) units in the polyester, based on reaction proportions, is between 60:40 and 20:80 with the ratio, based on reactant proportions, of (c) units to (d) units being about 80:20.

The esters contemplated above as the polyester-forming precursor may be any of the well known esters e.g. aliphatic esters, or aromatic esters. Preferred aliphatic, or acyclic, esters are the alkyl esters having from 1 to 4 carbon atoms, with the methyl or ethyl ester being especially preferred. The phenyl esters are preferred aromatic esters. Instead of using the acid or esters, acid halides may likewise

be employed, with the acid chloride being quite suitable. Thus for example units (a) may be the polymerization radical obtained from p,p'-sulfonyldibenzoyldichloride and units (b) the polymerization radical obtained from isophthaloyldichloride.

The copolyesters may be synthesized by methods generally known in the art for producing polyesters wherein at least one polyester-forming dicarboxylic acid, ester, or halide thereof, is reactively combined with at least stoichiometric amounts of at least one polyester-forming dibasic alcohol under conditions of temperature, pressure and catalysis as to form the polyester. In the usual procedure the method of reactively combining the acid, acid ester, or acid halide with the dibasic alcohol is a two-step process involving a transesterification step, or esterification step depending on the starting materials, followed by a polycondensation step with the reaction being done in a melt condition. Temperatures employed which are quite suitable for forming the present copolyesters are from 200° or 210°C. up to 300°C. Additionally in the usual procedure a stoichiometric excess of glycol will be employed, with the mole ratio of ethylene glycol to neopentyl glycol being about 80:20. Generally the amount will be between 2 and 3 moles, conveniently about 2.5 moles, of total glycol per mole of total dicarboxylic acid, or ester or halide, employed.

Conventional catalysts are likewise employed. For example transesterification is effected in the presence of effective catalytic amounts of transition metal compounds, alkaline earth metal compounds, or alkali metal compounds, for example the acetates, oxides, phenoxides, and alkoxides. Specific suitable catalysts will be, for example, zinc acetate, manganese acetate, magnesium acetate and calcium acetate, and titanium alkoxides like titanium tetrabutoxides. Suitable polycondensation catalysts include for example antimony acetate, antimony trioxide, titanium alkoxide, and organotin oxides, for example stannous alkoxides. Usually the catalysts will be present in an amount of 10^{-5} to 10^{-3} moles of catalyst per mole of total acid, ester or halide employed. In performing the reaction the reactant proportions of course will be selected as indicated previously. Additionally units (a) and (b) of the copolyester are, relative to themselves, present in about the same ratio as that of their precursors in the reaction charge. Similarly the ratio of (d) to (c) units will be about the same as the molar ratio used in the reaction for their precursors.

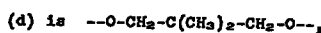
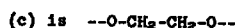
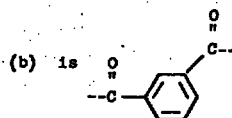
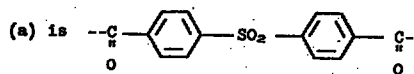
The copolyesters of the present invention can be melt-molded into containers, for example bottles, and these containers will be clear, i.e. to the unaided eye the container will be transparent thereby allowing for the visual observation of the packaged product

through the container walls. In passing it should be mentioned that when the term "melt-molded" is employed herein this contemplates conventional known processes wherein thermoplastic materials, for example polyethylene terephthalate, are first taken to a melt state and then molded for example by blow molding techniques, or injection molding techniques, or combinations thereof, into a final container or bottle. Thus for example the copolyesters can be melt-molded into bottles or jars by techniques wherein, for example, a parison is first formed by a blow molding or injection molding operation and wherein the parison is biaxially stretched or oriented and formed into a final configuration, again, for example, by blow molding. Thus the copolyesters of the present invention may be melt-molded to clear bottles and containers for use in the packaging industry using any of the techniques known in the art for forming melt molded containers.

The following Examples are given for the purpose of illustrating the invention.

EXAMPLE I

A polyester was prepared having the following repeating units in its backbone.



Based on the proportions of the polyester forming precursors used in the reaction the mole ratio of b:a was about 60:40 and the mole ratio of c:d was 80:20. The specific charge of ingredients, or precursors, was about 0.0309 moles of dimethyl sulfonyldibenzoate (DMS), about 0.0463 moles of dimethyl isophthalate (DMI), about 0.154 moles of ethylene glycol (EG), and about 0.038 moles of neopentyl glycol (NPG). For catalytic purposes the charge also included about 3.86×10^{-5} moles of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ and about 1.46×10^{-5} moles of Sb_2O_3 .

The mixture of the starting materials was weighed into a 300 ml, 3-necked round bottom flask equipped with a stirrer, nitrogen inlet tube, and a condenser. The contents of the flask were heated at 195° to 205°C. for 3 hours with nitrogen flowing into the reaction flask to provide a nitrogen blanket. About 80% of the theoretical methanol by-product was removed. After this three hour period at

195° to 205°C. the contents were heated to about 260°C. and a vacuum of about 24 mm Hg was applied and the system held for about 1 hour. Ethylene glycol, neopentyl glycol, and by-product methanol was removed. The condensation of the prepolymer was then continued at a temperature of about 285° to about 295°C. and was maintained there for a period of 3—4 hours under a vacuum of about 0.5 millimeters of mercury. During this time excess ethylene glycol and neopentyl glycol was further removed by distillation. After this period the polymer was removed and found to have a glass transition temperature, as measured with a Differential Scanning Calorimeter, of about 93°C., and an oxygen permeability, as measured by ASTM D-1434-66, of about 11.2 cc·mil/100 in.²·day·atm. at about 73°F. and 50% relative humidity and a CO₂ permeability of about 40.6 cc·mil/100 in.²·day·atm. The polymer was easily formed into flexible clear films.

Following the known forming procedures of the prior art, e.g. U.S. Patent No. 3,733,309, a biaxially oriented container (i.e. a container having a bottom wall and a circumferential side wall merging with and proceeding upwardly from the bottom wall, the sidewall at its upper margin tapering inwardly and merging with a neck portion defining a mouth opening) is formed from the above-produced polymer. This container is clear and upon being filled by placing foodstuffs, beverages or medicines therein and closing the container shows excellent characteristics for packaging of such products. A similar bottle, but one which is not oriented, also shows excellent characteristics for packaging but is weaker.

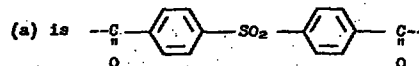
EXAMPLES II & III

Following the procedure of Example I two copolyesters were prepared. The mole ratio of DMI to DMS in the reactant charge was 30:70 for one polyester and 20:80 for the other. In both cases the reactant charge mole ratio of EG to NPG was about 80:20. The former copolyester had an oxygen permeability of 10.2, a carbon dioxide permeability of 72.2, a glass transition temperature of 117°C. and an inherent viscosity of 0.49. The values for the latter copolyester were 12.4, 95.0, 127°C. and 0.64 respectively. These copolyesters are excellent materials for forming transparent containers for the packaging of foodstuffs, beverages and medicines, for example.

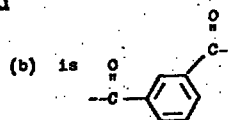
In a similar manner a polyester was produced using the polyester synthesis procedure as above but without any dimethyl isophthalate. That is the ratio of c:d was about 80:20 and the ratio of b:a was 0:100. The polyester had a glass transition temperature of about 137°C. but its permeability characteristics were unsatisfactory (O₂=20.3 and CO₂=147).

WHAT WE CLAIM IS:—

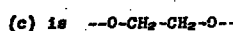
1. A linear copolyester which can be melted and molded to a clear container, the repeating units of said polyester consisting essentially of



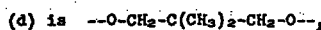
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said copolyester having an oxygen permeability of less than 15 cc·mil/100 in.²·day·atm. and a glass transition temperature in excess of 72°C., said (a) and (b) units and said (c) and (d) units respectively being the units formed by reactively combining polyester-forming precursors thereof in an amount of at least one mole of the precursors of said (c) and (d) units per mole of precursors of said (a) and (b) units and wherein the precursors of said units are in a molar ratio of said (b) unit precursor to said (a) unit precursor of 80:20 to 20:80 and a molar ratio of said (c) unit precursor to said (d) unit precursor of about 80:20.

2. The copolyester of claim 1 wherein said precursor mole ratio of (b) to (a) units is 60:40 to 20:80 said copolyester having an oxygen permeability of less than 12.4 and a glass transition temperature between 93°C. and 127°C. and a CO₂ permeability of less than 95.

3. The copolyester of claim 2 wherein said ratio of (b) units to (a) units is 30:70 to 20:80, said copolyester having a glass transition temperature between 117°C. and 127°C. and an oxygen permeability between 10.2 and 12.4.

4. A method of forming a copolyester by reactively combining at least one polyester forming dicarboxylic acid, ester or halide thereof with at least a stoichiometric amount of at least one polyester forming dibasic alcohol, under conditions of temperature, pressure and catalysis so as to form a polyester, wherein said acid, ester or halide consists essentially of (1) p,p'-sulfonyldibenzoic acid, an ester thereof or a halide thereof and (2) isophthalic acid, an ester thereof or a halide thereof, and wherein said alcohol consists essentially of (3) ethylene glycol and (4) neopentyl alcohol, the mole ratio of (2) to (1) being 80:20 to 20:80 and the mole ratio of (3) to (4) being about 80:20.

5. A method of producing a polyester as



195° to 205°C. the contents were heated to about 260°C. and a vacuum of about 24 mm Hg was applied and the system held for about 1 hour. Ethylene glycol, neopentyl glycol, and by-product methanol was removed. The condensation of the prepolymer was then continued at a temperature of about 285° to about 295°C. and was maintained there for a period of 3-4 hours under a vacuum of about 0.5 millimeters of mercury. During this time excess ethylene glycol and neopentyl glycol was further removed by distillation. After this period the polymer was removed and found to have a glass transition temperature, as measured with a Differential Scanning Calorimeter, of about 93°C., and an oxygen permeability, as measured by ASTM D-1434-66, of about 11.2 cc·mil/100 in.²·day·atm. at about 73°F. and 50% relative humidity and a CO₂ permeability of about 40.6 cc·mil/100 in.²·day·atm. The polymer was easily formed into flexible clear films.

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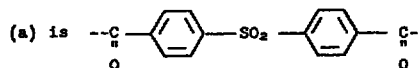
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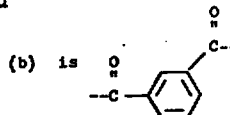
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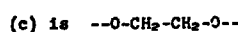
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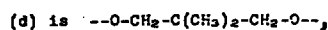
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said copolyester having an oxygen permeability of less than 15 cc·mil/100 in.²·day·atm. and a glass transition temperature in excess of 72°C., said (a) and (b) units and said (c) and (d) units respectively being the units formed by reactively combining polyester-forming precursors thereof in an amount of at least one mole of the precursors of said (c) and (d) units per mole of precursors of said (a) and (b) units and wherein the precursors of said units are in a molar ratio of said (b) unit precursor to said (a) unit precursor of 80:20 to 20:80 and a molar ratio of said (c) unit precursor to said (d) unit precursor of about 80:20.

2. The copolyester of claim 1 wherein said precursor mole ratio of (b) to (a) units is 60:40 to 20:80 said copolyester having an oxygen permeability of less than 12.4 and a glass transition temperature between 93°C. and 127°C. and a CO₂ permeability of less than 95.

3. The copolyester of claim 2 wherein said ratio of (b) units to (a) units is 30:70 to 20:80, said copolyester having a glass transition temperature between 117°C. and 127°C. and an oxygen permeability between 10.2 and 12.4.

4. A method of forming a copolyester by reactively combining at least one polyester forming dicarboxylic acid, ester or halide thereof with at least a stoichiometric amount of at least one polyester forming dibasic alcohol, under conditions of temperature, pressure and catalysis so as to form a polyester, wherein said acid, ester or halide consists essentially of (1) p,p'-sulfonyldibenzoic acid, an ester thereof or a halide thereof and (2) isophthalic acid, an ester thereof or a halide thereof, and wherein said alcohol consists essentially of (3) ethylene glycol and (4) neopentyl alcohol, the mole ratio of (2) to (1) being 80:20 to 20:80 and the mole ratio of (3) to (4) being about 80:20.

5. A method of producing a polyester as



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claimed in claim 4, substantially as herein-
before described.

6. A polyester when produced by a method
as claimed in claim 4 or claim 5.

5 7. A container made of a polyester as
claimed in any of claims 1—3 and 6.

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