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PATENT SPECIFICATION

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(54) LINEAR COPOLYESTERS

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

This invention relates to linear copolyesters, and especially to linear copolyesters formed from isophthalic acid and, optionally, terephthalic acid and bis(4-beta-hydroxyethoxyphenyl) sulfone and ethylene glycol.

At present there is a strong interest in manufacturing plastic bottles or containers from poly(ethylene terephthalate), which is essentially a homopolymer formed from terephthalic acid and ethylene glycol. Such bottles or containers, whether they be oriented or unoriented, possess many desirable characteristics but there is a need to provide a polyester composition which will have oxygen and carbon dioxide permeabilities which are lower than that of poly(ethylene terephthalate) and which will have a glass transition temperature higher than that of poly(ethylene terephthalate). Such a polyester would enable containers made therefrom to be much more versatile in their utilization, e.g. it would allow for the containers to be used to package materials for which the poly(ethylene terephthalate) would not be well suited and would also allow the containers to be subjected to environments, for example high temperatures, to which poly(ethylene terephthalate) may not be subjected.

U.S. Patent No. 2,593,411 suggests that polyesters may be formed from dicarboxylic acids and from bis(4-beta-hydroxy-alkoxyphenyl) sulfones and that mixed polyesters can likewise be obtained by employing such sulfones in combination with other dihydric and polyhydric alcohols. British Patent Specification 678,264 suggests linear polyesters formed from an aromatic dicarboxylic acid and a glycol, e.g. bis(4-beta-hydroxyethoxyphenyl) sulfone. Also in this regard reference may be had to British Patent Specification 1,196,911 which discloses the reaction of ethylene glycol with for example bis(4-chlorophenyl) sulfone and indicates that such materials may be employed in forming polyesters. Vol. 83 of *Chemical Abstracts*, No. 206808s (1975) discloses polyesters formed from 4,4'-biphenyldicarboxylic acid and aliphatic glycols and bis(4-beta-hydroxyethoxyphenyl) sulfone. Similarly Vol. 83 of *Chemical Abstracts*, Nos. 165136a and 165644q (1975) disclose the use of such hydroxyethoxy sulfones with naphthalene dicarboxylic acids to form polyesters. None of the foregoing are directed to forming polyesters having an oxygen permeability and a carbon dioxide permeability lower than that of poly(ethylene terephthalate) and which have a glass transition temperature higher than that of poly(ethylene terephthalate).

Japanese unexamined (Kokai) Patent Publication No. Showa 50—51595 (Patent Appl. No. Showa 48—101837) discloses transparent, dimensionally stable, linear polyesters having high glass transition points but has no recognition, or teachings, with regard to oxygen permeability and carbon dioxide permeability. It is taught therein to employ, for example, bis(4-beta-hydroxyethoxyphenyl) sulfone with a diol and a dicarboxylic acid which is primarily terephthalic acid. In order to obtain polyesters suitable for the purposes of this invention it is taught that, of the dicarboxylic acid used for forming the polyester, at least 70 mole percent, and preferably 80%, should be terephthalic acid and, based on the acid employed, at least 60% and preferably 65—95% should be the described sulfone. A wide variety of optional bifunctional carboxylic acids are set forth from which it is possible to select isophthalic acid. Similarly a wide variety of diols are disclosed, including ethylene glycol.

8

In accordance with this invention applicant has satisfied the need for low oxygen permeabilities, low carbon dioxide permeabilities, and high glass transition temperatures and provides copolyesters which, as contemplated herein, will have oxygen and carbon dioxide permeabilities lower than that of poly(ethylene terephthalate) and glass transition temperatures higher than that of poly(ethylene terephthalate). These linear copolyesters are ideally suited for forming clear bottles for packaging carbonated beverages and are the polymeric reaction product of polyester forming reactants consisting essentially of:

(A.) isophthalic acid and, optionally, terephthalic acid and, (B.) bis(4-beta-hydroxyethoxyphenyl) sulfone and ethylene glycol, the amount of said (A) reactants being between 50 mole percent and 100 mole percent of isophthalic acid and between 50% and 0% of terephthalic acid, based only on reactants (A) and the amount of the bis(4-beta-hydroxyethoxyphenyl) sulfone being between 20 and 90 mole percent of the combined amount of the (A) reactants and the combined amounts of the (B) reactants, i.e., bis(4-beta-hydroxyethoxyphenyl) sulfone and ethylene glycol, being 110 to 300 mole percent of the combined amounts of the (A) reactants. The percentages are based on the reactant feed. Most suitably bis(4-beta-hydroxyethoxyphenyl) sulfone will be employed as a reactant in an amount between 80 mole percent and 90 mole percent, based on the combined amounts of isophthalic acid and, when employed, terephthalic acid. Excellent copolyesters are produced by employing about 85 mole percent of bis(4-beta-hydroxyethoxyphenyl) sulfone based on the total molar amount of isophthalic and, when employed, terephthalic acid. With respect to the isophthalic acid and terephthalic acid generally it is preferred to employ the isophthalic acid in an amount of between 60 mole percent and 100 mole percent and terephthalic acid in an amount between 0 and 40 mole percent, with these percentages being based on the amount of isophthalic and terephthalic acid being employed. In passing it should be mentioned that when reference is made to the oxygen and CO₂ permeability of poly(ethylene terephthalate) it is generally considered that that homopolymer has an oxygen permeability of about 8-9 cc·mil/100 in²·day·atm. and a CO₂ permeability of about 62 cc·mil/100 in²·day·atm. when measured on pressed films. Generally the glass transition temperature of unoriented poly(ethylene terephthalate) is considered to be about 72°C.

When reference is made herein to bis(4-beta-hydroxyethoxyphenyl) sulfone and to ethylene glycol it is contemplated that this likewise includes esters thereof as being employed for the reactants. Similarly when reference is made to isophthalic acid and/or terephthalic acid, that terminology likewise contemplates not only the acid but also the esters and acid halides thereof for use as reactants. Preferably in practicing the invention the ethylene glycol and bis(4-beta-hydroxyethoxyphenyl) sulfone will be used as the glycol per se, whereas the diesters of isophthalic acid and, when employed, terephthalic acid, will be the preferred (A) reactants. These esters may be the aliphatic esters or aromatic esters with the preferred esters being the alkyl esters having from 1 to 4 carbon atoms, with methyl being especially highly preferred. The phenyl esters are the preferred aromatic esters.

The copolyesters as contemplated herein are synthesized by methods generally known in the art for producing polyesters. The reactants may all be reacted in a single operation by first charging them to an appropriate reactor or a sequential operation may be employed by first reacting isophthalic acid and ethylene glycol to form bis(beta-hydroxyethyl) isophthalate and then in turn reacting the latter with the remaining ingredients. Since, as indicated, in the preferred practice the diesters of isophthalic acid and terephthalic acid will be employed, conventional transesterification followed by polycondensation is contemplated as the preferred approach. Temperatures employed which will be quite suitable for forming the copolyesters will generally range between 200 or 210°C. up to 295°C., with the preferred range being between 225°C. and 285°C. Of course the reaction will be done under an inert atmosphere.

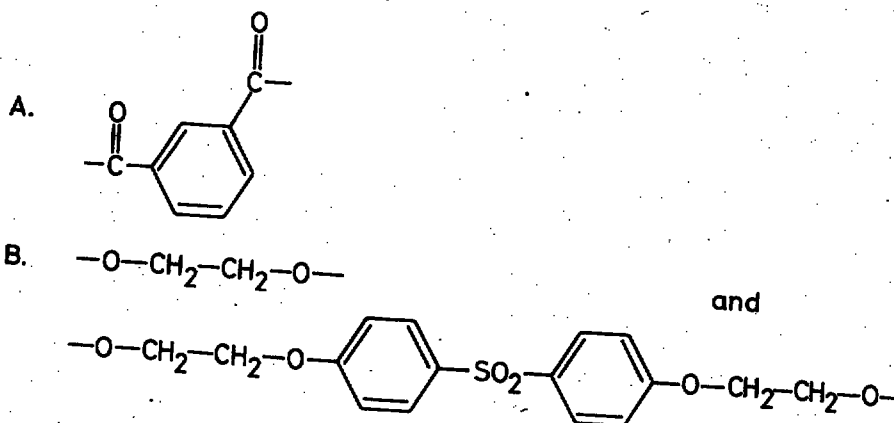
Conventional catalysts are likewise employed for example transesterification is effected in the presence of effective catalytic amounts of transition metal compounds, alkaline earth metal compounds, or alkali metal compounds, for example the acetates, oxides, phenoxides, and alkoxides. Specific suitable catalysts will be, for example, zinc acetate, manganese acetate, magnesium acetate, calcium acetate, and titanium alkoxides, e.g. 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 about 10⁻⁵ to about 10⁻³ moles of catalysts per mole of total acid employed.

Of course suitable adjuvants, such as antioxidants and stabilizers may be employed and they may be added directly to the reaction mass or added to the final polymer.

While the foregoing describes the present invention with sufficient particularity to enable those skilled in the art to make and use same there nonetheless follow, for exemplary purposes only, two specific Examples which are given for the purpose of illustrating the invention.

EXAMPLE 1.

A linear polyester was prepared having the following units in its backbone:



The specific reactant materials employed were about 0.1 mole of dimethyl isophthalate (DMI), about 0.2 mole of ethylene glycol (EG), and about 0.085 mole of bis(4-beta-hydroxyethoxyphenyl) sulfone (BSE). Additionally, about 6.5×10^{-5} moles of Sb_2O_3 and about 5×10^{-5} mole of $\text{Mn}(\text{C}_2\text{H}_5\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ were employed for catalytic purposes.

The mixture of the reactants along with the catalysts were weighed into a 300 ml three-necked round bottom flask equipped with a stirrer, nitrogen inlet tube, and a condenser. The contents of the flask were heated to and held at about 225°C . for about 3 hours with nitrogen flowing into the reaction flask to provide a nitrogen blanket and with methanol being removed. The reactant system was then heated to about 265°C . and held there for about 45 minutes during which time additional methanol was removed. A vacuum of 0.2 to 0.45 mm Hg was then applied and the reactants heated to between 275°C . and 285°C . with ethylene glycol being removed. The system was held at that latter temperature under that vacuum for approximately 6 hours after which time the polymer was removed. Table A sets forth the glass transition temperature of the polymer, as well as the carbon dioxide and oxygen permeability of films which were pressed from that polymer. In Table A the percentages are based on feed stock.

EXAMPLE 2.

The procedure of Example 1 was substantially repeated except that the charge instead of being 0.1 mole of DMI was a charge of 0.1 mole of a mixture of DMI and dimethyl terephthalate (DMT), the latter being used in an amount of about 0.04 mole, and the former being used in an amount of about 0.06 mole. The characteristics of the linear copolyester formed from these reactants is set forth in Table A below.

In Table A, O_2 and CO_2 respectively refer to the oxygen permeability and carbon dioxide permeability of pressed films as measured by ASTM D-1434-66 at about 73°F . and 50% relative humidity in $\text{cc} \cdot \text{mil}/100 \text{ in}^2 \cdot \text{day} \cdot \text{atm}$. and T_g represents the glass transition temperature as measured with a Differential Scanning Calorimeter.

TABLE A

Example	% DMI	% DMT	% BSE	Mole Ratio of EG/BSE	O_2	CO_2	T_g
1	100	0	85	70/30	4.5	11.2	112°C .
2	60	40	85	70/30	5.9	38.5	117°C .

12

While the above sets forth the contemplated utility for the copolyesters described herein, these copolyesters may also be used as coatings and may be used to form numerous types of molded objects.

WHAT WE CLAIM IS:—

- 5 1. A linear copolyester having a glass transition temperature higher than that of
poly(ethylene terephthalate) and an O₂ and CO₂ permeability lower than that of poly- 5
(ethylene terephthalate) and being the polymeric reaction product of:
(A) isophthalic acid and, optionally, terephthalic acid and,
(B) bis(4-beta-hydroxyethoxyphenyl) sulfone and ethylene glycol, 10
the amount of said (A) reactants being between 50% and 100% (mole) of isophthalic
acid and between 50% and 0% terephthalic acid, the amount of said bis(4-beta-
hydroxyethoxyphenyl) sulfone being between 20% and 90% (mole) of the combined 10
amount of said (A) reactants and the combined amounts of said (B) reactants being
from 110 to 300% (mole) of the combined amounts of said (A) reactants.
15 2. A copolyester as claimed in claim 1 wherein in said (A) reactants the amount
of said isophthalic acid is 60 to 100% and the amount of said terephthalic acid is 40
to 0%. 15
3. A copolyester as claimed in claim 1 or claim 2 wherein the amount of said
bis(4-beta-hydroxyethoxyphenyl) sulfone is between 80 and 90% of the combined 20
amount of said (A) reactants. 20
4. A copolyester as claimed in claim 3 wherein the amount of said bis(4-beta-
hydroxyethoxyphenyl) sulfone is about 85% and wherein said polyester has a CO₂
permeability of less than 38.5 cc-mil/100 in²·day·atm., and an O₂ permeability
of less than 5.9 and a glass transition temperature of at least 112°C.
25 5. A linear copolyester as claimed in claim 1, substantially as hereinbefore 25
described.

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While the above sets forth the contemplated utility for the copolyesters described herein, these copolyesters may also be used as coatings and may be used to form numerous types of molded objects.

WHAT WE CLAIM IS:—

- 5 1. A linear copolyester having a glass transition temperature higher than that of poly(ethylene terephthalate) and an O₂ and CO₂ permeability lower than that of poly(ethylene terephthalate) and being the polymeric reaction product of: 5
- (A) isophthalic acid and, optionally, terephthalic acid and,
- 10 (B) bis(4-beta-hydroxyethoxyphenyl) sulfone and ethylene glycol, the amount of said (A) reactants being between 50% and 100% (mole) of isophthalic acid and between 50% and 0% terephthalic acid, the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone being between 20% and 90% (mole) of the combined amount of said (A) reactants and the combined amounts of said (B) reactants being from 110 to 300% (mole) of the combined amounts of said (A) reactants. 10
- 15 2. A copolyester as claimed in claim 1 wherein in said (A) reactants the amount of said isophthalic acid is 60 to 100% and the amount of said terephthalic acid is 40 to 0%. 15
- 20 3. A copolyester as claimed in claim 1 or claim 2 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is between 80 and 90% of the combined amount of said (A) reactants. 20
- 25 4. A copolyester as claimed in claim 3 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is about 85% and wherein said polyester has a CO₂ permeability of less than 38.5 cc·mil/100 in²·day·atm., and an O₂ permeability of less than 5.9 and a glass transition temperature of at least 112°C. 25
5. A linear copolyester as claimed in claim 1, substantially as hereinbefore described.

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