

# PATENT SPECIFICATION

(11) 1 585 404

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## (54) LINEAR COPOLYESTERS

(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:—

This invention relates to the packaging of comestibles, and especially to a molded container for use therein.

At present there is a strong interest in protecting comestibles by enveloping these comestibles, for example foodstuffs, e.g. carbonated beverages, and medicines in packages, for example molded containers and, especially, biaxially oriented molded containers, which packages are formed from materials which comprise poly(ethylene terephthalate). Such molded containers, whether they be biaxially oriented or unoriented possess many desirable characteristics for certain products, but there is a need to provide for a polymer composition which will have a glass transition temperature higher than that of poly(ethylene terephthalate) whereby containers made of such a polymer may be subjected to environments, for example higher temperatures, to which poly(ethylene terephthalate) may not be subjected. Additionally, in order to achieve wider versatility in the types of products which are packaged therein, for example, comestibles, there is also a need to provide for polymer compositions which have an oxygen permeability which is lower than that of poly(ethylene terephthalate). Additionally, many products, for example carbonated beverages, need to be packaged in containers having low carbon dioxide permeability and accordingly there is also a need to provide containers having carbon dioxide permeabilities which are lower than that of poly(ethylene terephthalate).

According to the present invention there is provided a clear molded container which is formed from an organic polymer having an oxygen permeability of less than about 7.0 cc.mil/100 in<sup>2</sup>.day.atm., a carbon dioxide permeability of less than about 50.3 and a glass transition temperature in excess of about 121°C.

The invention also includes a package comprising comestibles enveloped in a molded container as set out above.

A particularly suitable organic polymer for forming the containers of the invention is the linear copolyester which is the reaction product of (A) isophthalic acid and 4,4'-sulfonyldibenzoic acid, and (B) bis-(4-beta-hydroxyethoxy-phenyl) sulfone and ethylene glycol, wherein the (A) reactants comprise 60% to 80% of isophthalic acid and 20% to 40% of 4,4'-sulfonyldibenzoic acid, and the amount of bis(4-beta-hydroxyethoxyphenyl) sulfone is between 60% and 85% of the combined amount of the (A) reactants, these percentages being on a mole basis. These polymers are of outstanding utility for the packaging of carbonated beverages, e.g. pop, and exhibit excellent heat stability. These polymers are claimed *per se* in our Application No. 21826/77 (serial no. 1585403), from which the present application is divided.

In passing it should be mentioned that when reference is made to oxygen and carbon dioxide permeability of poly(ethylene terephthalate) it is generally considered that the homopolymer has an oxygen permeability of about 8—9 cc.mil/100 in<sup>2</sup>.day.atm. and a carbon dioxide permeability of about 62 cc.mil/100 in<sup>2</sup>.day.atm. when measured on pressed films. Generally the glass transition

temperature of unoriented poly(ethylene terephthalate) is considered to be about 72°C.

Biaxially oriented molded containers formed from the polymers contemplated herein are of especially outstanding characteristics. Packages which comprise comestibles, for example carbonated beverages, or medicines, enveloped in a molded container formed from such polymers find utilization, and a flexibility of use, not possessed by that of poly(ethylene terephthalate). The present application likewise contemplates improvements in methods for protecting comestibles wherein the comestibles are enveloped in packages which are formed from the polymers contemplated herein.

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 to 4,4'-sulfonyldibenzoic acid that terminology likewise contemplates not only the acid but also the esters and acid halides thereof for use as reactants. Preferably in practising the invention the ethylene glycol and bis(4-beta-hydroxyethoxyphenyl) sulfone will be used as the diol *per se*, whereas the diesters of isophthalic acid and the 4,4'-sulfonyldibenzoic acid will be used as the (A) reactants. These esters may be the aliphatic esters or aromatic esters with the preferred esters being the alkyl esters having from 1-4, carbon atoms, with methyl being especially highly preferred. The phenyl esters are the preferred aromatic esters.

The copolyesters 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 4,4'-sulfonyldibenzoic 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 polyesters will generally range between 200 or 210°C. and 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, calcium acetate, and titanium alkoxides, like titanium tetrabutoxides as well as mixed metal salts for example potassium titanium oxalate. 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.

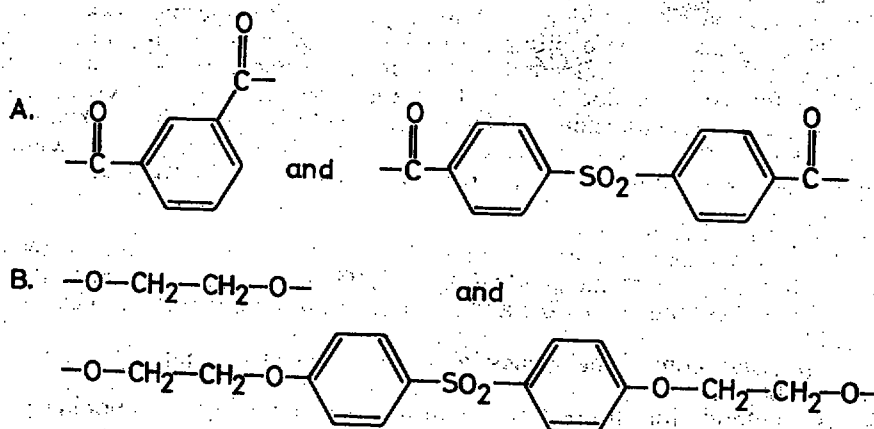
Of course suitable adjuvants, such as antioxidants and stabilizers may be employed and they may be added directly to the reaction mass or added to the final polymer.

The polymers contemplated herein may be formed into molded containers, and preferably biaxially 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 foodstuffs, for example carbonated soft drinks and beer, or medicines, by simply enveloping those substances in these packages.

The following Examples illustrate the present invention.

## Example 1:

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



The specific reactant materials employed in the feed stock was about 0.1 mole of an admixture of dimethyl isophthalate (DMI) and dimethyl 4,4'-sulfonyldibenzoate acid (DMS) with the former being present in an amount of about .08 mole and the latter in an amount of about .02 mole. About 0.2 mole of ethylene glycol (EG) and about .085 mole of bis(4-beta-hydroxyethoxyphenyl) sulfone (BSE) were employed as the glycol. Additionally about  $6.5 \times 10^{-5}$  mole of  $\text{Sb}_2\text{O}_3$  and about  $5 \times 10^{-5}$  mole of  $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$  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 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 about 0.2 to about 0.45 mm Hg was then applied and the reactants heated to between about 275°C. to about 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. The carbon dioxide permeability and the oxygen permeability were measured on pressed films employing ASTM D-1434-66 at a temperature of about 73°F. and 50% relative humidity and is in the units cc.mil/100 in<sup>2</sup>.day.atm. The glass transition temperature was measured with a Differential Scanning Calorimeter. In Table A the percentages are based on feed stock.

## Examples 2 and 3.

The procedure of Example 1 was substantially repeated using a total molar charge of the (A) reactants of about 0.1 mole with the mole percentage of the respective (A) constituents being varied as indicated in Table A. Additionally in Example 3 instead of employing .085 moles of BSE there was employed about .060 moles of BSE and about 0.19 moles of ethylene glycol.

TABLE A.

| Example | % DMI | % DMS | % BSE | Mole Ratio<br>EG/BSE | O <sub>2</sub> | CO <sub>2</sub> | T <sub>g</sub> |
|---------|-------|-------|-------|----------------------|----------------|-----------------|----------------|
| 1       | 80    | 20    | 85    | 70/30                | 5.5            | 35.4            | 121°C.         |
| 2       | 60    | 40    | 85    | 70/30                | 7.0            | 50.3            | 129°C.         |
| 3       | 60    | 40    | 60    | 76/24                | 5.1            | 46              | 124°C          |

Following the known forming procedures of the prior art, for example U.S. Patent No. 3,733,309, a 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 above polyesters of Examples 1—3. The containers are clear and upon being filled with comestibles, for example foodstuffs such as apple sauce, or medicines, so as to envelope these substances, show outstanding characteristics for the packaging of such products. The organic polymers of Examples 1—3 show particularly outstanding characteristics for the packaging of carbonated beverages.

**WHAT WE CLAIM IS:—**

1. A clear molded container formed from an organic polymer having an oxygen permeability of less than about 7.0 cc.mil/100 in<sup>2</sup>.day.atm., a carbon dioxide permeability of less than about 50.3 and a glass transition temperature in excess of about 121°C.

2. A package comprising comestibles enveloped in a molded container as claimed in claim 1.

3. A method for protecting comestibles comprising enveloping said comestibles in a molded container as claimed in claim 1.

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

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10      No. 3,733,309, a biaxially oriented molded container (i.e. a container having a  
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