

PATENT SPECIFICATION

(11) 1 582 167

1 582 167

- (21) Application No. 21827/77 (22) Filed 24 May 1977
(31) Convention Application No. 690 483
(32) Filed 27 May 1976 in
(33) United States of America (US)
(44) Complete Specification published 31 Dec. 1980
(51) INT CL³ C08G 63/68
(52) Index at acceptance
C3R 3D13 3N1 D2D D2E
C3Y B200 B262 B284 F224 G320 H260



(54) PACKING METHODS AND CONTAINER EMPLOYING 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:—

The present invention relates to packages and methods for protecting comestibles; more specifically, it is directed to molded containers which are formed from linear copolyesters.

At present there is a strong interest in the packaging industry for protecting comestibles like foodstuffs, medicines, and especially carbonated beverages, or other related substances, by enveloping the substances in packages, for example molded containers, which are formed from various polymers. One polymer in which there is an especially strong interest is poly(ethylene terephthalate) and containers formed from this material, which are biaxially oriented, possess many desirable characteristics. Molded biaxially oriented containers which are formed from poly(ethylene terephthalate) and certain copolyesters are disclosed in U.S. Patent No. 3,733,309. While molded containers formed from poly(ethylene terephthalate) have, as indicated, many desirable characteristics, there is a need in the art to provide an improved polyester which will have oxygen and carbon dioxide permeabilities which are lower than that of poly(ethylene terephthalate) and which will have glass transition temperatures higher than that of poly(ethylene terephthalate). Packages formed from such a polyester would be much more versatile in their utilization and, for example, would allow for the containers to package substances for which the poly(ethylene terephthalate) may not be suitable and would also allow for such packages to be subjected to environments, for example higher temperatures, to which poly(ethylene terephthalate) may not suitably 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 being formed from 4,4'-biphenyldicarboxylic acid and aliphatic glycols and bis(4-beta-hydroxyethoxyphenyl) sulfone. Similarly Vol. 83 *Chemical Abstracts* Nos. 165136a and 165644q (1975) disclose the use of such hydroxyethoxyphenyl sulfones with naphthalene dicarboxylic acids to form polyesters. None of the foregoing are directed to forming polyesters having oxygen permeabilities and CO₂ permeabilities which are lower than that of poly(ethylene terephthalate) and which have glass transition temperatures 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 patent application 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 dicarboxylic acids are set forth from which it is possible to select isophthalic acid. Similarly a wide variety of diols are disclosed, including ethylene glycol.

In accordance with this invention applicant has satisfied the need in the art by providing for improved packaging methods and improved packages, such as a molded container whether it be oriented or unoriented, which packages are formed from copolyesters having a lower carbon dioxide and lower oxygen permeability than poly(ethylene terephthalate) and a higher glass transition temperature than poly(ethylene terephthalate).

Thus in accordance with the present invention an improved molded container is provided which is formed from a prescribed linear copolyester. In accordance with another feature of this invention, an improved package is provided which comprises comestibles like foodstuffs, medicines, and other related substances, enveloped in a molded container which molded container comprises a prescribed linear copolyester. In accordance with another feature of this invention an improved method for protecting such comestibles is provided which comprises enveloping such substances in packages which are formed from materials which comprise prescribed linear copolyesters.

The linear copolyesters, which form clear packages contemplated for use herein for packaging comestibles, 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 the (A) reactants, on a mole basis of feed stock, being between 15% and 100% of isophthalic acid and 0% to 85% of terephthalic acid, the amount of bis(4-beta-hydroxyethoxyphenyl) sulfone being at least 20 mole percent based on the combined amount of the (A) reactants employed, and the combined amounts of the (B) reactants being 110 to 300 mole percent of the combined amounts of the (A) reactants. Desirably the bis(4-beta-hydroxyethoxyphenyl) sulfone will be employed as a reactant in an amount of between 20 mole percent to 90 mole percent based on the combined amounts of isophthalic acid and, when employed, terephthalic acid; most suitably, the amount will be between 80 and 90 mole percent thereof. Excellent linear copolyesters are formed for example using about 85 mole percent of the bis(4-beta-hydroxyethoxyphenyl) sulfone. Most desirably the (A) reactants will be employed in molar amounts of 50% to 100% of isophthalic acid and 50% to 0% of terephthalic acid. Linear copolyesters having an outstanding balance of properties will be formed by employing between 60% and 100% of isophthalic acid and 40% to 0% of terephthalic acid. When reference is made herein to carbon dioxide and oxygen permeability of poly(ethylene terephthalate) reference is made to an unoriented pressed film of that material and the oxygen permeability thereof is about 8—9 cc·mil/100 in²·day·atm. and the carbon dioxide permeability is about 62 cc·mil/100 in²·day·atm. Generally the glass transition temperature of unoriented poly(ethylene terephthalate) is considered to be about 72°C.

When reference is made herein to the 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 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 used as 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 contemplated herein, which are claimed *per se* in copending Application No. 21828/77 (Serial No. 1,582,168) 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 the 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 transesteri-

9

fication followed by polycondensation is contemplated as the preferred approach. Temperatures employed which will be quite suitable for forming the polyesters will generally range between 200 or 210°C. up to 295°C., with the preferred ranges being between 225°C. and 285°C. Of course the reaction will be done under an inert atmosphere.

Convention 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.

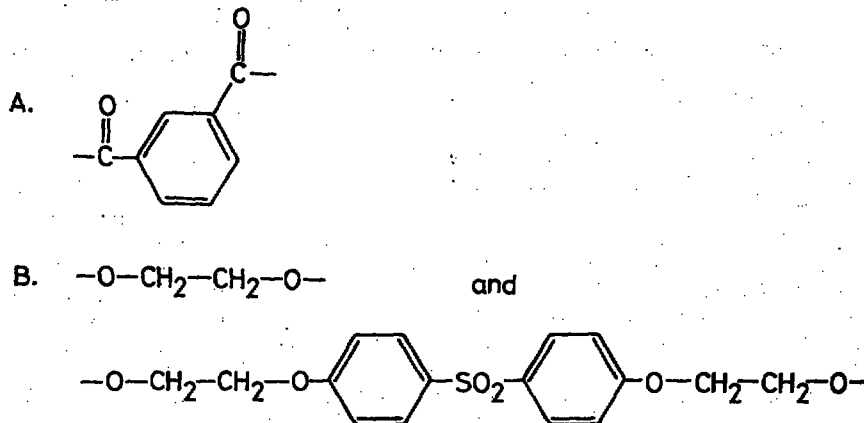
Of course suitable adjuvants, such as antioxidants and stabilizers may be employed and they may be added directly to the reaction mass or added to the final polymer.

The linear copolyesters contemplated may be formed into packages, for example molded containers and preferably biaxially oriented molded containers, using conventional plastic forming techniques such as, for example, that disclosed in U.S. Patent No. 3,733,309. These packages are ideally suited for protecting comestibles, like food-stuffs e.g. carbonated soft drinks, or medicines, or other related substances, by simply enveloping those substances in these packages.

The following Examples 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 $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ 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 hrs. 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 0.45mm Hg was then applied and the reactant 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 and 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.

10

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 present in amount of about 0.04 mole, and the former being present in an amount of about 0.06 mole. The characteristics of the linear polyester formed from these reactants is set forth in Table A below.

In Table A, O₂ and CO₂ 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 cc · mil/100 in² · day · atm. and T_g represents the glass transition temperature as measured with a Differential Scanning Calorimeter.

EXAMPLES 3 & 4.

The procedure of Example 2 was substantially repeated. The only difference was that the 0.1 mole of total DMI and DMT was varied as indicated in Table A with regard to their molar proportions. The characteristics of these polyesters is set forth in Table A.

Following the known forming procedures of the prior art, for example U.S. Patent No. 3,733,309, a clear biaxially oriented molded container (i.e., a container having a bottom wall and circumferential sidewall 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 polyesters of Examples 1 to 4. The containers are clear and upon being filled with foodstuffs or medicines, so as to envelope these substances, show outstanding characteristics for the packaging of such products. The polyesters of Examples 1 and 2 are especially outstanding for packaging carbonated beverages.

COMPARATIVE EXAMPLES 5, 6 & 7.

The procedure of Examples 1-4 was generally followed but no dimethyl isophthalate was employed. In Examples 5 & 6 the molar amount of constituent A was solely supplied by dimethyl terephthalate. Additionally in Examples 5 & 6 the percent of bis(4-beta-hydroxyethoxyphenyl) sulfone employed was first about 70% based on the dimethylterephthalate in accordance with the general teachings of the above-referred to Japanese Showa Publication 50-51595 and in Example 6 the percent of bis(4-beta-hydroxyethoxyphenyl) sulfone was 50% which closely approximates that employed in Comparative Example 1 of that Japanese Publication. Table B below summarizes the oxygen permeability, the carbon dioxide permeability, and the glass transition temperatures of those two polyesters. Example 7 also relates to that Japanese Publication by employing 85 mole percent of dimethyl terephthalate as a constituent and, from the list of optional dicarboxylic acids of that Japanese Publication, the dimethyl ester of diphenyl sulfone dicarboxylic acid (DMS) was employed in an amount of 15 mole percent. Table B below shows the oxygen and carbon dioxide permeabilities of that polyester and its glass transition temperature. As will be readily apparent from Table B, illustrating the inferior permeability characteristics of the polyesters of Examples 5, 6, & 7, there is no recognition in the Japanese Publication of the present inventive concept.

TABLE A

Example	% DMI	% DMT	% BSE	Mole Ratio EG/BSE	O ₂	CO ₂	T _g
1	100	—	85	70/30	4.5	11.2	112°C.
2	60	40	85	70/30	5.9	38.5	117
3	30	70	85	70/30	—	54	117
4	15	85	85	70/30	7.2	56	121

TABLE B

Example	% DMT	% DMS	% BSE	Mole Ratio EG/BSE	O ₂	CO ₂	T _g
5	100	—	70	74/26	9.0	75.0	119
6	100	—	50	80/20	9.6	77.9	115
7	85	15	85	70/30	8.9	86	124

WHAT WE CLAIM IS:—

1. A molded container formed from a material which comprises a linear copolyester consisting essentially of the polymeric reaction product of
 (A) isophthalic acid and, optionally, terephthalic acid, and
 (B) bis(4-beta-hydroxyethoxyphenyl) sulfone and ethylene glycol
 the amount of said (A) reactants, in mole percent, being between 15% and 100% isophthalic acid and 0% to 85% terephthalic acid, the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone being at least 20 mole percent of the combined amounts of said (A) reactants and the combined amounts of said (B) reactants being 110% to 300% of the combined amounts of said (A) reactants, said copolyester having an O₂ and CO₂ permeability less than that of poly(ethylene terephthalate) and a glass transition temperature greater than that of poly(ethylene terephthalate).
2. The molded container of claim 1 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is between 20% and 90% of the combined amounts of said (A) reactants.
3. The molded container of claim 2 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is between 80% and 90%, on the same basis.
4. The molded container of claim 3 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is about 85%.
5. The molded container of any of claims 1 to 4 wherein the amount of isophthalic acid is between 50 to 100% and the amount of terephthalic acid is between 50 and 0%, based on the weight of (A) reactants.
6. The molded container of claim 5 wherein the amount of isophthalic acid is between 100% and 60% and the amount of terephthalic acid is between 0% and 40%, on the same basis.
7. The molded container of claim 6 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is 80% to 90%, based on the combined amounts of said (A) reactants.
8. The molded container of claim 7 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is about 85%, said copolyester having an O₂ and CO₂ permeability of less than about 5.9 and 38.5 cc·mil/100 in²·day·atm. respectively, and a glass transition temperature of at least about 112°C.
9. The molded container of claim 1 wherein said container which is formed from said copolyester is a biaxially oriented container.
10. A package comprising comestibles enveloped in a molded container, wherein said molded container is a container as claimed in any of claims 1 to 9.
11. A method for protecting a foodstuff, medicine, or other related substance, comprising enveloping said foodstuff, medicine or other related substance in a package constructed of a material which comprise a linear copolyester as defined in claim 1.
12. The method of claim 11 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is between 20% and 90% of the combined amounts of said (A) reactants.
13. The method of claim 12 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is between 80% and 90%, on the same basis.
14. The method of any of claims 11 to 13 wherein the amount of said isophthalic acid is between 50% and 100% and the amount of said terephthalic acid is between 50% and 0%, based on the weight of (A) reactants.
15. The method of claim 14 wherein the amount of said isophthalic acid is between 60% and 100% and the amount of said terephthalic acid is between 0 and 40%, on the same basis.



1,582,167

TABLE B

Example	% DMT	% DMS	% BSE	Mole Ratio EG/BSE	O ₂	CO ₂	T _g
5	100	—	70	74/26	9.0	75.0	119
6	100	—	50	80/20	9.6	77.9	115
7	85	15	85	70/30	8.9	86	124

WHAT WE CLAIM IS:—

1. A molded container formed from a material which comprises a linear copolyester consisting essentially of the polymeric reaction product of
5 (A) isophthalic acid and, optionally, terephthalic acid, and
(B) bis(4-beta-hydroxyethoxyphenyl) sulfone and ethylene glycol
the amount of said (A) reactants, in mole percent, being between 15% and 100% isophthalic acid and 0% to 85% terephthalic acid, the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone being at least 20 mole percent of the combined amounts
10 of said (A) reactants and the combined amounts of said (B) reactants being 110% to 300% of the combined amounts of said (A) reactants, said copolyester having an O₂ and CO₂ permeability less than that of poly(ethylene terephthalate) and a glass transition temperature greater than that of poly(ethylene terephthalate).
2. The molded container of claim 1 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is between 20% and 90% of the combined amounts
15 of said (A) reactants.
3. The molded container of claim 2 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is between 80% and 90%, on the same basis.
4. The molded container of claim 3 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is about 85%.
20 5. The molded container of any of claims 1 to 4 wherein the amount of isophthalic acid is between 50 to 100% and the amount of terephthalic acid is between 50 and 0%, based on the weight of (A) reactants.
6. The molded container of claim 5 wherein the amount of isophthalic acid is
25 between 100% and 60% and the amount of terephthalic acid is between 0% and 40%, on the same basis.
7. The molded container of claim 6 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is 80% to 90%, based on the combined amounts of
said (A) reactants.
30 8. The molded container of claim 7 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is about 85%, said copolyester having an O₂ and CO₂ permeability of less than about 5.9 and 38.5 cc·mil/100 in²·day·atm. respectively, and a glass transition temperature of at least about 112°C.
9. The molded container of claim 1 wherein said container which is formed from
35 said copolyester is a biaxially oriented container.
10. A package comprising comestibles enveloped in a molded container, wherein said molded container is a container as claimed in any of claims 1 to 9.
11. A method for protecting a foodstuff, medicine, or other related substance, comprising enveloping said foodstuff, medicine or other related substance in a package
40 constructed of a material which comprise a linear copolyester as defined in claim 1.
12. The method of claim 11 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is between 20% and 90% of the combined amounts of said
(A) reactants.
13. The method of claim 12 wherein the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is between 80% and 90%, on the same basis.
45 14. The method of any of claims 11 to 13 wherein the amount of said isophthalic acid is between 50% and 100% and the amount of said terephthalic acid is between 50% and 0%, based on the weight of (A) reactants.
15. The method of claim 14 wherein the amount of said isophthalic acid is
50 between 60% and 100% and the amount of said terephthalic acid is between 0 and 40%, on the same basis.

(12)



1,582,167

6

6

16. The method of claim 15 wherein the amount of said bis(4-beta-hydroxy-ethoxyphenyl) sulfone is about 85%, said copolyester having an O₂ and CO₂ permeability of less than about 5.9 and 38.5 cc·mil/100 in²·day·atm. respectively, and a glass transition temperature of at least about 112°C.

5

17. A molded container as claimed in claim 1, substantially as described.

5

For the Applicants,
CARMAELS & RANSFORD,
Chartered Patent Agents,
43, Bloomsbury Square,
London, WC1A 2RA.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.