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Señora Jefe de la
DIVISION DE NUEVAS CREACIONES
Superintendencia de Industria y Comercio
E. S. D.

SUPERINTENDENCIA Y COMERCIO
Radicacion : 02066657 / 00000006 Folios: 2
Fecha (AMD): 2004-02-17 16:47:19
Tramite : 002 PATENTES D 1 REGISTRO/ 538 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Trámite : 002
Evento : 538
Actuación: 411

Referencia : Expediente No. 02.066.657
Solicitante : NESTLE WATERS MANAGEMENT &
TECHNOLOGY SA ET TERGAL FIBRES SA
Asunto : Solicitud de patente para: PROCEDIMIENTOS DE
FABRICACIÓN DE PREFORMAS Y DE ENVASES
EN PET TALES COMO BOTELLAS DE USO
ALIMENTICIO, ENVASES Y PREFORMAS
INTERMEDIAS OBTENIDOS

Publicada en : La Gaceta No. 537 Del 27 de febrero de 2004

1. Yo, Emilio FERRERO, identificado como aparece al pie de mi firma, actuando como apoderado en el asunto de la referencia, atentamente, solicito se efectúe el examen de patentabilidad de la solicitud en referencia presentada de acuerdo con el artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina. Para tal efecto presento junto con este escrito el recibo No. 04 -28.002 por valor de \$ 353.000.00, que corresponde a la tasa fijada según lo dispuesto en la resolución No. 37323 del 30 de diciembre de 2003.

2. Ruego atentamente a la Señora Jefe se sirva ordenar que se anexe este recibo para que se efectúe dicho examen y se continúe con el trámite de la solicitud.

Bogotá, 17 AGO. 2004
Señora Jefe,



EMILIO FERRERO
T.P.A. No. 31.929

COLO 13366 801 002 7
MRE/MRM/
ID-000018/WPC13366

112

SUPERINDUSTRIA Y COMERCIO
Radicacion : 82966657 80888886 Folios: 2
Fecha (RMB): 2004-04-17 16:47:19
Tramite : 002 PATENTES D 1 REGISTRO/ 538 PETICION
Dependencia: 2000 DIVISION DE NUEVAS CREACIONES

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 04 - 28,002
FECHA : ABRIL 5 DE 2004

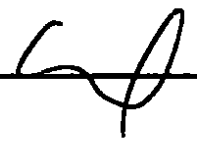
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	22136876	05/04/2004	42,043,800.00

***** C O N C E P T O *****

CANT. HISTORICO	CONCEPTO	TOTAL CONCEPTO
1 50005-01-01 SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN	333,000.00
	TOTAL :	\$ 333,000.00

SOM: TRESCIENTOS CINCUENTA Y TRES MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

13366-801-002-7

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 02- 66657

EL EXTRACTO DE LA PRESENTE SOLICITUD DE PATENTE DE INVENCION FUE PUBLICADO

EN LA GACETA DE PROPIEDAD INDUSTRIAL No 537, DE FECHA 27 DE FEBRERO DE 2004,

EL TERMINO HABIL SEÑALADO POR LA LEY EXPIRA EL 27 DE MAYO DE 2004.

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI

NO **X**

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá, D. C., 1 de Febrero de 2006

Doctor

EMILIO FERRERO

Representante **NESTLE WATERS MANGEMENT & TECHNOLOGY S.A.**
TERGEL FIBRES S. A.

ASUNTO

Radicación • No. 02-66657

Trámite 002

Evento 001

Actuación 430 : 1420

Oficio

Folios 082

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica

1) Documentos estudiados:

- a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 4 a 22 de la solicitud en estudio.
- b) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 10 reivindicaciones en los folios 23 a 24 de la solicitud en estudio.
- c) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 31 de julio de 2002, y en el momento de la radicación SI se reclamo prioridad de la primera solicitud presentada en Francia FR0110280

2) Objeto de la Invención

- a) Las reivindicaciones 1 a 10 de la solicitud en estudio se refieren a
 - i) (1.-) Utilización de una resina PET que presenta una viscosidad intrínseca (VI) inferior a 0,65 dl/g para la fabricación de preformas en resina PET luego de envases realizados en la citada resina PET.
 - ii) (4.-) Preforma en resina PET obtenida por la utilización según una cualquiera de las reivindicaciones 1 a 3, caracterizada porque la viscosidad intrínseca (VI) del poliéster que forma las paredes de la citada preforma está comprendida entre 0,45 dl/g y 0,65 dl/g.
 - iii) (5.-) Envase en resina PET, caracterizado porque está compuesto de una resina PET de viscosidad intrínseca inferior a 0,65 dl/g.

- b) Los anteriores productos buscan mejorar las botellas plásticas para alimentos.
- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a B 65 D 01/02

3) Reivindicaciones de uso

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los Países Miembros otorgarán patentes para las invenciones sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial".

Las reivindicaciones 1 a 4 y 10 explícitamente hablan sobre el uso de una resina PET con viscosidad intrínseca entre 0,45 dl/g y 0,65dl/g y sobre el uso de un envase. Tal como está contemplado en la legislación el uso no se protege. Se protegen los productos o procedimientos, donde el producto esté correctamente definido por su conformación o su composición, y los procedimientos por la serie de etapas que busquen un fin. El uso no corresponde ni a un producto ni a un procedimiento. El uso es simplemente la aplicación industrial de esos productos o procedimientos.

Por lo anterior, las reivindicaciones 1 a 4 y 10 no son patentables de acuerdo al Art. 14 de la Decisión 486.

4) Determinación del Estado de la Técnica

El artículo 16 de la Decisión 486 de la Comisión establece:

"El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones B 65 D 01/02 y las más cercanas a ellas, se encontró que antes del 31 de julio de 2001 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con envases fabricados con compuestos tipo PET.

De acuerdo con lo establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente:

Nº	Documento	Título	Fecha de Publicación
D1	EP 0 368 278	Copolyester, polyester composition containing the Copolyester, and polyester laminated structure...	1989.11.08
D2	US 0 492 999	Copolyester and hollow container and oriented film comprising the copolyester	1992.07.01
D3	US 5 641 548	Blow molded articles	1997.01.24
D4	US 4 254 080	Forming substantially rectangular articles from performs of polyalkylene terephthalate	1981.03.03

5) Evaluación de los requisitos de patentabilidad

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicación industrial".

En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación Industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

a) Evaluación de novedad

El art. 16 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Una invención se considerará nueva cuando no está comprendida en el estado de la técnica." "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fechas de prioridad cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

El art. 21 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los productos o procedimiento ya patentados, comprendidos en el estado de la técnica, no serán objeto de nueva patente, por el simple hecho de atribuirse un uso distinto al originalmente comprendido por la patente inicial."

Evaluación del Nivel Inventivo

El art. 18 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en el arte en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

De acuerdo a lo encontrado en las anterioridades relacionadas, el emplear polímeros como el PET (o muy similares al mismo) con viscosidades intrínsecas del orden de 0,45 dl/g y 0,85 dl/g es muy común en el arte previo a la presente solicitud. Por tanto, la presente solicitud no cumpliría con los requisitos de patentabilidad necesarios para que se le conceda el privilegio solicitado.

b) Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud se podrían ver afectados así:

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	EP 0 368 278	5 – 9	Novedad
			Nivel inventivo
D2	US 0 492 999	5 – 9	Novedad
			Nivel inventivo
D3	US 5 641 548	5 – 9	Novedad
			Nivel inventivo
D4	US 4 254 080	5 - 9	Novedad
			Nivel inventivo

6) Notificación

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación debe responder a la notificación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto por el numeral 5.2, literal e) del capítulo quinto del título primero de la Circular Única Nº 10 de 2001


ALIX CESPEDES DE VERGEL
Jefe División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en la lista, de fecha

09 FEB. 2006

Concepto Técnico Nº	EXAMINADOR TÉCNICO Código No.	EXAMINADOR JURÍDICO Código No.
111	202003	

0902060

PL 87 5



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number: **0 368 278 A2**

EUROPEAN PATENT APPLICATION

Application number: 88120885.5
Date of filing: 08.11.88
Int. Cl.⁷: C08G 63/18, C08G 63/20, B32B 27/36, B65D 65/38, C08L 67/02, //(C08L67/02, 67:00)

Priority: 08.11.88 JP 281800/88
28.12.88 JP 328733/88
28.12.88 JP 328737/88
Date of publication of application: 18.05.90 Bulletin 90/20
Designated Contracting States: AT BE CH DE ES FR GB GR IT LI LU NL SE

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Copolyester, polyester composition containing the copolyester, and polyester laminated structure having layer composed of the copolyester or the polyester composition.

A copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 g/g and being derived from dicarboxylic acid units composed of 85 to 90 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 85 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units; a gas barrier imparting agent composed of the copolyester; a polyester composition composed of (A) a polyethylene terephthalate and (B) the copolyester; and a film, a preform and a container composed of the polyester composition. Also provided are a polyester laminated structure, a stretched laminated structure, a preform and a laminated blow-molded article each composed of (C) a polyalkylene terephthalate layer and (D) a copolyester layer composed of the copolyester or the polyester composition.

EP 0 368 278 A2

Copolyester, polyester composition containing the copolyester, and polyester laminated structure having layer composed of the copolyester or the polyester composition

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a copolyester and a gas-barrier property imparting agent, and more specifically, to a copolyester having excellent gas-barrier property and surface properties and a high glass transition temperature and a gas-barrier property imparting agent composed of the copolyester.

The invention also relates to a polyester composition and a film, a preform and a container composed of the polyester composition, and more specifically, to a polyester composition having excellent gas-barrier property, surface properties and transparency and comprising (A) polyethylene terephthalate and (B) the aforesaid copolyester, and to a film, a preform and a container composed of the polyester composition.

Furthermore, this invention relates to a polyester laminated structure, and its use, and more specifically, to a polyester laminated structure having excellent moldability, mechanical properties and composed of (C) a polyalkylene terephthalate layer and (D) a copolyester layer composed of the aforesaid copolyester or a polyester composition, and to its use.

2. Description of the Prior Art

Glass has widely been used as a material for containers for holding various articles, for example seasonings, oils, wines and liquors, beer, soft drinks including carbonated drinks, cosmetics, and detergents. Glass containers have excellent gas-barrier property, but their cost of production is high. It is the usual practice therefore to recover the used empty containers and recycle them for use. The glass containers, however, are heavy and involve high transportation expenses. Moreover, they are susceptible to breakage and inconvenient to handle.

To solve this problem, the glass containers have been superseded by various plastic containers, and various plastic materials are used according to the kind of articles to be held and the purpose of use. Polyethylene terephthalate (PET) has excellent thermal resistance, impact strength, gas-barrier property and transparency, and is used as a material for containers used to hold seasonings, refreshing drinks, detergents and cosmetics. In the case of containers for beer and carbonated drinks which most rigorously require gas-barrier property, polyethylene terephthalate is still not entirely satisfactory. To use polyethylene terephthalate for such containers, it is necessary to improve gas-barrier property by increasing the thickness of the containers.

Polyester containers have shown an increasing demand, but to expand their use further, it is strongly desired to develop polyesters having excellent gas-barrier property and melt-moldability.

Japanese Laid-Open Patent Publication No. 84898/1981 discloses a multilayer container having a thin wall portion in which the outermost layer and the innermost layer are composed of a polyester having ethylene terephthalate as main recurring units, an interlayer is composed of a polyamide obtained by reacting a dibasic acid component and a diamine component, the diamine component being m-xylenediamine or a mixture of it with p-xylenediamine, and the resin constituting the thin wall portion is oriented in at least one direction. This patent document describes that the above container has excellent oxygen gas-barrier property while retaining the excellent dynamical properties, transparency and chemical resistance of the polyester.

Japanese Laid-Open Patent Publication No. 163248/1983 discloses a biaxially stretched blow molded bottle in which both inside and outside surface layers are composed of polyethylene terephthalate and a layer intermediate between them is composed of a mixture of polyethylene terephthalate and a xylene group-containing polyamide.

Japanese Laid-Open Patent Publication No. 84824/1984 discloses a polyalkylene isophthalate such as polyethylene isophthalate and its copolymer, and a packaging material having good gas-barrier property with respect to oxygen and carbon dioxide gas which is molded from them.

Japanese Laid-Open Patent Publication No. 87048/1984 discloses a multilayer packaging material composed of a layer of a polyalkylene isophthalate or its copolymer and a layer of a polyalkylene terephthalate such as polyethylene terephthalate or its copolymer, and a molded article such as a bottle

formed from it.

Japanese Laid-Open Patent Publication No. 64656/1984 proposes a method of blending polyethylene isophthalate and polyethylene terephthalate.

However, the polyethylene isophthalates described in the above-cited patent documents contains high-melting oligomers, and these oligomers adversely affect the physical properties of the resulting molded articles.

To improve the gas-barrier property of PET, a copolyester was proposed which is prepared by copolymerizing isophthalic acid as a dicarboxylic acid component and ethylene glycol and 1,3-bis(2-hydroxyethoxy)benzene as a dihydroxy compound component (see Japanese Laid-Open Patent Publication No. 167617/1983).

If an article such as a container is molded from a polyester resin containing moisture, hydrolysis takes place and the mechanical properties of the molded article are degraded. It is necessary therefore to dry the polyester resin before molding. However, since an isophthalate-type copolyester containing a large amount of isophthalic acid as the dicarboxylic acid component has a lower crystallinity and glass transition temperature (T_g) than a terephthalate-type copolyester, it can be dried only at low temperatures. Accordingly, to obtain an isophthalate-type polyester having a low water content, long periods of time are required for its drying. If the isophthalate copolyester is dried at temperatures higher than the glass transition temperature, the copolyester will melt-adhere to itself.

Usually, polyethylene terephthalate is dried at a temperature of 110 to 180 °C. If the polyethylene terephthalate dried at the above temperatures and the isophthalate-type copolyester dried at lower temperatures are dry-blended immediately after drying, the isophthalate-type copolyester will be heated to a temperature higher than the glass transition temperature by the polyethylene terephthalate which is still at a considerably high resin temperature. Consequently, the pelletized isophthalate-type copolyester will get out of shape or the copolyester pellets melt-adhere to one another. Consequently, it is difficult to mix them uniformly.

For this reason, it has been desired to develop an isophthalate-type copolyester having a high glass transition temperature (T_g) and excellent thermal resistance.

An isophthalate-type copolyester having copolymerized therein bis(4-beta-hydroxyethoxyphenyl)sulfone was proposed as a copolyester having a high glass transition temperature (T_g) (see Japanese Laid-Open Patent Publication No. 167617/1983).

The use of bis(4-beta-hydroxyethoxyphenyl)sulfone makes the isophthalate-type copolyester slightly higher in glass transition temperature (T_g), but its T_g elevating effect is not sufficient. In addition, if its gas-barrier property is degraded, or the copolyester is colored or the monomeric components bleed out, the polyester is undesirable in view of food sanitation.

SUMMARY OF THE INVENTION

It is an object of this invention to solve the above problems in the prior art, and to provide an isophthalate-type copolyester being free from high-melting oligomers and having a high glass transition temperature and excellent gas-barrier property and surface properties.

Another object of this invention is to provide a gas-barrier property imparting agent comprising the above isophthalate-type copolyester. Another object of this invention is to solve the problems associated with the prior art discussed above, and to provide a polyester composition which does not contain high-melting oligomers, can be dried at a high speed and has excellent thermal resistance, impact strength, surface properties, transparency and gas-barrier properties.

Another object of this invention is to provide a film, a preform and a container composed of the above polyester composition.

Another object of this invention is to solve the problems associated with the prior art discussed above, and to provide a polyester laminated structure which is free from high-melting oligomers, and has excellent moldability, stretchability, gas-barrier property, especially with respect to oxygen and carbon dioxide gas, thermal resistance, impact strength, surface properties, transparency, electrical properties and chemical resistance.

Another object of this invention is to provide a stretched laminated structure, a preform for blow molding and a laminated blow-molded article each composed of the above polyester laminated structure and having excellent gas-barrier property, especially with respect to oxygen and carbon dioxide gas, thermal resistance, impact strength, surface properties, transparency, electrical properties and chemical resistance.

The above objects are achieved in accordance with this invention by a copolyester having an intrinsic

viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from a dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,8-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

5 The above objects are also achieved in accordance with this invention by a gas-barrier property imparting agent composed of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from a dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,8-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

10 The above objects are further achieved in accordance with this invention by a polyester composition comprising (A) 50 to 95 % by weight of polyethylene terephthalate and (B) 50 to 5 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from a dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,8-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

15 The above objects are further achieved in accordance with this invention by a film composed of a polyester composition comprising (A) 80 to 95 % by weight of polyethylene terephthalate and (B) 50 to 5 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from a dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,8-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

20 The above objects are further achieved in accordance with this invention by a preform composed of a polyester composition comprising (A) 80 to 95 % by weight of polyethylene terephthalate and (B) 50 to 5 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from a dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,8-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

25 The above objects are further achieved in accordance with this invention by a container composed of a polyester composition comprising (A) 80 to 95 % by weight of polyethylene terephthalate and (B) 50 to 5 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 12.5 dl/g and being derived from a dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,8-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

30 The above objects are also achieved in accordance with this invention by a polyester laminated structure composed of (C) a polyalkylene terephthalate layer and (D) a copolyester layer, the copolyester layer (D) derived from dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,8-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

35 The above objects are further achieved in accordance with this invention by a stretched polyester laminated structure composed of (C) a polyalkylene terephthalate layer and (D) a copolyester layer composed of a copolyester derived from a dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,8-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units or a copolyester composition comprising said copolyester and polyethylene terephthalate, said polyalkylene terephthalate layer (C) and the copolyester layer (D) being stretched.

40 The above objects are also achieved in accordance with this invention by a preform for a laminated blow-molded article, said preform composed of (C) a polyalkylene terephthalate layer and (D) a copolyester layer, the copolyester layer (D) being composed of a copolyester derived from a dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,8-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

45 The above objects are also achieved in accordance with this invention by a polyester laminated blowmolded article composed of (C) a polyalkylene terephthalate layer and (D) a copolyester layer, the copolyester layer (D) being composed of a copolyester derived from a dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,8-naphthalenedicarboxylic acid units and

dihydroxy compound units composed of 85 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The copolyester of this invention is characterized in that the dicarboxylic acid units (recurring units derived from a dicarboxylic acid) consist of 85 to 60 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and the dihydroxy compound units (recurring units derived from a dihydroxy compound) consist of 85 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, and that it has an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dL/g.

Since the copolyester of the invention uses isophthalic acid units and 2,6-naphthalenedicarboxylic acid units as the dicarboxylic acid units and ethylene glycol units and 1,3-bis(2-hydroxyethoxy)benzene units as the dihydroxy compound units, it does not contain high-melting oligomers and has excellent gas-barrier property and surface properties and a high glass transition temperature.

The copolyester of this invention will be described below specifically.

The copolyester of the invention can be obtained by co-condensation reaction of the following dicarboxylic acids and dihydroxy compounds.

The dicarboxylic acids used in this invention are 85 to 60 mole %, preferably 80 to 70 mole %, of isophthalic acid, and 5 to 40 mole %, preferably 10 to 30 mole %, of 2,6-naphthalenedicarboxylic acid.

If the isophthalic acid is used in an amount of more than 85 mole %, the resulting copolyester does not have so high a glass transition temperature. If it is used in an amount of less than 60 mole %, the glass transition temperature of the resulting copolyester has too high a glass transition temperature, and a blend of the resulting copolyester and polyethylene terephthalate, or a multilayer laminate of the copolyester cannot be sufficiently stretched.

In the present invention, another dicarboxylic acid may be used in addition to the isophthalic acid and 2,6-naphthalenedicarboxylic acid in an amount which does not impair the properties of the resulting copolyester. Examples of the other dicarboxylic acid are terephthalic acid, phthalic acid, and 2-methyl-terephthalic acid. As the dihydroxy compounds, ethylene glycol and 1,3-bis(2-hydroxyethoxy)benzene are used in the invention. These dihydroxy compounds are used in such amounts that the hydroxy compound component consists of 85 to 70 mole %, preferably 80 to 80 mole %, of ethylene glycol, and 5 to 30 mole %, preferably 10 to 20 mole %, of 1,3-bis(2-hydroxyethoxy)benzene. By using ethylene glycol and 1,3-bis(2-hydroxyethoxy)benzene in the above amounts as the dihydroxy compounds, a copolyester being free from high-melting oligomers and having excellent surface properties and a high glass transition temperature can be obtained.

In addition to ethylene glycol and 1,3-bis(2-hydroxyethoxy)benzene, another dihydroxy compounds may be used in an amount which does not impair the properties of the resulting copolyester. Examples of the other dihydroxy compound include dihydroxy compounds having 3 to 15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, cyclohexanedimethanol, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4-beta-hydroxyethoxyphenyl)propane and bis(4-beta-hydroxyethoxyphenyl)sulfone.

The copolyester of the invention may be composed only of the above dicarboxylic acid units and the above dihydroxy compound units, or of the dicarboxylic acid units, the hydroxy compound units and a small amount of trifunctional or higher polycarboxylic acid units or polyhydroxy compound units. Polycarboxylic acids having 4 to 15 carbon atoms may be used as the trifunctional or higher polycarboxylic acid. Specific examples may be trimellitic acid, trimesic acid and hemimellitic acid. The trifunctional or higher polyhydroxy compounds may be, for example, polyhydric alcohols having 3 to 15 carbon atoms. Typical examples include 1,1,1-trihydroxymethylpropane, glycerol, 1,2,3-butanetriol, 1,2,3-pentanetriol, and pentaerythritol. Polyesters obtained by co-condensing the trifunctional or higher polycarboxylic acid or polyhydroxy compound with the above dicarboxylic acid and dihydroxy compound are preferred because they have improved uniform stretchability in blow molding.

The proportion of the trifunctional or higher polycarboxylic acid units in the copolyester is 0.01 to 2 moles, preferably 0.005 to 1 mole, per 100 moles of the dicarboxylic acid units, and the proportion of the trifunctional or higher polyhydroxy compound units is 0.01 to 2 moles, preferably 0.05 to 1 mole, per 100 moles of the dihydroxy compound units.

The resulting copolyester of the invention has an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dL/g, preferably 0.8 to 1.0 dL/g. If the intrinsic viscosity is less than 0.3 dL/g, the mechanical

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strength of the copolyester is undesirably degraded. On the other hand, if it exceeds 1.5 dl/g, the copolyester undesirably has degraded melt-moldability.

The copolyester of the invention can be produced by known polycondensation reactions heretofore employed in the production of polyethylene terephthalate. The dicarboxylic acids may be fed to the reaction system as such or their dialkyl esters. They may also be fed as esters of the dicarboxylic acid with a diol such as bis(beta-hydroxyethyl) alcohol.

Likewise, the dihydroxy compounds may be fed as such or in the form of dihydroxy esters of the carboxylic acids.

Known catalysts used in the production of polyethylene terephthalate may be used in the copolycondensation. The catalysts may be, for example, metals such as antimony, germanium and titanium, or their compounds such as the oxides, hydroxides, halides, inorganic acid salts, organic acid salts, complex salts, double salts, alcoholates and phenolates. These catalysts may be used singly or in combination with each other. The catalyst may be supplied to the reaction system at the initial stage of the esterification reaction or ester interchange reaction, or may be supplied to the reaction system before it is switched to the polycondensation reaction stage.

At the time of the cocondensation, there may be used catalysts for ester-interchange reaction, and additives such as inhibitors against formation of diethylene glycol, heat stabilizers, light stabilizers, lubricants, pigments and dyes, which are used in the production of polyethylene terephthalate. Amines such as triethylamine and tri-n-butylamine and quaternary ammonium compounds such as tetraethyl ammonium hydroxide and tetrabutyl ammonium hydroxide may be used as the inhibitors against the formation of diethylene glycol. Examples of the stabilizers such as heat stabilizers are phosphorus compounds such as phosphoric acid, phosphorous acid, hypophosphoric acid and esters of these.

The copolyester of this invention may be produced by a known melt polycondensation method or at times by using a solid-phase polycondensation method after the melt polycondensation method.

In the above melt polycondensation, the so-called direct polycondensation or the so-called ester-interchange polycondensation may be used.

The melt polycondensation method will be described further more specifically. For example, isophthalic acid and 2,6-naphthalenedicarboxylic acid or dicarboxylic acids containing these as main ingredients and ethylene glycol and 1,3-bis(2-hydroxyethoxy)benzene or a condensate thereof with a dicarboxylic acid, and optionally a trifunctional or higher compound containing at least three carboxyl or hydroxyl groups are esterified or ester-interchanged simultaneously or consecutively at a temperature of preferably 100 to 280 °C, and then polycondensing the resulting pre-polycondensate at a temperature above its melting point, preferably 200 to 300 °C under vacuum or in the presence of a flowing inert gas with stirring.

Furthermore, the copolyester of the invention may be produced by subjecting the copolyester obtained by the above melt polycondensation method to solid-phase polycondensation method to increase its molecular weights. Specifically, this solid-phase polycondensation method is carried out by pelletizing the copolyester obtained by the melt polycondensation method and maintaining the pellets at a temperature below the melting point, preferably 180 to 240 °C, under vacuum or in a stream of an inert gas.

The copolyester of this invention has a higher glass transition temperature than a polyester obtained from isophthalic acid and ethylene glycol, and can be dried more rapidly. Furthermore, the copolyester of this invention has better gas-barrier property than a polyester obtained from terephthalic acid and ethylene glycol. The copolyester of the invention hardly contains high-melting oligomers, and can give a molded article having excellent surface properties.

The copolyester of the invention can be used as a gas-barrier imparting agent because it has excellent gas-barrier property and surface property and a high glass transition temperature.

The copolyester of the invention may, as required, contain other components such as coloring agents, fillers, polymerization catalysts, and crosslinking agents such as trimellitic anhydride, trimesic acid or triols.

The copolyester of the invention may be used in the unstretched state as a material for articles of various shapes such as films, sheets, fibers and containers to be obtained by ordinary molding methods. When the copolyester in the stretched state is molded into films, sheets and containers, these articles have further improved gas-barrier property.

Since the copolyester of the invention has excellent gas-barrier property, it can be used as a packaging material such as a bottle by using it as a single layer or as a laminate with another layer such as a layer of polyethylene terephthalate, nylon 6 or nylon 66.

Furthermore, a packaging material having excellent gas-barrier property can be prepared by blending the copolyester of the invention with another polyester such as polyethylene terephthalate.

Now, a stretched product of the copolyester of the invention will be described. This stretched product is monoaxially or biaxially stretched and may be in the form of a film, a sheet, a fiber, or a blow-molded

container. Where the copolyester is monoaxially stretched, the stretch ratio is usually from 1.1 to 10, preferably from 1.2 to 8, especially preferably from 1.5 to 7. Where the copolyester is stretched biaxially, the stretch ratio is usually from 1.1 to 8, preferably from 1.2 to 7, especially preferably from 1.5 to 6, in the longitudinal direction, and usually from 1.1 to 8, preferably from 1.2 to 7, especially preferably from 1.5 to 6, in the transverse direction. The stretched product may be heat-set according to the purpose for which it is to be used.

As required, the stretched product of the copolyester of the invention may contain suitable amounts of various additives incorporated in conventional polyesters, for example, nucleating agents, inorganic fillers, lubricants, slip agents, antiblocking agents, stabilizers, antistatic agents, antihaze agents, and pigments. The stretched product of the copolyester of the invention may be produced by any of known methods. Generally, a starting molded article such as a film-like material, a sheet-like material or a parison molded from the copolyester or its composition containing the above additives as required is subjected to a stretching treatment, either directly or after it is cooled to a temperature below its glass transition temperature and solidified and then re-heated, at a temperature ranging from its glass transition temperature to its melting point, preferably, from its glass transition temperature to a point 80 °C higher than it. The heat-setting of the stretched product is carried out for a short time at the above stretching temperature or a higher temperature.

If the starting molded article is a film-like article or a sheet-like article, it may be stretched, for example, by a monoaxial stretching method by which it is stretched in one direction, a biaxial stretching method in which it is stretched in the longitudinal direction and then in the transverse direction, a simultaneous biaxial stretching method in which it is stretched in the longitudinal and transverse directions simultaneously, a method by which it is biaxially stretched and then repeatedly stretched in either one direction, a method by which it is biaxially stretched and further in both directions, or a vacuum forming method by which a space between the film- or sheet-like article and the mold is maintained in vacuum to thereby stretch it.

The stretched product of the copolyester may also be produced in the form of a laminate with another resin such as polyethylene terephthalate. Such a laminate may be produced, for example, by a method in which one or more layers of the starting molded article such as a film- or sheet-like article of the copolyester are laminated to one or more layers of a starting molded article such as a film- or sheet-like article of another resin such as polyethylene terephthalate, and the laminate is then stretched, or a method in which a film- or sheet-like article of the other resin is bonded to the stretched product of the copolyester of the invention.

If the starting molded article is a parison, a stretch blow-molded container may be produced from it by stretching the parison at the above temperature in the longitudinal direction, and then blow-molded to stretch it further in the transverse direction (biaxial stretch blow molding). Furthermore, if a parison prepared from one or more layers of the copolyester and one or more layers of the other resin is subjected to the above stretch blow molding, laminated blow-molded article composed of the copolyester and the other resin (e.g., polyethylene terephthalate) can be produced.

Since the stretched product of the copolyester of the invention has excellent gas-barrier property, it can be used in various applications. In particular, biaxially stretched blow-molded containers of the copolyester, because of their excellent gas-barrier property, are useful for holding various articles, for example seasonings, oils, beer, wines and liquors, soft or carbonated drinks such as cola, cider and juices, cosmetics and detergent. Particularly, for holding beer or carbonated drinks, the thickness of the containers can be decreased, and the taste of these goods can be preserved for an extended period of time.

The stretched film of the copolyester of the invention may be used for example, as electrically insulating film, magnetic tapes, photographic films, and metal-vapor deposited films.

The polyester composition of this invention comprises (A) 50 to 95 % by weight of polyethylene terephthalate and (B) 50 to 5 % by weight of a copolyester.

The polyester film, polyester preform and polyester container in accordance with this invention are composed of the above polyester composition.

The polyester composition of this invention consists essentially of the polyethylene terephthalate (A) and the copolyester (B). The dicarboxylic acid units of the copolyester (B) are composed of isophthalic acid units and 2,6-naphthalenedicarboxylic acid units and the dihydroxy compound units are composed of ethylene glycol units and 1,3-bis(2-hydroxyethoxy)benzene units. Accordingly, the composition can be dried at a high speed, and had excellent thermal resistance, impact strength, transparency and gas-barrier property. Furthermore, since it does not contain high-melting oligomers, it has excellent surface properties.

Now, the polyester composition, the polyester film, the polyester preform and the polyester container in accordance with this invention will be described in detail.

The polyethylene terephthalate (A) used in the polyester composition of the invention is a crystalline

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thermoplastic polyester composed of usually at least 80 mole %, preferably at least 90 mole %, of terephthalic acid units based on the entire dicarboxylic acid units and usually at least 80 mole %, preferably at least 90 mole %, of ethylene glycol based on the entire dihydroxy compound units.

Examples of dicarboxylic acid units other than the terephthalic acid units include units derived from aromatic dicarboxylic acids such as isophthalic acid, diphenylether-4,4-dicarboxylic acid, naphthalene-1,4-dicarboxylic acid and naphthalene-2,6-dicarboxylic acid, aliphatic dicarboxylic acids such as oxalic acid, succinic acid, adipic acid, sebacic acid and undecanedicarboxylic acid, or aliphatic dicarboxylic acids such as hexahydroterephthalic acid.

Examples of dihydroxy compounds units other than the ethylene glycol units are units derived from aliphatic dihydroxy compounds such as propylene glycol, 1,4-butanediol and neopentyl glycol, aliphatic dihydroxy compounds such as propylene glycol, 1,4-butanediol and neopentyl glycol, alicyclic dihydroxy compounds such as cyclohexanediol and cyclohexanedimethanol, and aromatic dihydroxy compounds such as 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4-beta-hydroxyethoxyphenyl)propane, bis(4-beta-hydroxyethoxyphenyl)sulfone and bisphenol A.

The polyethylene terephthalate (A) may contain the other dicarboxylic acid units and the other dihydroxy compound units if it contains terephthalic acid units and ethylene glycol units in the amounts indicated above. The polyethylene terephthalate (A) may be used as a mixture with another polyester.

The molecular weight of the polyethylene terephthalate (A) is not particularly limited if it is within a range which can give various molded articles such as a container from the resulting polyester composition. However, polyethylene terephthalate (A) used in this invention desirably has an intrinsic viscosity $[\eta]$, measured in o-chlorophenol at 25 °C, of at least 0.8 dl/g, preferably at least 0.8 dl/g.

The copolyester (B) contained in the polyester composition is composed of the dicarboxylic acid units and the dihydroxy compound units to be described below, and can be obtained by the copolycondensation of the corresponding dicarboxylic acids and dihydroxy compounds.

If the amount of the isophthalic acid units exceeds 85 mole %, the glass transition temperature of the copolyester (B) does not so much increase. If, on the other hand, it is less than 80 mole %, the glass transition temperature of the copolyester (B) rises too much, and a blend of the copolyester (B) and polyethylene terephthalate (A) cannot sufficiently be stretched.

Since the copolyester (B) contains 2,6-naphthalenedicarboxylic acid units derived from a rigid comonomer, the copolyester has a high glass transition temperature and a high level of gas-barrier property. Accordingly, the polyester composition composed of the copolyester (B) and polyethylene terephthalate (A) can be dried at a high speed during production.

Various known methods may be used to prepare the polyester composition from the polyethylene terephthalate (A) and the copolyester (B). For example, there may be used a method by which the polyethylene terephthalate (A) and the copolyester (B) are mixed by using a Henschel mixer, a V-blender, a ribbon blender, a tumbler blender, etc. Since the copolyester has a high glass transition temperature, even when the two polyesters (A) and (B) are mixed immediately after drying, the copolyester hardly melt-adhere to itself. Accordingly, the two polyesters (A) and (B) can be rapidly mixed after drying. The mixture so prepared may be melt-kneaded by a single-screw extruder, a twin-screw extruder, a kneader or a Bambury mixer, and then granulated or pulverized.

In the resulting polyester composition, the amount of the polyethylene terephthalate (A) is 50 to 95 % by weight, preferably 70 to 90 % by weight, and the amount of the copolyester (B) is 50 to 5 % by weight, preferably 30 to 10 % by weight, based on the total weight of the polyester composition.

If the amount of the polyethylene terephthalate (A) is less than 50 % by weight, the properties of the polyethylene terephthalate cannot sufficiently be exhibited. On the other hand, if it exceeds 95 % by weight, the properties of the copolyester (B) are not fully exhibited.

The resulting polyester composition has a glass transition temperature of usually 75 to 85 °C, preferably 80 to 85 °C. Since the polyester composition of the invention has a higher glass transition temperature than a polyester composition comprising a conventional isophthalate-type copolyester, it can be dried at high temperatures, and therefore rapidly.

The polyester composition of this invention may contain ordinary various additives for polyesters, such as heat stabilizers, weather stabilizers, antistatic agents, lubricants, mold releasing agents, pigment dispersing agents, pigments and dyes in amounts which do not impair the objects of this invention.

The polyester composition may be used in various shapes such as a sheet, a plate, a tube, a hollow article or a container.

The polyester film in accordance with this invention is prepared by an ordinary method from the polyester composition described above. The polyester film may either be stretched or unstretched.

The unstretched polyester film desirably has a thickness of usually 50 to 600 micrometers, preferably

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200 to 800 micrometers.

The stretched film may be a monoaxially or biaxially stretched film. The stretch ratio of the monoaxially stretched film is desirably from 1.1 to 10, preferably from 1.2 to 8, especially preferably from 1.5 to 7. In the biaxially stretched film, the stretch ratio is usually from 1.1 to 8, preferably from 1.2 to 7, especially from 1.5 to 7.

In the biaxially stretched film, the stretch ratio is desirably from 1.1 to 8, preferably from 1.2 to 7, especially preferably from 1.5 to 8, in the longitudinal direction, and from 1.1 to 8, preferably from 1.2 to 7, especially preferably from 1.5 to 8, in the transverse direction.

The polyester film of this invention can be produced by any known method. Generally, a film-like material molded from the above polyester composition optionally containing the additives, as such or after it is cooled and solidified at a temperature below the glass transition temperature, is re-heated, and this starting molded product is subjected to a stretching treatment at a temperature ranging from the glass transition temperature to its melting point, preferably from the glass transition temperature to a point about 80 °C higher than the glass transition temperature. Heat-setting of the stretched film may be carried out at a temperature higher than the above stretching temperature for a short period.

In the production of the stretched polyester film of this invention, the starting film-like product in the unstretched state may be stretched monoaxially (monoaxial stretching method); stretched in the longitudinal direction and then in the transverse direction (biaxial stretching method); stretched simultaneously in the longitudinal and the transverse directions (simultaneous biaxial stretching method); stretched biaxially and then repeatedly stretching in either direction; stretched biaxially and further in both directions; or may be processed by a so-called vacuum forming method in which a space between the film-like product and a mold is reduced in pressure, thereby to stretch-molding the film-like product.

The polyester composition of this invention may be processed into a sheet-like article substantially in accordance with the methods of producing the polyester film described above.

The polyester preform of this invention may be produced by using the polyester composition.

For example, it may be prepared by injection-molding the polyester composition.

The polyester container in accordance with this invention may be produced by press-forming a sheet of the polyester composition, or stretch blow-molding the polyester preform mentioned above.

Stretch blow-molding may be carried out, for example, by stretching the preform in the longitudinal direction at the stretching temperature for the polyester composition, and then blow-molding it to stretch it also in the transverse direction (biaxial stretch blow molding method).

To produce the polyester container from the biaxial stretch blow molding method, a bottomed preform molded by an ordinary injection-molding machine or a parison obtained by bottoming one end of a parison molded by an extrusion-molding machine is stretched to 1.5 to 3.5 times, preferably 2 to 3 times in the longitudinal direction, and 2 to 5 times, preferably 3 to 4.5 times, in the transverse direction at a stretching temperature of 80 to 120 °C, preferably 90 to 110 °C by a rod moving longitudinally within a blow molding mold and the blowing of a pressurized gas. Molding by an injection molding machine may be carried out by a two-stage method using a cold parison or a one-stage method using a hot parison.

To improve the rigidity of the polyester container, a layer of polyethylene terephthalate may be laminated to the inside and outside layers of the polyester composition.

The polyester container of this invention may be used in various applications because of its excellent transparency and gas-barrier property. In particular, biaxial stretch blow-molded containers have excellent gas-barrier property and transparency and can be used not only for holding seasonings, oils, wines and liquors, cosmetics and detergents, but also holding sparkling drinks such as cola, cider and beer. The polyester containers of the invention permit prolongation of the period within which goods held therein can be taken with their original tastes and flavors without increasing the thickness of the container wall as in conventional containers.

The polyester laminated structure of this invention is composed of (C) a polyalkylene terephthalate layer and (B) a copolyester layer. The copolyester layer (D) is a layer of the copolyester of the invention described hereinabove, or the above polyester composition of the invention comprising the copolyester and polyethylene terephthalate, in which the layers (C) and (D) are stretched.

The preform for the polyester laminated blow-molded product of this invention is composed of (C) a polyalkylene terephthalate and (D) a copolyester layer which is a layer of the copolyester of the invention described hereinabove, or the above polyester composition of the invention comprising the copolyester and polyethylene terephthalate.

The polyester laminated blowmolded product of this invention is composed of (A) a polyalkylene terephthalate and (D) a copolyester layer. The copolyester layer is a layer of the copolyester of the invention described above and the polyester composition of the invention comprising the copolyester and

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polyethylene terephthalate.

The polyester laminated structure, the preform for a laminated blow-molded article, and the laminated blow-molded article in accordance with this invention are each composed of the above described specific layers mentioned above, and therefore, have excellent gas-barrier property particularly with respect to oxygen and carbon dioxide, thermal resistance, impact strength, surface properties, transparency, electrical properties and chemical resistance and hardly contain high-melting oligomers.

The polyester laminated structure, the preform for a laminated blow-molded article, and the laminated blow-molded article in accordance with this invention will be described below specifically.

The polyalkylene terephthalate layer (C) of the polyester laminated structure of the invention is formed of a polyalkylene terephthalate such as polyethylene terephthalate and polypropylene terephthalate, preferably polyethylene terephthalate.

The polyethylene terephthalate used in this invention is as described hereinabove.

The molecular weight of polyethylene terephthalate used in this invention is not particularly limited if the resulting polyester laminated structure can be molded into various articles such as a container. Desirably, however, the polyethylene terephthalate has an intrinsic viscosity $[\eta]$, measured at 25 °C in o-chlorophenol, of usually at least 0.8 dl/g, preferably at least 0.8 dl/g.

When polypropylene terephthalate, for example, is used as the polyalkylene terephthalate, propylene glycol may be used in place of ethylene glycol. The polypropylene terephthalate so obtained has an intrinsic viscosity, measured at 25 °C in o-chlorophenol, of usually 0.8 to 1.2 dl/g. This polypropylene terephthalate may be used as a mixture with another polyester.

The copolyester layer (D) of the polyester laminated structure in this invention may be formed from the above copolyester or a polyester composition comprising the copolyester and polyethylene terephthalate described hereinabove. If the proportion of isophthalic acid units constituting the above copolyester exceeds 95 mole %, the glass transition temperature of the copolyester do not so much increase. If it is less than 90 mole %, the glass transition temperature of the copolyester increases excessively, and the polyester laminated structure composed of the copolyester layer (D) and the polyalkylene terephthalate layer (C) can be stretched only with reduced stretchability of the copolyester layer (D).

In the present invention 2,6-naphthalenedicarboxylic acid units derived from a rigid comonomer component are included as units constituting the copolyester. Hence, the copolyester has a high glass transition temperature and hardly contain high-melting oligomers. The gas-barrier property of the laminated structure can be maintained at a high level.

The polyester composition used in the production of the polyester laminated structure has a higher glass transition temperature than a polyester composition comprising a conventional isophthalate-type copolyester, and therefore can be dried rapidly at a high temperature, and the polyester laminated structure of the invention can be produced efficiently.

Specific examples of the laminated structure are shown below.

A two-layer laminated structure composed of one copolyester layer (D) and one polyalkylene terephthalate layer (C);

a three-layer laminated structure composed of two outside layers of the polyalkylene terephthalate (C) and an interlayer of the copolyester (D);

a multilayer laminated structure having four or more layers composed of alternately laminated layers of the copolyester (D) and layers of alkylene terephthalate (C), in which both outermost layers are composed of the polyalkylene terephthalate (C);

a multilayer laminated structure having four or more layers composed of alternately laminated layers of the copolyester (D) and layers of alkylene terephthalate (C), in which both outermost layers are composed of the copolyester (D); and

a multilayer laminated structure having four or more layers composed of alternately laminated layers of the copolyester (D) and layers of alkylene terephthalate (C), in which one of the outermost layers is composed of the copolyester layer (D) and the other, of the polyalkylene terephthalate layer (C).

The laminated structures may be used in the form of a sheet, a plate, a tube, a hollow body or a container, and can be produced by known methods.

There is no particular restriction on the thicknesses of the copolyester layer (D) and the polyalkylene terephthalate layer (C) and may be determined according to the use to which the resulting laminate structure is to be put. For example, when this laminated structure is a two-layer structure, the thickness of the copolyester layer (D) is usually 50 to 600 micrometers, preferably 90 to 300 micrometers, and the thickness of the polyalkylene terephthalate layer (C) is 50 to 300 micrometers, preferably 50 to 200 micrometers. When the laminated structure is the first-mentioned three layer structure, the thickness of the copolyester layer (D) is usually 50 to 800 micrometers, preferably 50 to 200 micrometers. The thickness of

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each of the outside polyalkylene terephthalate layer (C) is usually 50 to 500 micrometers, preferably 50 to 300 micrometers. If the laminated structure is the latter-mentioned three-layer structure, the thickness of the polyalkylene terephthalate interlayer is usually 50 to 500 micrometers, preferably 50 to 300 micrometers, and the thickness of copolyester outside layers (C) is usually 50 to 500 micrometers, preferably 50 to 200 micrometers. When the laminated structure is a multilayer structure, the thicknesses of the intermediate layer and both outside layers of the copolyester (D) and the thicknesses of the intermediate layer and outermost layers composed of the polyalkylene terephthalate layer (C) may be prescribed in the same way as above.

The laminated structure of the invention has excellent stretchability, electrical properties, particularly electrical insulation, mechanical strength, transparency and gas-barrier property.

The polyester stretched laminated structure of the invention may be produced by any known methods. Generally, a starting molded article such as a film or sheet obtained by laminating the polyalkylene terephthalate layer (C) and the copolyester layer (D), either as such or after cooling and solidifying it to a temperature below the glass transition temperature of the polyalkylene terephthalate and the copolyester, is stretched at a temperature above the glass transition temperature of both, preferably 70 to 100 °C.

The polyester stretched laminated molded structure of the invention can be produced by, for example, stretching an unstretched film or sheet (when the starting molded article is film or sheet) is stretched monodially (monodial stretching method); stretched in the longitudinal direction and then in the transverse direction (biaxial stretching method); stretched biaxially and then repeatedly stretched in either direction; or biaxially stretched and then further stretched in both directions. When the starting structure is to be monodially, the stretch ratio is usually from 1.1 to 10, preferably from 1.2 to 8, especially preferably from 1.5 to 7. In the production of the starting molded structure by biaxial stretching, the stretch ratio is usually from 1.1 to 8, preferably from 1.2 to 7, especially preferably from 1.5 to 6, in the longitudinal direction, and usually from 1.1 to 8, preferably from 1.2 to 7, especially preferably from 1.5 to 6, in the transverse direction. The resulting stretched laminated molded structure may be heat-set.

The polyester stretched laminated structure of the invention has excellent mechanical strength, transparency, electrical properties and gas-barrier property. In particular, by using this molded structure for forming electrical and electronic component parts and metallic parts, it is effective for protecting electrical and electronic circuits and preventing corrosion of metals. The polyester stretched laminated structure in the form of a film can also be effectively used for capacitors, motors, transformers and wire and cable coatings by utilizing its electrical properties. Furthermore, by utilizing its excellent gas-barrier property, it may be used as a film for food packaging.

The preform for the polyester laminated blow-molded article of the invention may be produced by using the polyester laminated structure of the invention.

For example, by molding and processing the polyester laminated structure in tubular form, the preform of the invention can be obtained.

The polyester laminated blow-molded article of this invention is a stretch blow-molded article formed from the above polyester laminated structure. The stretched blow-molded article may be produced by stretch blow-molding the above preform.

The polyester laminated blow-molded article may be monodially or biaxially stretched. The biaxially stretched polyester laminated blow-molded article has outstanding mechanical strength and gas-barrier property.

The stretch ratios used in the production of the polyester laminated blow-molded article in this invention may be the same as those described above with regard to the stretched polyester laminated structures.

The polyester laminated blow-molded article may be produced by stretching and blow-molding the preform described above. The stretch blow molding may be carried out by stretching the preform in the longitudinal direction at temperatures within the range of the stretching temperatures for the laminated structure, and further blow-molding the stretched preform to stretch it in the transverse direction (biaxial stretching blow-molding method).

For example, a polyester container may be produced in accordance with the biaxial stretching blow-molding method by stretching a bottomed parison molded by an ordinary injection-molding machine, or a parison obtained by bottoming one end of a parison molded by an extrusion molding machine at a temperature of 80 to 120 °C, preferably 80 to 110 °C, to 1.5 to 3.5 times in the longitudinal direction, and to 2 to 6 times, preferably 3 to 4.5 times in the transverse direction by a rod moving longitudinally within a blow-molding mold and the blowing of a pressurized gas. Particularly, a biaxially stretched blow-molded container as the polyester laminated blow-molded article of the invention has excellent gas-barrier property and transparency, and is suitable therefor for holding not only seasonings, oils, wines and liquors, cosmetics and detergents but also for holding sparkling drinks such as cola, cider and beer as stated hereinabove.

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The following examples illustrate the present invention specifically.
In these examples, the various properties were measured by the following methods.

5 Intrinsic viscosity of the polyester

Measured in an o-chlorophenol solution of the polymer at 25 °C.

10 Composition of the polyester

Determined by measuring the nuclear magnetic resonance spectrum of the polyester in a trichloroacetic acid solution.

15 Glass transition temperatures of the polyester

Measured by a differential scanning calorimeter at a temperature elevating rate of 10 °C/min.

20 Oxygen gas permeation coefficient

Measured at 25 °C by an OXTRAN device made by MOCON company.

25 Carbon dioxide gas permeability coefficient

Measured at 25 °C by using a PERMATRAN C-IV device made by MOCON company.

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EXAMPLE A1

A copolyester composed of isophthalic acid (IA), 2,6-naphthalenedicarboxylic acid (NDA), 1,3-bis(2-hydroxyethoxy)benzene (DER) and ethylene glycol (EG) was produced by the following procedure.

A 1-liter stainless steel reactor equipped with a stirrer, a nitrogen gas inlet and a condenser was charged with 122.5 g of isophthalic acid, 17.7 g of naphthalenedicarboxylic acid, 84.8 g of ethylene glycol, 24.4 g of 1,3-bis(2-hydroxyethoxy)benzene, 0.33 g of 1,1,1-tris(hydroxymethyl)propane, 0.058 g of titanium acetylacetonate, 0.077 g of Sb₂O₃, 0.010 g of tetrasodium ethylenediaminetetraacetate, and 0.027 g of manganese hypophosphate monohydrate.

The reaction mixture was heated in an atmosphere of nitrogen at 220 °C for 1 hour and then at 240 °C for 25 minutes. During this time, water was continuously evaporated.

Then, 0.184 g of tris(nonylphenyl) phosphite was added to the mixture in the reactor.

The reaction temperature was raised to 250 °C, and maintained for 35 minutes in a nitrogen atmosphere.

The flowing of the nitrogen gas was stopped, and a reduced pressure of less than 4 mmHg was applied. The reaction was continued at 275 °C for 4 hours under less than 0.4 mmHg. The resulting copolyester had an intrinsic viscosity of 0.83 dl/g. It had a glass transition temperature of as high as 70 °C. The carbon dioxide gas permeability coefficient was 3.0 cc.mm/m².day.atm, and it had good gas-barrier property.

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EXAMPLES A2 and A3 and COMPARATIVE EXAMPLES A-1 to A-6

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Copolyesters having the compositions indicated in Table 1 were synthesized as in Example A1. Sheets were formed from the copolyesters, and their gas-barrier properties were measured.

The results are shown in Table 1.

Table 1

Run (°)	Composition of the copolyester	T _g	Pco ₂	[η]
	(mole%)	(° C)	(cc.mm/m ² .day.atm)	(dl/g)
Ex. A1	IA/NDA/DER/EG	73	3.0	0.83
	80/10/15/85			
Ex. A2	IA/NDA/DER/EG	78	3.1	0.81
	80/20/15/85			
Ex. A3	IA/NDA/DER/EG	84	3.3	0.83
	70/30/15/85			
CEx. A1	TA/EG	78	21.8	0.76
	100/100			
CEx. A2	IA/EG	87	3.0	0.80
	100/100			
CEx. A3	NDA/EG	124	7.2	0.80
	100/100			
CEx. A4	IA/NDA/DER/EG	80	4.2	0.80
	50/50/15/85			
CEx. A5	IA/TA/EG/DER	89	3.8	0.78
	70/30/85/15			
CEx. A6	IA/TA/EG/DER/BSE	78	5.1	0.81
	70/30/72/15/12			
Ex. = Example; CEx. = Comparative Example				

The total amount of the dicarboxylic acid and the dihydroxy compound was 100 mole %.
The following abbreviations were used.

- IA: isophthalic acid
- NDA: 2,6-naphthalenedicarboxylic acid
- TA: terephthalic acid
- DER: 1,3-bis(2 hydroxyethoxy)benzene
- EG: ethylene glycol
- BSE: bis(4-beta-hydroxyethoxyphenyl)sulfone

EXAMPLES B1 to B6 and COMPARATIVE EXAMPLES B1 to B6

One hundred parts of polyethylene terephthalate (Mitsui PET J135, a product of Mitsui PET Resin Co., Ltd.) dried at 150 °C for 10 hours was mixed with each of the amounts indicated in Table 2 of the copolyester obtained in Example A1. The mixture was melt-extruded at a molding temperature of about 250 to 290 °C by an extruder, cooled and cut by a cutter to form pellets of a polyester composition composed of polyethylene terephthalate and the copolyester. The pellets were press-formed to prepare a press sheet having a thickness of about 800 micrometers. The press sheet was stretched simultaneously by a biaxially stretching device to three times both in the longitudinal and transverse directions to obtain a biaxially stretched film.

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The resulting biaxially stretched film has a thickness of about 50 microns, there was no thickness unevenness, and it was uniformly stretched. The transparencies and the carbon dioxide gas permeability coefficients of the press sheet and the biaxially stretched film are shown in Table 2.

The compositions obtained by mixing PET with the copolyesters of Comparative Examples A2 and A5 had a decreased glass transition temperature as compared with the compositions prepared by mixing PET with the copolyesters of Examples A1, A2 and A3. Furthermore, when the copolyesters of Comparative Examples A5 and A8 were mixed with PET, the effect of improving the oxygen gas permeability coefficient was small.

Table 2

Run	Copolyester		Tg of the composition (°C)	Properties of the biaxially stretched film of the composition	
	Type	Amount		Haze	CO ₂ gas permeability coefficient
	(example designation)	(wt.%)		(%)	(cc.mm/m ² .day.atm)
Ex. B1	Ex. A1	10	77	0.8	9.1
Ex. B2	Ex. A2	10	78	0.8	9.3
Ex. B3	Ex. A3	10	79	0.8	9.5
CEx. B1	CEx. A2	10	73	2.0	9.1
CEx. B2	CEx. A4	10	79	1.0	10.1
CEx. B3	CEx. A5	10	73	0.7	9.9
CEx. B4	CEx. A8	10	78	1.2	10.6
Ex. B4	Ex. A1	20	77	0.8	7.5
Ex. B5	Ex. A2	20	78	0.8	7.8
Ex. B6	Ex. A3	20	79	0.9	7.9
CEx. B5	CEx. A2	20	70	2.8	7.5
CEx. B6	CEx. A4	20	80	1.2	8.7
CEx. B7	CEx. A5	20	70	0.8	8.7
CEx. B8	CEx. A8	20	78	1.4	9.4

EXAMPLES B7 to B8 and COMPARATIVE EXAMPLES B9 to B11

The composition of polyethylene terephthalate and the copolyesters prepared in Examples 1B, B3 and B5 were each injection-molded at a molding temperature of about 270 °C by an injection-molding machine to form preforms (cold parison). Each of the preforms was biaxially stretched and blow-molded to about 2.5 times in the longitudinal direction and about 4 times in the transverse direction to produce a stretched bottle having an inner capacity of about 1 liter.

The above procedure was repeated using the polyester compositions of Comparative Examples B3, B5 and B7.

The hazes of the side surfaces of the stretched bottles and their carbon dioxide gas permeabilities were measured, and the results are shown in Table 3.

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Table 3

Run	Composition (example designation)	Properties of the biaxially stretched bottle	
		Haze (%) of the side surface of the bottle	CO ₂ gas permeation coefficient
			(cc/day.bottle.atm)
Ex. B7	Ex. B1	1.8	1.5
Ex. B8	Ex. B3	2.0	1.5
Ex. B9	Ex. B5	2.4	1.8
CEx. B9	CEx. B3	2.8	2.1
CEx. B10	CEx. B6	2.0	1.8
CEx. B11	CEx. B7	3.0	2.8

EXAMPLE C1

Polyethylene terephthalate (Mitsui PET J135, a product of Mitsui PET Resin Co., Ltd.) dried at 150 °C for 10 hours was press-formed at about 280 °C to prepare a press sheet having a thickness of about 100 micrometers.

Separately 100 parts of the polyethylene terephthalate was mixed with 20 parts of the copolyester of Example A1, and the mixture was melt-extruded at 280 to 290 °C by using an extruder to produce pellets of the composition. The pellets of the composition were press-formed at about 280 °C to prepare a press sheet having a thickness of about 100 micrometers. The above polyethylene terephthalate press sheet was laid over the press sheet of the composition, and the assembly was press-formed at about 280 °C to give a two-layer laminated sheet having a thickness of about 800 micrometers. The resulting laminated sheet had good adhesion between the polyethylene terephthalate layer (C) and the polyester composition layer (D) and had a haze of 1.2 %. The carbon dioxide gas permeability coefficient was 15.5 cc.mm/m².day.atm.

The laminated sheet was simultaneously stretched in the longitudinal and transverse direction to 3 times by a biaxially stretching device to prepare a biaxially stretched film having a thickness of about 80 micrometers. The film was in the uniformly stretched state. The biaxially stretched film also shows good adhesion between the polyethylene terephthalate layer (C) and the polyester composition layer (D). The film had a haze of 0.8 %, and a carbon dioxide gas permeability coefficient of 10.0 cc.mm/m².day.atm.

EXAMPLES C2 AND C3 and COMPARATIVE EXAMPLES C1 to C4

In the same way as in Example C1, press sheets and biaxially stretched films were prepared except that the copolyesters indicated in Table 4 were used. The haze values and carbon dioxide gas permeability coefficients of the products are shown in Table 4.

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Table 4

Run	Copolyester		Properties of the press sheet of the laminated structure		Properties of the biaxially stretched film of the laminated structure	
	Type	Amount	Haze	CO ₂ gas permeability coefficient	Haze	CO ₂ gas permeability coefficient
	(example designation)	(parts by weight)	(%)	(cc.mm/m ² .day.atm)	(%)	(cc.mm/m ² .day.atm)
Ex. C1	Ex. A1	20	1.2	15.5	0.8	10.0
Ex. C2	Ex. A2	20	1.8	15.7	0.8	10.1
Ex. C3	Ex. A3	20	1.8	18.0	0.9	10.2
CEx. C1	CEx. A2	20	6.2	15.5	2.1	10.0
CEx. C2	CEx. A4	20	2.4	17.2	1.2	10.8
CEx. C3	CEx. A5	20	1.8	17.0	0.8	11.0
CEx. C4	CEx. A8	20	2.8	19.0	1.4	11.0

EXAMPLE C4

The polyethylene terephthalate in Example C1 was injection-molded, and then a composition composed of 100 parts of the polyethylene terephthalate in Example C1 and 20 parts of the copolyester in Example A1 was also injection-molded to form a preform having an inside layer of the polyethylene terephthalate (C) and an outside layer of the polyester composition (D) composed of the copolyester and the polyethylene terephthalate each of the layers having a thickness of about 1.8 mm.

The resulting preform was heated to 85 to 95 °C by using a far-infrared heater, and then stretched to about 2.5 times in the longitudinal direction and to about 4.3 times in the transverse direction by stretching blow-molding machine to prepare a two-layer stretched bottle having an inner capacity of about 1 liter in which the polyethylene terephthalate layer (C) in the minimum thickness portion was about 150 micrometers thick, and the polyester composition layer (D) was about 150 micrometers thick. The haze of the side surface of the stretched bottle was 1.5 %. The carbon dioxide gas permeability of this bottle was 2.0 ml/day.bottle.atm.

COMPARATIVE EXAMPLE C5

A preform composed only of polyethylene terephthalate and having the same thickness (about 3.2 mm) of the preform in Example C5 was prepared by injection-molding the polyethylene terephthalate used in Example 1. The preform was then stretched and blow-molded to prepare a stretched bottle having an inner capacity of about 1 liter in which the minimum thickness portion was about 300 micrometers thick.

The side surface of the stretched bottle had a haze of 4.5 %, and the carbon dioxide gas permeability of the stretched bottle was 2.0 ml/day.bottle.atm.

Claims

1. A copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from dicarboxylic acid units composed of 85 to 90 mole % of isophthalic acid units and 5

to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

2. A copolyester according to claim 1 having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.8 to 1.0 dl/g and being derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

3 The copolyester of claim 2 which further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

4. The copolyester of claim 2 which further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-tris(hydroxymethyl)propane units.

5. A gas-barrier property imparting agent comprising a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

6. A gas-barrier property imparting agent according to claim 5 comprising a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.8 to 1.0 dl/g and being derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

7. The gas-barrier imparting agent of claim 6 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

8. The gas-barrier property imparting agent of claim 6 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-tris(hydroxymethyl)propane units.

9. A polyester composition comprising (A) 50 to 95 % by weight of polyethylene terephthalate and (B) 50 to 5 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

10. A polyester composition according to claim 9 comprising (A) 70 to 90 % by weight of polyethylene terephthalate and (B) 30 to 10 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.8 to 1.0 dl/g and being derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

11. The polyester composition of claim 10 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

12 The polyester composition of claim 10 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-tris(hydroxymethyl)propane units.

13. A film composed of a polyester composition comprising (A) 50 to 95 % by weight of polyethylene terephthalate and (B) 50 to 5 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from dicarboxylic acid units composed of 95 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

14. A film according to claim 13 which is composed of a polyester composition comprising (A) 70 to 90 % by weight of polyethylene terephthalate and (B) 30 to 10 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.8 to 1.0 dl/g and being derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

15. The film of claim 14 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

16. The film of claim 14 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the

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dihydroxy compound units, of 1,1,1-tris(hydroxymethyl)propane units.

17. A preform composed of a polyester composition comprising (A) 50 to 95 % by weight of polyethylene terephthalate and (B) 50 to 5 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from dicarboxylic acid units
5 composed of 95 to 60 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

18. A preform according to claim 17 which is composed of a polyester composition comprising (A) 70 to 90 % by weight of polyethylene terephthalate and (B) 30 to 10 % by weight of a copolyester having an
10 intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.8 to 1.0 dl/g and being derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

19. The preform of claim 18 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of
15 the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

20. The preform of claim 18 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-tris(hydroxymethyl)propane units.

21. A container composed of a polyester composition comprising (A) 50 to 95 % by weight of polyethylene terephthalate and (B) 50 to 5 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from dicarboxylic acid units
20 composed of 95 to 60 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

22. A container according to claim 21 wherein the polyester composition comprises (A) 70 to 90 % by
25 weight of polyethylene terephthalate and (B) 30 to 10 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.8 to 1.0 dl/g and being derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

23. The container of claim 22 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole
30 of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

24. The container of claim 22 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-tris(hydroxymethyl)propane units.

25. A polyester laminated structure composed of (C) a polyalkylene terephthalate layer and (D) a
35 copolyester layer, the copolyester layer (D) being composed of a copolyester derived from dicarboxylic acid units composed of 95 to 60 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

26. A polyester laminated structure according to claim 25 composed of (C) a polyalkylene terephthalate
40 layer and (D) a copolyester layer, the copolyester layer (D) being composed of a copolyester derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

27. The polyester laminated structure of claim 26 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

28. The polyester laminated structure of claim 26 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-tris(hydroxymethyl)propane units.

29. A stretched polyester laminated structure composed of (C) a polyalkylene terephthalate layer and (D) a copolyester layer composed of a copolyester derived from a dicarboxylic acid units composed of 95 to 60 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of
45 1,3-bis(2-hydroxyethoxy)benzene units or a copolyester composition comprising said copolyester and polyethylene terephthalate, said polyalkylene terephthalate layer (C) and the copolyester layer (D) being stretched.

30. A stretched polyester laminate structure according to claim 29 which is composed of (C) a

polyethylene terephthalate layer and (D) a copolyester layer composed of a copolyester derived from dicarboxylic acid units composed of 80 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 80 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units or a copolyester composition comprising said copolyester and polyethylene terephthalate, said polyalkylene terephthalate layer (C) and the copolyester layer (D) being stretched.

31. The polyester stretched laminated structure of claim 30 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

32. The polyester stretched laminated structure of claim 30 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-tris(hydroxymethyl)propane units.

33. A preform for a laminated blow-molded article, said preform being composed of (C) a polyalkylene terephthalate layer and (D) a copolyester layer, the copolyester layer (D) being composed of a copolyester derived from dicarboxylic acid units composed of 85 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 85 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

34. A preform for a laminated blow-molded article according to claim 33, said preform composed of (C) a polyethylene terephthalate layer and (D) a copolyester layer, the copolyester layer (D) being composed of a copolyester derived from a dicarboxylic acid units composed of 80 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 80 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

35. The preform of claim 34 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

36. The preform of claim 34 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-tris(hydroxymethyl)propane units.

37. A polyester laminated blow-molded article composed of (C) a polyalkylene terephthalate layer and (D) a copolyester layer, the copolyester layer (D) being composed of a copolyester derived from dicarboxylic acid units composed of 85 to 80 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 85 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

38. A polyester laminated blow-molded article according to claim 37 which is composed of (C) a polyethylene terephthalate layer and (D) a copolyester layer, the copolyester layer (D) being composed of a copolyester derived from dicarboxylic acid units composed of 80 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 80 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

39. The polyester laminated blow-molded article of claim 38 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

40. The polyester laminated blow-molded article of claim 38 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-tris(hydroxymethyl)propane units.



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(54) Copolyester and hollow container and oriented film comprising the copolyester.

(57) A copolyester comprising:
a dicarboxylic acid component comprising:
(a) 80 to 99.5 mol% of units derivable from terephthalic acid or an ester forming derivative thereof, and
(b) 0.5 to 4.5 mol% of units derivable from a phenylenedioxy diacetic acid or an ester forming derivative thereof; and
a diol component

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The present invention relates to a copolyester having a high transparency, superior strength and superior gas barrier property, and to a packaging material comprising the copolyester.

Polyethylene terephthalate (hereinafter sometimes abbreviated to "PET") has excellent mechanical strength, chemical safety, transparency and hygienic properties and is light in weight and low in cost. Therefore PET is widely used in packaging materials such as sheets, films and containers.

However, although the gas barrier property of PET is superior to other resins including polyolefins, it is not considered to be sufficient in some applications where a higher performance is required. For instance, a packaging material for a carbonated beverage, beer or wine is required to have a high oxygen and carbon dioxide gas barrier property in order to preserve the contents. A hollow container of a generally-used biaxially oriented PET cannot satisfy these strict requirements. Moreover, there is a demand for a film which has a low permeability to gases such as oxygen or moisture, and which does not have lowered performance under a freezing process, boiling treatment or retort treatment, for the packaging of, for example, fresh food or medical equipment.

Various methods have been proposed to improve the gas barrier property of packaging materials comprising polyethylene terephthalate. For example various gas barrier materials may be blended with PET and various gas barrier materials can be laminated or coated on a PET film.

The present inventors have found that a specific copolyester obtained using isophthalic acid and a phenylenedioxy diacetic acid as the main acid components can be used as a superior gas barrier material (JP-A-1-247422(1989), JP-A-21-47423(1989), JP-A-1-167331(1989), JP-A-2-182455(1990) and JP-A-2-14238(1990), and US-A-4,959,421).

It is also known that a polyester copolymer prepared from 5 to 100 mol% of a phenylenedioxy diacetic acid and 0 to 95 mol% of terephthalic acid as acid component has an excellent gas barrier property (JP-A-60-501080(1985), US-A-4,440,982 and US-A-4,652,948).

However, these gas barrier materials do not generally have sufficient mechanical strength and heat resistance so it is difficult to mold these materials singly. When a gas barrier material is blended with PET, it is difficult to maintain, for example, the mechanical strength and heat resistance which are inherent in PET. When coating or laminating a gas barrier material onto PET, there are various problems to be considered in the selection of molding conditions, adhesive properties between layers or the thickening of a container wall.

The present invention provides a copolyester comprising:

a dicarboxylic acid component comprising:

- (a) 80 to 99.5 mol% of units derivable from terephthalic acid or an ester forming derivative thereof, and
 - (b) 0.5 to 4.5 mol% of units derivable from a phenylenedioxy diacetic acid or an ester forming derivative thereof; and
- a diol component.

The present invention also provides a container, sheet or film which comprises the copolyester defined above.

The present invention further provides a process for forming a copolyester hollow container which comprises:

forming a preform by injection molding or extrusion molding of the copolyester defined above, and subjecting the preform to a biaxial-stretching blow molding.

The present invention additionally provides a process for forming a stretched copolyester film which comprises: injection molding or extrusion molding the copolyester defined above to obtain a sheet, and stretching the sheet in the machine direction or transverse direction.

The copolyester of the present invention has superior physical properties such as gas barrier property, mechanical strength, heat resistance and water resistance and has a high transparency.

The present inventors have found that the copolyester comprising a dicarboxylic acid component comprising units derivable from terephthalic acid as the main ingredient and a small amount of units derivable from phenylenedioxy diacetic acid in a specified range is unexpectedly superior in all physical properties including mechanical strength, heat resistance, water resistance and gas barrier property. It is possible to produce a molded article by a single use of the copolyester.

The terephthalic acid or ester forming derivative thereof may be any compound based on terephthalic acid which is reactive with diol components, and may include terephthalic acid, a nucleus-substituted derivative such as 2-chloroterephthalic acid and 2-methoxyterephthalic acid, an ester derivative such as dimethyl terephthalate and diethyl terephthalate, and an acid halide derivative such as terephthaloyl dichloride.

The phenylenedioxy diacetic acid or ester forming derivative thereof may include 1,2-phenylenedioxy diacetic acid, 1,3-phenylenedioxy diacetic acid, 1,4-phenylenedioxy diacetic acid, 2-methyl-1,3-phenylenedioxy diacetic acid, 5-methyl-1,3-phenylenedioxy diacetic acid, 6-methyl-1,3-phenylenedioxy diacetic acid, 5-ethyl-1,3-phenylenedioxy diacetic acid, 6-ethyl-1,3-phenylenedioxy diacetic acid, 5-methoxy-1,3-phenylenedioxy diacetic acid, 6-methoxy-1,3-phenylenedioxy diacetic acid, 4-chloro-1,2-phenylenedioxy diacetic

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acid, 4-chloro-1,3-phenylenedioxy diacetic acid, acid anhydrides thereof, acid halides thereof, and esters thereof. These compounds may be used singly or in combination of two or more compounds, for example, a combination of position isomers such as a combination of 1,2-isomer and 1,3-isomer. Among these, the preferable compound are 1,3-phenylenedioxy diacetic acid or the ester forming derivatives thereof and a more preferable compound is 1,3-phenylenedioxy diacetic acid.

In the dicarboxylic acid component constituting the copolyester of the present invention, the ratio of the unit derived from terephthalic acid is 80 to 99.5 mol%, preferably 90 to 99.0 mol%, and the ratio of the unit derived from the phenylenedioxy diacetic acid is 0.5 to 4.5 mol%, preferably 1.0 to 4.0 mol%. When the unit derived from terephthalic acid is below 80 mol %, the mechanical strength and the heat resistance are insufficient. On the other hand, when the unit derived from the phenylenedioxy diacetic acid is below 0.5 mol%, the improvement of gas barrier property is not sufficient and in case it exceeds 4.5 mol%, there is a tendency to give rise to such troubles as heat decomposition, adhesion and the like during molding process. Moreover, the transparency, mechanical strength and heat resistance of molded article are considerably decreased so that such polymer is not suitable to be used alone as a starting material for a molded article. In addition, if the unit derived from the phenylenedioxy diacetic acid is contained over 4.5 mol%, the gas barrier property of a non-stretched sheet is improved, however, a stretched sheet obtained therefrom surprisingly is not always improved in the gas barrier property.

The copolyester of the present invention, as far as each of the units derived from terephthalic acid and phenylenedioxy diacetic acid satisfies respectively the ratio range described above, it may contain a small amount of other unit derived from other dicarboxylic acid, hydroxycarboxylic acid or their derivatives. These other dicarboxylic acids may contain an aromatic dicarboxylic acid such as phthalic acid, isophthalic acid, 4,4'-diphenoxyethanedicarboxylic acid, 4,4'-diphenylsulfonedicarboxylic acid, 4,4'-biphenyldicarboxylic acid and their structural isomers, and an aliphatic dicarboxylic acid such as malonic acid, succinic acid, and adipic acid. And p-hydroxybenzoic acid, esters of p-hydroxybenzoic acid and glycolic acid may be mentioned as the hydroxycarboxylic acid and its derivatives.

The diol components of the copolyester may include an aliphatic glycol such as ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, pentamethylene glycol, hexamethylene glycol, neopentyl glycol, diethylene glycol, etc., an alicyclic glycol such as cyclohexane dimethanol, and an aromatic dihydroxy compound such as bisphenol A and bisphenol S. Among these compounds, generally, ethylene glycol is most preferred. The diol component is used in an amount substantially equivalent to the dicarboxylic acid component described above.

The copolyester of the present invention may contain as the constitutional component a mono-functional compound such as o-benzoylbenzoic acid or a poly-functional compound such as trimethylolpropane, pentaerythritol, glycerin, trimellitic acid, trimaleic acid, pyromellitic acid and a glycidyl ether of aromatic dihydroxy compounds such as bisphenol A glycidyl ether, as far as these additional components do not injure requirement of the present invention. These mono-functional or poly-functional components can be used up to 20 mol%, preferably up to 10 mol%, and further preferably up to 5 mol% of the diol component.

A conventionally known additive, for example, antioxidant, UV absorber, fluorescent brightening agent, mold release agent, antistatic agent, dispersant and colorant such as dye and pigment can be added to the copolyester. These additives may added in any step during polyester manufacturing or in masterbatching step before molding process.

The intrinsic viscosity of the copolyester of the present invention as measured in a mixed solvent of phenol and tetrachloroethane (weight ratio 1/1) at 30°C is preferred in the range from 0.4 to 2.0, preferably 0.5 to 1.5. When the intrinsic viscosity is below 0.4, the strength of the copolyester is poor so that it is impossible to obtain the physical properties required for practical use when the copolyester is taken out of the reaction vessel after completion of polymerization and cut it into chips, or molded it into sheets, films or containers such as bottles, barrels and cans. In case the intrinsic viscosity is over 2.0, there are problems that the melt viscosity becomes so high that the molding process such as injection molding, extrusion molding and blow molding becomes very difficult to be carried out.

The copolyester of the present invention can be produced by any polymerization method which is conventionally known as a polymerization method for polyethylene terephthalate. For example, there is a method comprising the steps of directly esterifying terephthalic acid, 1,3-phenylenedioxy diacetic acid and ethylene glycol under pressure and thereafter gradually reducing the pressure while raising the temperature to polycondense the esterified product. The copolyester of the present invention can be further produced by another method wherein an ester of terephthalic acid such as dimethyl terephthalate, an ester of the 1,3-phenylenedioxy diacetic acid such as dimethyl 1,3-phenylenedioxydiacetate and ethylene glycol are subjected to ester interchange reaction, and thereafter the reaction product is further subjected to polycondensation. In these production reactions, the phenylenedioxy diacetic acid can be added at any stage during the ester interchange

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reaction or the initial stage of polycondensation reaction. For example, ester interchange reaction between an ester of terephthalic acid and ethylene glycol is first carried out, and then the phenylenedioxy diacetic acid is added to the reaction product to carry out polycondensation. Further, if necessary, it is possible to attain higher degree of polymerization, low acetaldehyde formation and low oligomerization degree by subjecting the copolymer to heat treatment after the polymerization. The heat treatment is preferably carried out in the range from a temperature just below the melting point of the copolyester to a temperature 80°C below the melting point for several ten hours or less, after the surface of chip is crystallized at 80 to 180°C.

In the production method of the copolyester described above, it is preferable to use esterification catalyst, ester interchange catalyst, polycondensation catalyst, and stabilizer. As the ester interchange catalyst, at least one known compound selected from calcium, manganese, zinc, sodium and lithium compounds can be used. A manganese compound is preferable because it can provide a copolyester of a higher transparency. As the polycondensation catalyst, at least one known compound selected from antimony, germanium, titanium and cobalt compounds can be used. Antimony, germanium and titanium compounds are preferred.

The copolyester thus obtained can be molded into films, sheets, containers and other packaging materials by a melt molding method usually employed in PET molding. The non-stretched sheet or film obtained from the copolyester of the present invention can be used as a high gas barrier material. Moreover, the gas barrier property and mechanical strength can be improved by stretching the non-stretched film or sheet in at least to one direction.

The oriented copolyester film of the present invention is obtained by subjecting a non-stretched sheet obtained by injection molding or extrusion molding of the copolyester to any stretching method of uniaxial stretching, successive biaxial stretching, and simultaneous biaxial stretching which are usually employed in PET stretching. The copolyester can be molded into cups and trays by air-pressure molding or vacuum molding.

When producing these oriented films, the stretching temperature may be selected between the glass transition temperature of the polyester of the present invention and a temperature 70°C higher than the glass transition temperature, usually between 40 and 170°C, preferably 80 and 140°C. Both uniaxial and biaxial stretching method are applicable, but biaxial stretching is preferred because a biaxially oriented film has physical properties required in practical use. The stretching ratio is usually 1.1 to 10 times for the uniaxial stretching, and preferably 1.5 to 8 times. In the case of biaxial stretching, the stretching ratio is 1.1 to 8 times, preferably 1.5 to 5 times, for each of the machine and transverse directions. The stretching ratio in the machine direction is preferred to be 0.5 to 2 times, more preferably 0.7 to 1.3 times the stretching ratio in the transverse direction.

The thickness of a non-stretched sheet is 50 to 2000µm, preferably 100 to 1000µm. If it is below 50µm, the non-stretched sheet has a tendency to break during the stretching step and if it is over 2000µm, the quenching thereof becomes difficult and simultaneously a uniform stretching becomes difficult because of the increase in tension of stretching.

The oriented film thus obtained can be used as it is, however the gas barrier property and the mechanical strength can be further improved by subjecting an oriented film to heat setting for 0.1 to 30 minutes, preferably 0.5 to 5 minutes at a temperature from 100°C to the melting point of the copolyester, preferably 150 to 230°C, under the tension.

The hollow molded article of the copolyester of the present invention is produced by the stretching-blow molding of a preform prepared from the copolyester. The apparatus conventionally used in blow molding of PET can be used in the production of the hollow molded article. More specifically, a biaxial stretching blow molding such as a hot parison process or a cold parison process is adopted in which a preform is first produced by ordinary extrusion molding or injection molding of the copolyester, and the thus obtained preform is reheated and biaxially stretched as it is or after processing the mouth portion and the bottom portion thereof. The stretching temperature is 70 to 120°C, preferably 80 to 110°C, and the stretching ratio is 1.5 to 3.5 times in the machine direction and 2 to 5 times in the circumferential direction.

The hollow molded article obtained can be directly used, but in the case where it is used for a container for a liquid content requiring hot filling such as fruits juice drinks, it is preferred to improve the heat resistance thereof by heat setting in the same blow mold as used for molding or another mold equipped separately. This heat setting is usually carried out for from 2 seconds to 2 hours, preferably 10 seconds to 30 minutes, at 100 to 200°C, preferably 120 to 180°C, under tension by compressed air or mechanical stretching.

Further, the molded article of the present invention can be also produce from a blend of the copolyester and a polyalkylene terephthalate mainly comprising PET, or it may be formed in a laminated structure of a layer of the copolyester and a layer of a polyalkylene terephthalate mainly comprising PET.

The present invention, hereinafter, will be explained in more detail referring to the following examples, but the present invention is not restricted to the following examples.

In the following examples, "part" means "weight part" and the methods for measurements shown in examples are as follows.

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1. Intrinsic viscosity

The intrinsic viscosity was determined in a mixed solvent of phenol and tetrachloroethane (Weight ratio 50/50) at 30°C.

2. Acetaldehyde content

5 The content was determined by gas chromatography after water extraction of a copolyester for 2 hours at 160°C.

3. Flow rate of inactive gas

10 The flow amount of inactive gas per unit time (hour) and per unit resin weight (kg) was determined. The flow rate was expressed by a converted value of this flow amount to a gas volume (liter) at one atmospheric pressure and 25°C.

4. Gas permeability

15 The gas permeability was determined with oxygen permeability measuring equipment "OX-TRAN 10/60A" (manufactured by Modern Controls, USA) and carbon dioxide permeability measuring equipment "PERMATRAN C-IV" (manufactured by Modern Controls, USA) at 100% RH and 23°C, and expressed in cc-mm/m²-day-atm.

5. Creep resistance test

20 Into distilled water adjusted at 0°C, were dissolved 12.5 g of citric acid hydrate, and then the total aqueous solution was filled into a sample bottle made from a copolyester. Further, the sample bottle was added with 15.0 g of sodium bicarbonate, immediately sealed tightly, and shaken for several ten seconds to dissolve the sodium bicarbonate. The condition in the sample bottle thus treated corresponded to that filled with carbon dioxide gas in a volume 4.0 times the volume of the sample bottle at 0°C and 1 atm. The sample bottle was placed onto a flat plane in an atmosphere of 23°C and 50% humidity or 38°C and 90% humidity, and the height of the fill point was read after 2 hours and after 3 to 12 weeks of the storage under the same condition to obtain the fill point drop variation. A smaller fill point drop variation means a better creep resistance.

6. Mechanical strength and elongation

25 Mechanical strength and elongation of the body of a sample bottle were determined in accordance with the method of JIS-K 7113 under the condition of 23°C and 50% humidity using a tensile tester manufactured by INTESCO Co.

7. Heat resistance

30 Into a sample bottle, was filled 990 ml of hot water of a predetermined temperature, and the bottle was tightly sealed and left at room temperature for 1 hour. Then the bottle emptied with the content is visually observed whether its deformation occurs or not. Three bottles were examined for each run by this method and the lowest temperature at which deformation was observed was expressed as the critical temperature for heat resistance.

8. Cyclic trimer content (CT content)

35 In 2 ml of solution of chloroform/hexafluoroisopropanol (volume ratio 3/2), were dissolved 200 mg of a copolyester and the solution was diluted by further adding 20 ml of chloroform. By adding 10 ml of methanol to this solution, the copolyester was precipitated and the precipitate was filtered off to obtain a filtrate. The filtrate was evaporated to dryness and the residue was dissolved in 25 ml of dimethylformamide. This solution was subjected to quantitative analysis by liquid chromatography to determine the CT content.

40 The cyclic trimer is the main component of oligomers which are by-produced during copolymerization. The oligomer adheres to a mold and contaminates it during the molding of a copolyester, thereby causing lowering in production efficiency. Therefore, a lower CT content is preferred.

Example 1

45 Into a reaction vessel, were charged 9583 parts of dimethyl terephthalate (96 mol% of the acid component), 6390 parts of ethylene glycol and 2.1 parts of manganese acetate tetrahydrate. The mixture was heated gradually from 160 to 220°C over 4 hours to complete ester interchange reaction. To the reaction product, were added 470 parts of 1,3-phenylenedioxycacetic acid (4 mol% of the acid component), 1.5 parts of orthophosphoric acid and 1.5 parts of germanium dioxide and the temperature was raised gradually from 220°C while gradually decreasing the pressure in the polymerization vessel to carry out polycondensation at 275°C under 0.5 torr for three hours. As a result, transparent copolyester chips having an intrinsic viscosity of 0.63 were obtained.

50 After the surface of the copolyester chips was crystallized in a stirring crystallization apparatus (manufactured by Bepax Co., USA) at 160°C, the copolyester was transferred into a stationary solid phase polymerization tower, dried for 3 hours at 120 to 160°C under the stream of 20 liter/kg-hr nitrogen gas, and polymerized for 10 hours at 200°C. The solid-phase polymerized copolyester had an intrinsic viscosity of 0.66, an acetaldehyde

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content of 2.2 ppm and a CT content of 0.37 wt%.

A preform was prepared from the copolyester chips subjected to solid phase polymerization by using an injection molding machine IS-60B manufactured by Toshiba Corporation under the following conditions:

temperature of nozzle and each part of cylinder: 275°C,

screw rotation: 100 rpm,

injection time: 10 seconds, and

temperature of cooling water for mold: 10°C.

A bottle having 1 liter volume and 300µm of average body thickness was obtained from this preform using biaxial stretching blow molding machine of the following conditions:

preheater temperature: 80°C,

blow pressure: 20 kg/cm², and

molding cycle: 10 seconds.

The results of the measurements on gas permeability, CT content, fill point drop variation and mechanical strength and elongation of the bottle body are shown in Table 1.

Example 2

Into an autoclave, were charged 8200 parts of terephthalic acid (96 mol% of the acid component), 470 parts of 1,3-phenylenedioxy dicarboxylic acid (4 mol% of the acid component), and 3635 parts of ethylene glycol, and esterification reaction was carried out at 220 to 245°C for 3 hours with stirring under nitrogen gas atmosphere (2.5 kg/cm²) while distilling off the water produced during the reaction. The esterified product was added with 1.5 parts of orthophosphoric acid and 1.5 parts of germanium dioxide. After 3-hour polycondensation reaction carried out in accordance with the method in Example 1, transparent copolyester chips having 0.85 of intrinsic viscosity were obtained. The thus obtained chips were further subjected to the same solid phase polymerization as in Example 1 to obtain chips having 0.86 of intrinsic viscosity, 2.0 ppm of acetaldehyde content and 0.37 wt% of CT content. One liter bottle was obtained by the same blow molding procedure as in Example 1. The results of measurements on gas permeability, CT content, fill point drop variation, and mechanical strength and elongation of the body of the bottle are shown in Table 1.

Example 3

Copolyester chips having 0.86 of intrinsic viscosity, 2.0 ppm of acetaldehyde content and 0.39 wt% of CT content after solid phase polymerization was obtained in the same procedures as in Example 1 except for using 9712 parts of dimethyl terephthalate (97 mol% of the acid component), 6500 parts of ethylene glycol, and 350 parts of 1,3-phenylenedioxy dicarboxylic acid (3 mol% of the acid component). A smaller preform, in which the neck length, the outer diameter of the body and the body thickness were respectively 0.8, 0.8 and 1.32 times those of the preform in Example 1, was produced from the copolyester chips thus obtained. One liter bottle was prepared by the same blow molding method as in Example 1. The results of measurements on gas permeability, CT content, fill point drop variation, and mechanical strength and elongation of the body of the obtained bottle are shown in Table 1.

Comparative Example 1

One liter bottle was obtained using polyethylene terephthalate for molding bottle (manufactured by Japan Unipet Co., Ltd., RT-543C) by the same blow molding method as in Example 1. The results of measurements on gas permeability, CT content, fill point drop variation, and mechanical strength and elongation of the body of the bottle are shown in Table 1.

Comparative Example 2

Solid phase polymerized chips having 0.87 of intrinsic viscosity, 2.0 ppm of acetaldehyde content and 0.48 wt% of CT content were obtained by the same procedure as in Example 1 except the use of 8392 parts of dimethyl terephthalate (84 mol% of the acid component), 6450 parts of ethylene glycol and 698 parts of 1,3-phenylenedioxy dicarboxylic acid (8 mol% of the acid component). One liter bottle was obtained from these chips by the same blow molding procedure as in Example 1. The results of measurements on gas permeability, fill point drop variation, and mechanical strength and elongation of the body of the bottle are shown in Table 1.

Considerable amount of adhesion between the chips was observed when the prepolymer of the chips were

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crystallized in a stirring crystallization apparatus, and many deformed chips or fused chips of 3 or 4 pieces were recognized even after the solid phase polymerization.

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Table 1

			Example 1	Example 2	Example 3	Comp. Ex. 1	Comp. Ex. 2
Copolyester Composition (PDDA/TPA) (mol ratio)			4/96	4/96	3/97	0/100	6/94
O ₂ gas Permeability (cc mm/m ² day atm)			1.30	1.28	1.10	1.95	1.45
CO ₂ gas Permeability (cc mm/m ² day atm)			6.51	6.50	5.71	9.96	7.01
CT content (wt %)			0.41	0.41	0.43	0.62	0.53
Fill point drop variation (mm)	Temp 23°C Humi 50%	6 weeks	2.9	3.0	2.7	2.9	6.4
		12 weeks	3.2	3.2	2.9	3.1	8.6
	Temp 38°C Humi 90%	3 weeks	3.9	3.9	3.9	3.8	9.8
		6 weeks	5.7	5.8	5.3	5.5	14.1
		12 weeks	6.2	6.3	5.5	6.0	-
Mechanical strength and elongation	Machine Directio	Yield strength (kg/mm ²)	10.7	10.7	10.5	10.1	7.8
		Tensile strength (kg/mm ²)	13.5	13.6	13.4	13.1	9.1
		Elongation at break (%)	61.6	61.8	60.5	59.6	71.3
	Transverse directio	Yield strength (kg/mm ²)	11.4	11.5	11.9	12.5	9.5
		Tensile strength (kg/mm ²)	15.0	15.0	15.3	16.0	11.8
		Elongation at break (%)	38.1	38.1	37.5	37.3	53.0

Note PDDA is Phenylenedioxy diacetic acid unit and TPA is terephthalic acid unit

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Example 4

A similar preform as in Example 3 was prepared from the solid phase polymerized chips obtained in Example 3. The preform was blow-molded to one liter bottle using a stretching blow molding machine equipped with a heat setting device, and the thus molded bottle was subjected to heat setting at 150°C for 10 seconds to obtain a heat-resistant bottle for fruit juice. The results of measurements on gas permeability and heat resistance of the body of the heat-resistant bottle are shown in Table 2. There was no deformation in the bottle when the bottle was filled with a fruit juice which was sterilized at 80°C and cooled to 85°C, turned upside down after tightly sealing the bottle, and allowed to stand for 15 minutes

Comparative example 3

One liter heat-resistant bottle for fruit juice was obtained from a polyethylene terephthalate for molding heat-resistant bottle (manufactured by Nihon Unipet, RT-543G) by the same blow molding and heat setting procedures as in Example 4. The results of measurements on gas permeability and heat resistance of the bottle body are shown in Table 2. No bottle deformation was found when the bottle was filled with a fruit juice of 85°C, turned upside down and allowed to stand in the same manner as in Example 4. The bottle in this Comparative Example 3 showed a heat resistance comparative to that of Example 4, but was inferior in gas barrier property.

Comparative Example 4

A bottle for fruit juice was obtained from the solid polymerized chips obtained in Comparative Example 2 by the same blow molding and heat setting procedures as in Example 4. The result of measurement on heat resistance of the bottle body is shown in Table 2. Considerable deformation was observed through entire bottle when the bottle was filled with a fruit juice of 85°C in the same manner as in Example 4.

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Table 2

		Example 4	Comp Ex 3	Comp Ex 4
Polyester composition (PPDA/TPA) (mol ratio)		3/97	0/100	6/94
O ₂ gas Permeability (cc mm/m ² day atm)		1.04	1.43	—
CO ₂ gas Permeability (cc mm/m ² day atm)		5.30	6.90	—
Heat resistance	Water temperature (83°C)	000	000	00A
	Water temperature (85°C)	000	000	xΔx
	Water temperature (87°C)	000	000	xxx
	Water temperature (89°C)	0AΔ	000	—
	Water temperature (91°C)	—	AAA	—
	Critical heat resistant temp. (°C)	89	91	83

Note PPDA Phenylenedioxydiacetic acid unit
TPA Terephthalic acid unit
0 No deformation
Δ Slight deformation
x Large deformation

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Example 5

Into a reaction vessel, were charged 9583 parts of dimethyl terephthalate (98 mol% of the acid component), 6390 parts of ethylene glycol and 2.1 parts of manganese acetate tetrahydrate. The temperature of the mixture was gradually raised from 160°C to 220°C over 4 hours to carry out ester interchange reaction. To the resultant product, were added 470 parts of 1,3-phenylenedioxy diacetic acid (4 mol% of the acid component), 1.5 parts of orthophosphoric acid and 1.5 parts of germanium dioxide. The temperature of the mixture was gradually raised from 220°C while gradually reducing the pressure in the vessel from ordinary pressure, and polycondensation was carried out at 273°C and 0.5 torr for total polycondensation time of 3.5 hours to obtain transparent copolyester chips having 0.98 of intrinsic viscosity.

After the chips were dried in vacuum, a sheet having 1200µm thickness was formed using 40 mmφ extruder (manufactured Modern Machinery Co.) under the following conditions:

cylinder temperature: 275°C,
nozzle temperature: 275°C, and
screw rotation: 40 rpm.

The extruded sheet was subjected to simultaneous biaxial stretching in a ratio of 3 times in both the machine and transverse directions by a Long Stretching Machine (manufactured by T.M. Long Co. USA) having an inner temperature of 90°C, and then heat set at 200°C under tension for 120 seconds in an oven.

The stretched film obtained showed good appearance and superior oxygen gas barrier property (oxygen gas permeability of 07 cc-mm/m²-day-atm).

The stretched film was further subjected to retort treatment for one hour in an atmosphere of 120°C and 100% relative humidity in a pressure cooker (manufactured by Hirayama Seisakusho K.K.), and oxygen gas permeability was again measured. The oxygen gas permeability was 1.09 cc-mm/m²-day-atm, which was substantially the same as that before the retort treatment. Also, no change in its appearance was observed.

Example 6

Into an autoclave, were charged 8200 parts of terephthalic acid (98 mol% of the acid component), 470 parts of 1,3-phenylenedioxy diacetic acid (4 mol% of the acid component), and 3835 parts of ethylene glycol, and esterification reaction was carried out at 220 to 245°C for 3 hours with stirring under nitrogen gas atmosphere (2.5 kg/cm²) while distilling off the water produced during the reaction. The esterified product was added with 1.5 parts of orthophosphoric acid and 1.5 parts of germanium dioxide. Then, in accordance with the method in Example 5, colorless and transparent copolyester chips having 0.85 of intrinsic viscosity were obtained.

A stretched film having good appearance was obtained from the chips in the same procedure as in Example 5, except that the stretching ratios in both the machine and transverse directions were changed to 3.5 times respectively. The oxygen gas permeability of the stretched film was 0.85 cc-mm/m²-day-atm. Also, there was no change in oxygen gas permeability and its appearance before and after retort treatment similar to Example 5.

Example 7

Colorless and transparent copolyester chips having 0.87 of intrinsic viscosity was obtained in the same procedure as in Example 5 except the use of 9712 parts of dimethyl terephthalate (97 mol% of the acid component), 6500 parts of ethylene glycol and 350 parts of 1,3-phenylenedioxy diacetic acid (3 mol% of the acid component).

A stretched film having good appearance was obtained from the chips in the same procedure as in Example 5, except that the stretching ratios in both the machine and transverse directions were changed to 3.8 times respectively. The oxygen gas permeability of the stretched film was 0.86 cc-mm/m²-day-atm. Also, there was no change in oxygen gas permeability and its appearance before and after the retort treatment similar to Example 5.

Comparative Example 5

A stretched film having good appearance was obtained from PET for packaging film (Dialfol-H manufactured by Dialfol Company, Limited) in the same procedure as in Example 5. The oxygen permeability of the stretched film was 1.58 cc-mm/m²-day-atm. Although almost no change was observed in the oxygen gas permeability before and after the same retort treatment as in Example 5, the oxygen barrier property was inferior to those of Examples 5 to 7.

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Comparative Example 6

Transparent copolyester chips having 0.86 of intrinsic viscosity was obtained in the same procedure as in Example 5 except the use of 9392 parts of dimethyl terephthalate (94 mol% of the acid component), 6460 parts of ethylene glycol and 698 parts of 1,3-phenylenedioxy diacetic acid (6 mol% of the acid component).

The oxygen gas permeability of a stretched film obtained from the chips in the same procedure as in Example 5 was 1.16 cc-mm/m²-day-atm, being a little inferior in gas barrier property compared with that of the film in Example 5. The film of Comparative Example 6 had a bad stretching property, a tendency of non-uniform stretching, uneven film thickness and inferior appearance.

Comparative Example 7

A stretched film was obtained in the same procedure as in Comparative Example 6 except that the stretching ratios in both the machine and transverse directions were changed to 3.8 times respectively. The stretching property of the film was poor and the film had a tendency of non-uniform stretching, uneven film thickness and inferior appearance.

Claims

1. A copolyester comprising:
a dicarboxylic acid component comprising:
(a) 80 to 99.5 mol% of units derivable from terephthalic acid or an ester forming derivative thereof, and
(b) 0.5 to 4.5 mol% of units derivable from a phenylenedioxy diacetic acid or an ester forming derivative thereof; and
a diol component.
2. A copolyester according to claim 1 which has an intrinsic viscosity of 0.4 to 2.0, the intrinsic viscosity being determined at 30°C in a 1:1 by weight mixed solvent of phenol and tetrachloroethane.
3. A copolyester according to claim 1 or 2 wherein the dicarboxylic acid component comprises:
(a) 80 to 99.0 mol% of the units derivable from terephthalic acid or an ester forming derivative thereof, and
(b) 1.0 to 4.0 mol% of the units derivable from phenylenedioxy diacetic acid or an ester forming derivative thereof.
4. A copolyester according to any one of the preceding claims wherein the phenylenedioxy diacetic acid is 1,3-phenylenedioxy diacetic acid.
5. A copolyester according to any one of the preceding claims wherein the diol component comprises ethylene glycol.
6. A container, sheet or film which comprises a copolyester as defined in any one of the preceding claims.
7. A process for forming a copolyester hollow container which comprises:
forming a preform by injection molding or extrusion molding of a copolyester as defined in any one of claims 1 to 5, and
subjecting the preform to a biaxial-stretching blow molding.
8. A process according to claim 7 which further comprises heat setting the blown-molded product obtained in the biaxial-stretching blow molding step.
9. A process for forming a stretched copolyester film which comprises:
injection molding or extrusion molding a copolyester as defined in any one of claims 1 to 5 to obtain a sheet, and
stretching the sheet in the machine direction or transverse direction.
10. A process according to claim 9 which further comprises heat setting the stretched film obtained in the stretching step.

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US005641548A

United States Patent [19]
Yamamoto et al.

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[45] **Date of Patent:** **Jun. 24, 1997**

[54] BLOW MOLDED ARTICLES

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[21] **Appl. No.:** 301,440
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doned, which is a continuation of Ser. No. 369,993, Aug. 20,
1990, abandoned.

[30] Foreign Application Priority Data

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Aug. 31, 1989	[JP]	Japan	1-225761
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[51] **Int. Cl.⁶** B65D 23/00
[52] **U.S. Cl.** 428/35.7; 428/36.92; 264/512;
528/173
[58] **Field of Search** 428/35.7; 36.92;
264/512; 528/173; 215/1 C

[56] References Cited

U.S. PATENT DOCUMENTS

4,390,683	6/1983	Yatsu et al.	328/194
4,398,017	9/1983	Go	328/173
4,692,506	9/1987	Yatsu et al.	428/194

FOREIGN PATENT DOCUMENTS

0105825	7/1983	European Pat. Off.
0443640	5/1985	European Pat. Off.
0-383324	8/1990	European Pat. Off.
2032369	6/1979	United Kingdom B29C 17/03
2188032	9/1987	United Kingdom

OTHER PUBLICATIONS

Database WPI, accession No. 85-035365 [06] Derwent
Publ., Ltd. London, GB & IPA 59 230 022 (Mitsui Petro-
chemical) 24-12-1984.
Database WPI, accession No. 86-134847 [21] Derwent
Publ. Ltd., London, GB & IPA 61-072 051 (Mitsui Petro-
chemical) 14-04-1986.

Primary Examiner—Charles Nold
Attorney, Agent, or Firm—Sherman and Shalloway

[57] ABSTRACT

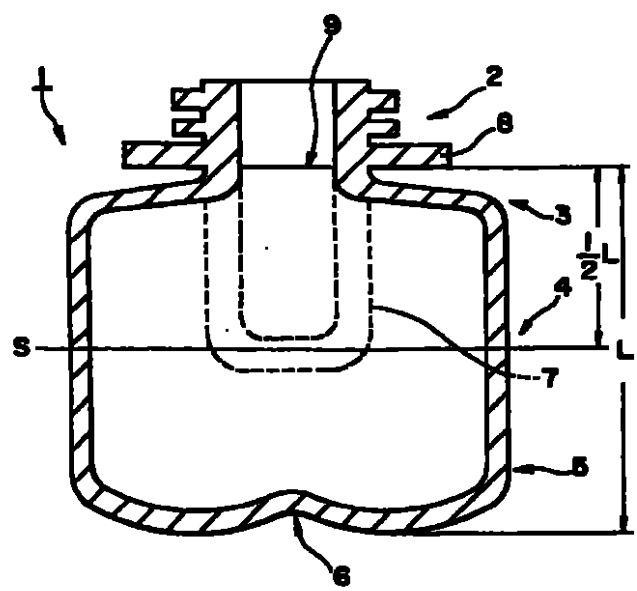
In accordance with the present invention, there are provided
blow molded articles which are composed of specific
copolyesters or specific polyester resin compositions and
which are highly oriented so that the stretch index as defined
by the following equations becomes not less than 130 cm.

$$\text{Stretch index} = \frac{\text{Internal volume (including stopper portion) of oriented bottle}}{\text{Internal volume (including stopper portion) of unoriented bottle}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area (including stopper portion) of oriented bottle}}{\text{Internal surface area (including stopper portion) of unoriented bottle}} \quad (\text{cm}^2)$$

The blow molded articles thus provided are excellent in
transparency and also excellent in moldability and gas
barrier properties and, moreover, excellent also in economi-
cal efficiency.

32 Claims, 1 Drawing Sheet



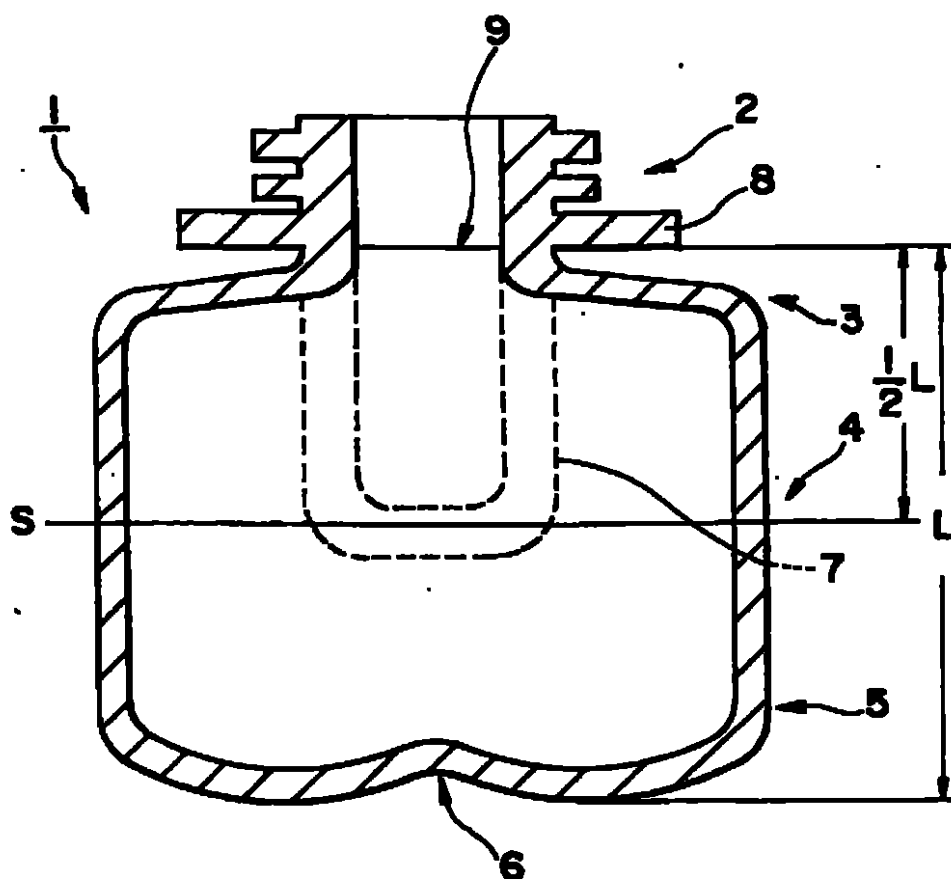
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FIG. 1



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BLOW MOLDED ARTICLES

This application is a continuation of application Ser. No. 08/029,914 filed Mar. 11, 1993, abandoned, which is a continuation of Ser. No. 07/569,993, filed Aug. 20, 1990, abandoned.

FIELD OF THE INVENTION

This invention relates to blow molded articles excellent in transparency, moldability, gas barrier properties and economical efficiency.

BACKGROUND OF THE INVENTION

Heretofore, glass has been widely used as a material for containers for seasonings, food oil, liquors such as beer and sake, cooling beverages such as carbonated drinks and the like, cosmetics, detergents, etc. However, glass containers are relatively high in manufacturing cost, though they are excellent in gas barrier properties, and therefore usually they are recovered after use and recycled for re-use. The drawbacks inherently associated with the glass containers, however, were such that because of heaviness for their size, they increase in shipping cost and, moreover, they are liable to break and not convenient for handling.

In order to overcome such drawbacks as mentioned above, various plastic containers have come to be used in place of the glass containers. Various plastic materials are used for the plastic containers, according to the kind of items to be preserved therein and the purpose for which the preserved items are used. Of these plastic materials, polyethylene terephthalate is used as a material, because of its excellent gas barrier properties and transparency, for containers for seasonings, cooling beverages, cosmetics and detergents. In these plastic containers especially for beer or carbonated drinks where the most severity of gas barrier properties is required, it may be said that even polyethylene terephthalate is not sufficient to meet such severe requirement. When these containers requiring severe gas barrier properties are intended to be manufactured from polyethylene terephthalate, it was necessary to improve gas barrier properties of the resulting container by increasing said container in wall thickness.

In the attempt as mentioned above, however, there was such a problem that the manufacturing cost of thick-wall bottles formed from polyethylene terephthalate becomes higher than that of thin-wall bottles, because the amount of the polyethylene terephthalate necessary for forming the thick-wall bottles are large in comparison with thin-wall bottles.

Under such circumstances, there is an attempt to obtain bottles excellent in gas barrier properties and economical efficiency from polyethylene terephthalate by highly orienting the polyethylene terephthalate used therefor. Bottles made of highly oriented polyethylene terephthalate may be obtained by orienting thick-wall preforms. In this case, however, there is brought about such a problem that the thick-wall preforms are gradually cooled in the course of the preparation thereof, and consequently highly oriented bottles obtained from these preforms undergo clouding and eventually deteriorate in transparency.

Such problem as mentioned above, on one hand, can be solved by using preforms formed from polyethylene terephthalate high in intrinsic viscosity. However, the use of polyethylene terephthalate high in intrinsic viscosity involves another problem that such polyethylene terephthalate as having a high intrinsic viscosity is poor in stretchability or moldability and also expensive.

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Japanese Patent L-O-P Publn. No. 64624/1984 discloses molded articles formed from polyalkylene isophthalate such as polyethylene isophthalate or copolymers thereof as packaging materials having good gas barrier characteristics against oxygen and carbon dioxide gas. Japanese Patent L-O-P Publn. No. 67049/1984 discloses multi-layer packaging materials comprising a layer of polyalkylene isophthalate such as mentioned above or copolymers thereof and a layer of polyalkylene terephthalate such as polyethylene terephthalate or copolymers thereof, and molded articles such as bottles composed of such multi-layer packaging materials.

There is proposed a process in which polyethylene and polyethylene terephthalate are blended (Japanese Patent L-O-P Publn. No. 64658/1984).

Japanese Patent L-O-P Publn. No. 167817/1983 discloses copolymers obtained by copolymerization of isophthalic acid as dicarboxylic acid, and ethylene glycol and 1,3-bis (2-hydroxyethoxy)benzene as a dihydroxy compound component.

Further, there has been made a proposal to manufacture bottles excellent in gas barrier properties by using polyethylene terephthalate resin compositions, prepared by mixing polyethylene terephthalate resins with other resins.

For example, in the specification of Japanese Patent Application No. 205739/1987 previously filed by the present applicant, there are proposed PET resin compositions having gas barrier properties capable of withstanding preservation and shipment of carbonated drinks, said resin compositions comprising a blend of PET resin and polyhydronopolpolyether resin. The containers molded from the above-mentioned PET resin compositions are superior in gas barrier properties to containers made of conventional PET resins.

Furthermore, the present applicant proposes by way of Japanese Patent L-O-P Publn. No. 72051/1986 PET resin compositions excellent in transparency, said PET resin compositions being obtained by mixing PET resin with copolymerized polyester resins.

Including of course such proposals as referred to above, the researches in improving transparency and gas barrier properties of PET resin compositions have heretofore been directed to place importance on the constitution of PET resin composition, and no attention has been focused on the draw ratio to be employed at the time when blow molded articles such as containers are prepared by stretching PET resin preforms.

OBJECT OF THE INVENTION

The present invention is intended to solve such drawbacks associated with the prior art as mentioned above, and an object of the invention is to provide blow molded articles molded from copolymers, said molded articles being excellent in moldability and gas barrier properties as well as in transparency, and also excellent in economical efficiency.

A further object of the invention is to provide blow molded articles molded from polyester resin compositions improved in gas barrier properties without marring transparency and mechanical properties of polyethylene terephthalate.

SUMMARY OF THE INVENTION

The first blow molded articles of the present invention are characterized in that the blow molded articles are composed of a copolyester having an intrinsic viscosity $[\eta]$ of 0.5-1.5 dl/g formed by esterification of dicarboxylic acid with a

Claim line 33

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dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 0-80 mol % of terephthalic acid and 20-100 mol % of isophthalic acid, said dihydroxy compound component comprising 10-95 mol % of ethylene glycol and 5-90 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxyl groups and being used in an amount of 0.05-1.0 mol by part based on 100 mol by part of the dicarboxylic acid, and are highly oriented so that the stretch index defined by the following equations becomes not less than 130 cm.

$$\text{Stretch index} = \frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented product (excluding stopper portion)}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area of oriented bottle (excluding stopper portion)}}{\text{Internal volume of oriented bottle (excluding stopper portion)}} \quad (\text{cm}^{-1})$$

The second blow molded articles of the invention are characterized in that the blow molded articles are composed of a copolyester having an intrinsic viscosity $[\eta]$ of 0.5-1.5 dl/g formed by esterification of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 85-99 mol % of terephthalic acid and 1-15 mol % of isophthalic acid, said dihydroxy compound component comprising 80-99 mol % of ethylene glycol and 1-20 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxyl groups and being used in an amount of 0.05-0.3 mol by part based on 100 mol by part of the dicarboxylic acid, and are highly oriented so that the stretch index as defined above becomes not less than 130 cm.

The third blow molded articles of the invention are characterized in that the blow molded articles are composed of a copolyester formed by esterification of dicarboxylic acid with a dihydroxy compound component, said dicarboxylic acid comprising 0-80 mol % of terephthalic acid and 20-100 mol % of isophthalic acid, and said dihydroxy compound component comprising 5-90 mol % of 1,3-bis(2-hydroxyethoxy)benzene or 1,4-bis(hydroxyethoxy)benzene and 10-95 mol % of ethylene glycol, and are highly oriented so that the stretch index as defined above becomes not less than 130 cm.

The fourth blow molded articles of the invention are characterized in that the blow molded articles are composed of a copolyester having an intrinsic viscosity $[\eta]$ of 0.5-1.5 dl/g formed by esterification of dicarboxylic acid with ethylene glycol, said dicarboxylic acid comprising 80-99.5 mol % of terephthalic acid and 0.5-20 mol % of 2,6-naphthalenedicarboxylic acid, and are highly oriented so that the stretch index as defined above becomes not less than 130 cm.

The fifth blow molded articles of the invention are characterized in that the blow molded articles are composed of a copolyester having an intrinsic viscosity $[\eta]$ of 0.5-1.5 dl/g formed by esterification of dicarboxylic acid with ethylene glycol, said dicarboxylic acid comprising 85-99.5 mol % of terephthalic acid and 0.5-15 mol % of isophthalic acid, and are highly oriented so that the stretch index as defined above becomes not less than 130 cm.

The sixth blow molded articles of the invention are characterized in that the blow molded articles are composed of a copolyester having an intrinsic viscosity $[\eta]$ of 0.5-1.5

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dl/g formed by esterification of dicarboxylic acid with ethylene glycol, said dicarboxylic acid comprising 85-99.5 mol % of terephthalic acid and 0.5-15 mol % of aliphatic dicarboxylic acid of 6-10 carbon atoms, and are highly oriented so that the stretch index as defined above becomes not less than 130 cm.

The seventh blow molded articles of the invention are characterized in that the blow molded articles are composed of a copolyester having an intrinsic viscosity $[\eta]$ of 0.5-1.5 dl/g formed by esterification of terephthalic acid with a dihydroxy compound component, said dihydroxy compound component comprising 85-99.5 mol % of ethylene glycol and 0.5-15 mol % of neopentyl glycol, and are highly oriented so that the stretch index as defined above becomes not less than 130 cm.

The eighth blow molded articles of the invention are characterized in that the blow molded articles are composed of a copolyester having an intrinsic viscosity $[\eta]$ of 0.5-1.5 dl/g formed by esterification of terephthalic acid with a dihydroxy compound component, said dihydroxy compound component comprising 85-99.5 mol % of ethylene glycol and 0.5-15 mol % of cyclohexanedimethanol, and are highly oriented so that the stretch index as defined above becomes not less than 130 cm.

The ninth blow molded articles of the invention are characterized in that the blow molded articles are composed of a copolyester having an intrinsic viscosity $[\eta]$ of 0.5-1.5 dl/g formed by esterification of terephthalic acid with a dihydroxy compound component, said dihydroxy compound component comprising 93-98 mol % of ethylene glycol and 2-7 mol % of diethylene glycol, and are highly oriented so that the stretch index as defined above becomes not less than 130 cm.

The tenth blow molded articles of the invention are characterized in that the blow molded articles are composed of a polyester resin composition comprising [A] 95-99% by weight of a polyethylene terephthalate resin and [B] 1-5% by weight of a copolyester formed by esterification of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 0-80 mol % of terephthalic acid and 20-100 mol % of isophthalic acid, said dihydroxy compound component comprising 10-95 mol % of ethylene glycol and 5-90 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxyl groups and being used in an amount of 0.05-1.0 part by mol based on 100 parts by mol of the dicarboxylic acid, and are highly oriented so that the stretch index as defined above becomes not less than 130 cm.

The eleventh blow molded articles of the invention are characterized in that the blow molded articles are composed of a polyester resin composition comprising [A] 95-99% by weight of a polyethylene terephthalate resin and [B] 1-5% by weight of a copolyester formed by esterification of dicarboxylic acid with a dihydroxy compound component, said dicarboxylic acid comprising 0-80 mol % of terephthalic acid and 20-100 mol % of isophthalic acid, and said dihydroxy compound component comprising 5-90 mol % of 1,3-bis(2-hydroxyethoxy)benzene or 1,4-bis(hydroxyethoxy)benzene and 10-95 mol % of ethylene glycol, and are highly oriented so that the stretch index as defined above becomes more than 130 cm.

The twelfth blow molded articles of the invention are characterized in that the blow molded articles are composed of a polyester resin composition comprising [A] 30-99% by weight of a polyethylene terephthalate resin and [B] 1-70%

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by weight of copolyesters formed by esterification of dicarboxylic acid with ethylene glycol, said dicarboxylic acid comprising 10-92 mol % of terephthalic acid and 8-90 mol % of isophthalic acid, and are highly oriented so that the orientation index as defined above becomes more than 130 cm.

The thirteenth blow molded articles of the invention are characterized in that the blow molded articles are composed of a polyester resin composition comprising [A] 80-99% by weight of a polyethylene terephthalate resin and [B] 5-20% by weight of a copolyester formed by esterification of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 0-80 mol % of terephthalic acid and 20-100 mol % of isophthalic acid, said dihydroxy compound component comprising 10-95 mol % of ethylene glycol and 5-90 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxyl groups and being used in an amount of 0.05-1.0 part by mol based on 100 parts by mol of the dicarboxylic acid, and are highly oriented so that the stretch index as defined above becomes not less than 130 cm.

The fourteenth blow molded articles of the invention are characterized in that the blow molded articles are composed of a polyester resin composition comprising [A] a polyethylene terephthalate resin and [B] at least one polyester resin selected from the group consisting of (i) a polyethylene naphthalate resin, (ii) a polyethylene isophthalate resin, (iii) a copolyester formed by esterification of dicarboxylic acid containing terephthalic acid and 2,6-naphthalenedicarboxylic acid with ethylene glycol, (iv) a copolyester formed by esterification of terephthalic acid with a dihydroxy compound component containing ethylene glycol and cyclohexanediethanol, (v) a copolyester formed by esterification of terephthalic acid with a dihydroxy compound component containing ethylene glycol and neopentyl glycol, (vi) a copolyester formed by esterification of terephthalic acid with a dihydroxy compound component containing ethylene glycol and diethylene glycol, and (vii) a copolyester formed by esterification of dicarboxylic acid containing terephthalic acid and an aliphatic dicarboxylic acid of 6-10 carbon atoms with ethylene glycol, and are highly oriented so that the stretch index as defined above becomes not less than 130 cm.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a rough sketch illustrative of the blow molded article of the present invention.

1	Blow molded article	2	Shoulder portion
3	Upper shoulder portion	4	Body portion
5	Lower shoulder portion	6	Bottom portion

DETAILED DESCRIPTION OF THE INVENTION

The blow molded articles of the present invention are illustrated below in detail. First, copolyesters and polyester resin compositions from which the blow molded articles are formed are illustrated hereinafter.

Copolyester

The first blow molded articles of the present invention are formed from a copolyester obtained by esterification of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound.

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In the copolyesters as illustrated above, the carboxylic acid used comprises 0-80 mol %, preferably 0.5-50 mol % and especially 2-30 mol % of terephthalic acid and 20-100 mol %, preferably 50-99.5 mol % and especially 50-98 mol % of isophthalic acid, and the dihydroxy compound component used comprises 10-95 mol %, preferably 15-90 mol % of ethylene glycol and 5-90 mol %, preferably 10-85 mol % of 1,3-bis(2-hydroxyethoxy)benzene.

Further, the polyfunctional hydroxy compound used has at least three hydroxyl groups and used in an amount of 0.05-1.0 part by mol, preferably 0.1-0.5 part by mol based on 100 parts by mol of the dicarboxylic acid.

When blow molded articles are prepared from copolyesters obtained by reacting dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound in the proportions as defined above, the resulting blow molded articles are found to have such advantages that they are excellent in gas barrier properties and transparency, favorable in moldability with no irregularity in thickness and small in shrinkage factor.

Examples of the polyfunctional hydroxy compound used preferably include trimethylolmethane, trimethylolpropane and trimethylolpropane, and of these compounds, preferred is trimethylolpropane.

The above-mentioned copolyesters desirably have an intrinsic viscosity $[\eta]$, as measured in o-chlorophenol at 25°C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g and especially 0.8-0.85 dl/g.

The above-mentioned copolyesters and such copolyesters as will be mentioned later may be prepared in accordance with the known polycondensation techniques employed conventionally in preparing polyethylene terephthalate. The dicarboxylic acid may be fed, as such, to the reaction system, or may be fed in the form of dialkyl ester or diol ester thereof.

Further, the dihydroxy compound component may be fed, as such, to the reaction system, or may be fed in the form of dihydroxy ester of carboxylic acid.

Catalysts used in the above-mentioned polycondensation may be those conventionally used in preparing polyethylene terephthalate. These catalysts used include metals such as antimony, germanium and titanium, or compounds thereof. The compounds of these metals used as the catalysts may be in the form of an oxide, hydride, halide, inorganic acid salt, organic acid salt, complex salt, double salt, alcoholate or phenolate. These catalysts may be used either singly or in admixture of two or more. The catalysts may be fed to the reaction system at the initial stage of esterification reaction or ester interchange reaction, or may be fed to the reaction system before said initial stage moves to the stage of polycondensation reaction.

At the time when the polycondensation is initiated, there may be used various additives such as catalysts for ester interchange reaction used at the time of preparing polyethylene terephthalate, inhibitors for diethylene glycol formation, heat stabilizers, light stabilizers, lubricants, pigments and dyes.

The catalysts for ester interchange reaction used herein include metallic compounds of calcium, magnesium, lithium, zinc, cobalt or manganese, and these metallic compounds may be in the form of an oxide, hydride, halide, inorganic acid salt or organic acid salt. The inhibitors for diethylene glycol formation include amines such as triethylamine and tri-n-butylamine, and quaternary ammonium compounds such as tetraethylammonium hydroxide and tetrabutylammonium hydroxide. The heat stabilizers include

phosphoric acid, phosphorous acid, hypophosphorous acid or phosphorus compounds such as esters thereof.

The copolyesters used in the invention may be prepared by the known melt polycondensation techniques, or may be prepared, under certain circumstances, by the solid phase polycondensation of the melt polycondensation techniques.

In the melt polycondensation as mentioned above, there may also be employed the so-called direct polycondensation technique or the so-called ester interchange polycondensation technique. That is, the melt copolycondensation may be carried out, for example, by a process wherein a condensate of terephthalic acid and isophthalic acid, or dicarboxylic acid consisting essentially of these acids, or ester derivative thereof with ethylene glycol, 1,3-bis(2-hydroxyethoxy)benzene, polyfunctional hydroxy compound or a condensate thereof with the dicarboxylic acid is allowed to undergo, either at a time or successively, esterification or ester interchange reaction, preferably at 100°-280° C., to form the initial polycondensate thereof, and the initial polycondensate thus formed is then allowed to undergo polycondensation reaction at a temperature higher than the melting point of said initial polycondensate, preferably at 200°-300° C., in vacuo or in an inert gas stream under agitation.

The copolyesters used in the invention may also be prepared by subjecting the copolyester obtained by the melt polycondensation technique further to solid phase polycondensation and thereby increasing the molecular weight of the resulting copolyester. The solid phase polycondensation may be carried out, for example, by a process wherein the copolyester obtained by the melt polycondensation is divided into fine particles which are then maintained at a temperature below the melting point of the copolyester, preferably 180°-240° C. in vacuo or in an inert gas stream.

The second blow molded articles of the invention are composed of a copolyester obtained by esterification of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound. In the copolyesters as illustrated above, the dicarboxylic acid used comprises 85-99 mol %, preferably 90-99 mol % of terephthalic acid and 1-15 mol %, preferably 1-10 mol % of isophthalic acid, and the dihydroxy compound component used comprises 80-99 mol %, preferably 85-99 mol % of ethylene glycol and 1-20 mol %, preferably 1-15 mol % of 1,3-bis(2-hydroxyethoxy)benzene.

Further, the polyfunctional hydroxy compound used has at least three hydroxyl groups and used in an amount of 0.05-0.3 part by mol, preferably 0.05-0.2 part by mol based on 100 parts by mol of the dicarboxylic acid.

The copolyesters mentioned above desirably have an intrinsic viscosity $[\eta]$, as measured in o-chlorophenol at 25° C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g.

In preparing the above-mentioned copolyesters, there may be used, in addition to terephthalic acid and isophthalic acid mentioned above, other dicarboxylic acids in such an amount that characteristics of the resulting copolyester are not marred, for example, not more than 1 mol %. The other dicarboxylic acids usable herein include phthalic acid, 2-methylterephthalic acid, 2,6-naphthalenedicarboxylic acid, etc.

In addition to ethylene glycol and 1,3-bis(2-hydroxyethoxy)benzene used in the invention as the dihydroxy compounds, there may also be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are dihydroxy compounds of 3-15 carbon atoms such as 1,3-

propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, cyclohexanedimethanol, 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4- β -hydroxyethoxyphenyl)propane and bis(4- β -hydroxyethoxyphenyl)sulfone.

The third blow molded articles of the invention are formed from a copolyester obtained by esterification of dicarboxylic acid with a dihydroxy compound component.

In the copolyesters mentioned above, the dicarboxylic acid comprises 0-80 mol %, preferably 0-30 mol % of terephthalic acid and 20-100 mol %, preferably 50-100 mol % of isophthalic acid, and the dihydroxy compound component comprises 5-90 mol %, preferably 10-85 mol % of 1,3-bis(2-hydroxyethoxy)benzene or 1,4-bis(2-hydroxyethoxy)benzene and 10-95 mol %, preferably 15-90 mol % of ethylene glycol.

The above-mentioned copolyesters desirably have an intrinsic viscosity $[\eta]$, as measured in o-chlorophenol at 25° C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g.

When blow molded articles are prepared from such copolyesters as mentioned above, the resulting blow molded articles are excellent in gas barrier properties and transparency, and also have excellent mechanical characteristics.

In preparing the above-mentioned copolyesters, there may also be used, in addition to terephthalic acid and isophthalic acid used as the dicarboxylic acid, other dicarboxylic acids, and there may also be used, in addition to 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene and ethylene glycol used as the dihydroxy compound component, other dihydroxy compounds.

The fourth blow molded articles of the invention are formed from a copolyester obtained by esterification of dicarboxylic acid with ethylene glycol.

In the copolyesters as obtained above, the dicarboxylic acid comprises 80-99.5 mol %, preferably 90-99.5 mol % of terephthalic acid and 0.5-20 mol %, preferably 0.5-10 mol % of 2,6-naphthalenedicarboxylic acid.

The above-mentioned copolyesters used in the invention desirably have an intrinsic viscosity $[\eta]$, as measured in o-chlorophenol at 25° C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g.

The copolyesters as illustrated above are excellent in gas barrier properties and transparency, and also excellent in moldability or stretchability.

In preparing the above-mentioned copolyesters, there may also be used, in addition to terephthalic acid and 2,6-naphthalenedicarboxylic acid used as the dicarboxylic acids, other dicarboxylic acids in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dicarboxylic acids usable herein include isophthalic acid, phthalic acid, 2-methylterephthalic acid, etc.

In addition to ethylene glycol used as the dihydroxy compound component in preparing the copolyesters mentioned above, there may also be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are dihydroxy compounds of 3-15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, cyclohexanedimethanol, 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4- β -hydroxyethoxyphenyl)propane and bis(4- β -hydroxyethoxyphenyl)sulfone.

The fifth blow molded articles of the invention are formed from a copolyester obtained by esterification of dicarboxylic acid with ethylene glycol.

In the copolyesters as mentioned above, the dicarboxylic acid comprises 80-99.5 mol %, preferably 90-99.5 mol % of terephthalic acid and 0.5-15 mol %, preferably 0.5-10 mol % of isophthalic acid.

The above-mentioned copolyesters used in the invention desirably have an intrinsic viscosity $[\eta]$, as measured in *o*-chlorophenol at 25° C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g. The copolyesters having this intrinsic viscosity of 0.5-1.5 dl/g are excellent in mechanical strength and also in melt moldability.

In preparing the above-mentioned copolyesters, there may also be used, in addition to terephthalic acid and isophthalic acid used as the dicarboxylic acid, other dicarboxylic acids in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dicarboxylic acids usable herein include phthalic acid, 2-methylterephthalic acid, 2,6-naphthalenedicarboxylic acid, etc.

In addition to ethylene glycol used as the dihydroxy compound component, there may also be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are dihydroxy compounds of 3-15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, cyclohexanedimethanol, 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4- β -hydroxyethoxyphenyl)propane and bis(4- β -hydroxyethoxyphenyl)sulfone.

The sixth blow molded articles of the invention are formed from a copolyester obtained by esterification of dicarboxylic acid with ethylene glycol.

In the copolyesters as mentioned above, the dicarboxylic acid comprises 85-99.5 mol %, preferably 90-99.5 mol % of terephthalic acid and 0.5-15 mol %, preferably 0.5-10 mol % of aliphatic dicarboxylic acid of 6-10 carbon atoms.

Examples of the aliphatic dicarboxylic acid used include adipic acid, sebacic acid, etc.

These aliphatic dicarboxylic acid may also be used as a mixture thereof.

Of these aliphatic dicarboxylic acids, particularly preferred is adipic acid or sebacic acid.

When the amount of the aliphatic dicarboxylic acid of 6-10 carbon atoms used is 0.5-15 mol %, the resulting copolyester is excellent in transparency and also excellent in moldability or stretchability.

In preparing the above-mentioned copolyesters, there may also be used, in addition to terephthalic acid and aliphatic dicarboxylic acid used as the dicarboxylic acid, other dicarboxylic acids in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dicarboxylic acids usable herein include isophthalic acid, phthalic acid, 2-methylterephthalic acid, 2,6-naphthalenedicarboxylic acid, etc.

In addition to ethylene glycol used as the dihydroxy compound component, there may also be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are dihydroxy compounds of 3-15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, cyclohexanedimethanol, 1,3-bis(2-

hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4- β -hydroxyethoxyphenyl)propane and bis(4- β -hydroxyethoxyphenyl)sulfone.

The above-mentioned copolyesters desirably have an intrinsic viscosity $[\eta]$, as measured in *o*-chlorophenol at 25° C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g. The copolyesters having this intrinsic viscosity $[\eta]$ of 0.5-1.5 are excellent in mechanical strength and also in melt moldability.

The seventh blow molded articles of the invention are formed from a copolyester obtained by esterification of terephthalic acid with a dihydroxy compound component.

In the copolyesters as obtained above, the dihydroxy compound component comprises 85-99.5 mol %, preferably 90-99.5 mol % of ethylene glycol and 0.5-15 mol %, preferably 0.5-10 mol % of neopentyl glycol.

In preparing the above-mentioned copolyesters, there may also be used, in addition to terephthalic acid used as the dicarboxylic acid, other dicarboxylic acids in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dicarboxylic acids usable herein include isophthalic acid, phthalic acid, 2-methylterephthalic acid, 2,6-naphthalenedicarboxylic acid, etc.

In addition to ethylene glycol and neopentyl glycol used as the dihydroxy compound component in preparing the above-mentioned copolyesters, there may also be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are dihydroxy compounds of 3-15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, cyclohexanediol, cyclohexanedimethanol, 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4- β -hydroxyethoxyphenyl)propane and bis(4- β -hydroxyethoxyphenyl)sulfone.

The above-mentioned copolyesters used in the invention desirably have an intrinsic viscosity $[\eta]$, as measured in *o*-chlorophenol at 25° C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g. The copolyesters having this intrinsic viscosity $[\eta]$ of 0.5-1.5 dl/g are excellent in mechanical strength and also excellent in melt moldability.

The eighth blow molded articles of the invention are formed from a copolyester obtained by esterification of terephthalic acid with a dihydroxy compound component.

In the copolyesters as obtained above, the dihydroxy compound component comprises 85-99.5 mol %, preferably 90-99.5 mol % of ethylene glycol and 0.5-15 mol %, preferably 0.5-10 mol % of cyclohexanedimethanol.

In preparing the above-mentioned copolyesters, there may also be used, in addition to terephthalic acid used as the dicarboxylic acid, other dicarboxylic acids in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dicarboxylic acids usable herein include isophthalic acid, phthalic acid, 2-methylterephthalic acid, 2,6-naphthalenedicarboxylic acid, etc.

In addition to ethylene glycol and cyclohexanedimethanol used as the dihydroxy compound component in preparing the above-mentioned copolyesters, there may also be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are dihydroxy compounds of 3-15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, 1,3-bis(2-hydroxyethoxy)

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benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4- β -hydroxyethoxyphenyl)propane and bis(4- β -hydroxyethoxyphenyl)sulfone.

The above-mentioned copolyesters used in the invention desirably have an intrinsic viscosity $[\eta]$, as measured in *o*-chlorophenol at 25° C., of 0.5–1.5 dl/g, preferably 0.6–1.2 dl/g. The copolyesters having this intrinsic viscosity $[\eta]$ of 0.5–1.5 dl/g are excellent in mechanical strength and also excellent in melt moldability.

The sixth blow molded articles of the invention are formed from a copolyester obtained by esterification of terephthalic acid with a dihydroxy compound component.

In the copolyesters as obtained above, the dihydroxy compound component comprises 93–98 mol %, preferably 95–98 mol % of ethylene glycol and 2–7 mol %, preferably 2–5 mol % of diethylene glycol.

In preparing the above-mentioned copolyesters, there may also be used, in addition to terephthalic acid used as the dicarboxylic acid, other dicarboxylic acids in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dicarboxylic acids usable herein include isophthalic acid, phthalic acid, 2-methylterephthalic acid, 2,6-naphthalenedicarboxylic acid, etc.

In addition to ethylene glycol and diethylene glycol used as the dihydroxy compound component in preparing the above-mentioned copolyesters, there may be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are dihydroxy compounds of 3–15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, cyclohexanediolmethanol, 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4- β -hydroxyethoxyphenyl)propane and bis(4- β -hydroxyethoxyphenyl)sulfone.

The above-mentioned copolyesters used in the invention desirably have an intrinsic viscosity $[\eta]$, as measured in *o*-chlorophenol at 25° C., of 0.5–1.5 dl/g, preferably 0.6–1.2 dl/g. The copolyesters having this intrinsic viscosity $[\eta]$ of 0.5–1.5 dl/g are excellent in mechanical strength and also excellent in melt moldability.

The tenth blow molded articles of the invention are formed from a polyester resin composition containing [A] 95–99% by weight, preferably 96–98% by weight of a polyethylene terephthalate resin and [B] 1–5% by weight, preferably 2–4% by weight of the copolyester used in the first blow molded articles of the invention, said copolyester being obtained by esterification of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 0–80 mol %, preferably 0.5–50 mol % and especially 2–50 mol % of terephthalic acid and 20–100 mol %, preferably 50–99.5 mol % and especially 50–98 mol % of isophthalic acid, said dihydroxy compound component comprising 10–95 mol %, preferably 15–90 mol % of ethylene glycol and 5–90 mol %, preferably 10–85 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxyl groups and being used in an amount of 0.05–1.0 part by mol, preferably 0.1–0.5 part by mol based on 100 parts by mol of the dicarboxylic acid.

The above-mentioned copolyesters desirably have an intrinsic viscosity $[\eta]$, as measured in *o*-chlorophenol at 25° C., of 0.5–1.5 dl/g, preferably 0.6–1.2 dl/g.

The polyethylene terephthalate resin [A] contained in the above-mentioned polyester resin compositions is a polyester containing ethylene terephthalate units as the main structural units.

The polyethylene terephthalate resin desirably contains usually not less than 50 mol %, preferably not less than 70 mol % of the ethylene terephthalate structural units. The polyethylene terephthalate resin containing such ethylene terephthalate structural units as mentioned above is composed of diol component units and dicarboxylic acid component units. The dicarboxylic acid component units which the polyethylene terephthalate resin comprises may contain, in addition to the terephthalic acid component units, small amounts of other aromatic dicarboxylic acid component units. Such aromatic dicarboxylic acid component units include, for example, component units derived from isophthalic acid, phthalic acid, naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, etc.

In the ethylene terephthalate units which the polyethylene terephthalate resin comprises, there are present the terephthalic acid component units in an amount of usually 50–100 mol %, preferably 70–100 mol %, the aromatic dicarboxylic acid component units other than the terephthalic acid component units in an amount of usually 0–50 mol %, preferably 0–30 mol %, the ethylene glycol component units, i.e. the diol component units, in an amount of usually 50–100 mol %, preferably 70–100 mol %, the diol component units other than ethylene glycol component units in an amount of usually 0–50 mol %, preferably 0–30 mol %, and the polyfunctional compound component units in an amount of usually 1–2 mol %, preferably 0–1 mol %.

The above-mentioned polyethylene terephthalate resin desirably has an intrinsic viscosity $[\eta]$ (as measured in a 1:1 by weight mixed solvent of phenol and tetrachloroethane) of usually 0.5–1.5 dl/g, preferably 0.6–1.2 dl/g, a melting point of usually 210°–265° C., preferably 220°–260° C., and a glass transition temperature of usually 50°–120° C., preferably 60°–100° C.

The polyester resin compositions containing the above-mentioned polyethylene terephthalate resin [A] and copolyester resin [B] in the proportions as defined above are excellent in gas barrier properties and moldability, while being freed from deterioration in transparency and mechanical properties owned by the polyethylene terephthalate used therein.

The above-mentioned polyester resin compositions and the polyester resin compositions as will be mentioned later may be prepared by mixing the polyethylene terephthalate resin with the copolyester resin using a mixing equipment such as a Henschel mixer, V blender, ribbon blender and tumbler blender, followed by melt mixing the resulting mixture using a single screw extruder, double-screw extruder, kneader or Banbury mixer, or by pulverizing said mixture.

The copolyester and polyester resin compositions used for preparing blow molded articles in the invention may be incorporated with various additives commonly added to polyester such as heat stabilizers, weathering agents, anti-static agents, slip agents, releasing agents, pigment dispersion agents, pigments or dyes in such an amount that no hindrances are thrown in the way of accomplishing the objects of the invention.

The eleventh blow molded articles of the invention are formed from a polyester resin composition containing [A] 95–99% by weight, preferably 96–98% by weight of a polyethylene terephthalate resin and [B] 1–5% by weight, preferably 2–4% by weight of the copolyester used in the third blow molded articles of the invention formed by esterification of dicarboxylic acid with a dihydroxy compound component, said dicarboxylic acid comprising 0–80

mol %, preferably 0-50 mol % of terephthalic acid and 20-100 mol %, preferably 50-100 mol % of isophthalic acid, and said dihydroxy compound component comprising 5-90 mol %, preferably 10-85 mol % of 1,3-bis(2-hydroxyethoxy)benzene or 1,4-bis(2-hydroxyethoxy)benzene and 10-95 mol %, preferably 15-90 mol % of ethylene glycol.

The polyethylene terephthalate resin used herein is the same as used in the tooth blow molded articles of the invention.

The above-mentioned copolyester desirably has an intrinsic viscosity $[\eta]$, as measured in *o*-chlorophenol at 25° C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g.

The polyester resin compositions containing the above-mentioned polyethylene terephthalate resin [A] and copolyester [B] in the proportions as defined above are excellent in gas barrier properties and moldability while being freed from deterioration in transparency and mechanical properties owned by the polyethylene terephthalate used therein.

The twelfth blow molded articles of the invention are formed from a polyester resin composition containing [A] 30-99% by weight, preferably 30-98% by weight and especially 30-97% by weight of a polyethylene terephthalate resin and [B] 1-70% by weight, preferably 2-70% by weight and especially 3-70% by weight of copolyester formed by esterification of dicarboxylic acid with ethylene glycol, said dicarboxylic acid comprising 10-92 mol %, preferably 50-92 mol % and especially 80-92 mol % of terephthalic acid and 8-90 mol %, preferably 8-50 mol % and especially 8-20 mol % of isophthalic acid.

The polyethylene terephthalate resin [A] used herein is the same as used in the tooth blow molded articles of the invention.

In preparing the above-mentioned copolyester, there may also be used, in addition to terephthalic acid and isophthalic acid used as the dicarboxylic acid, other dicarboxylic acids in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein include phthalic acid, 2-methylterephthalic acid, 2,6-naphthalenedicarboxylic acid, etc.

In addition to ethylene glycol used as the dihydroxy compound in preparing the above-mentioned copolyester, there may also be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are dihydroxy compounds of 3-15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, cyclohexanemethanol, 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4- β -hydroxyethoxyphenyl)propane and bis(4- β -hydroxyethoxyphenyl)sulfone.

The above-mentioned copolyester used in the invention desirably has an intrinsic viscosity $[\eta]$, as measured in *o*-chlorophenol at 25° C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g. The copolyester having this intrinsic viscosity $[\eta]$ of 0.5-1.5 dl/g is excellent in mechanical strength and also excellent in melt moldability.

The polyester resin compositions containing the above-mentioned polyethylene terephthalate resin [A] and copolyester [B] in the proportions as defined above are excellent in gas barrier properties and moldability while being freed from deterioration in transparency and mechanical properties owned by the polyethylene terephthalate used therein.

The thirteenth blow molded articles of the invention are formed from a polyester resin composition containing [A]

80-95% by weight, preferably 85-93% by weight of a polyethylene terephthalate resin and [B] 5-20% by weight, preferably 7-15% by weight of the copolyester used in the first blow molded articles of the invention formed by esterification of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 0-80 mol %, preferably 0.5-50 mol % and especially 2-50 mol % of terephthalic acid and 20-100 mol %, preferably 50-99.5 mol % and especially 50-98 mol % of isophthalic acid, said dihydroxy compound component comprising 10-95 mol %, preferably 15-90 mol % of ethylene glycol and 5-90 mol %, preferably 10-85 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxyl groups and being used in an amount of 0.05-1.0 part by mol based on 100 parts by mol of the dicarboxylic acid.

The polyethylene terephthalate resin [A] used herein is the same as used in the tooth blow molded articles of the invention.

The fourteenth blow molded articles of the invention are formed from a polyester resin composition containing [A] a polyethylene terephthalate resin and [B] at least one polyester resin selected from the group consisting of (i) a polyethylene naphthalate resin, (ii) a polyethylene isophthalate resin, (iii) a copolyester formed by esterification of dicarboxylic acid containing terephthalic acid and 2,6-naphthalenedicarboxylic acid with ethylene glycol, (iv) a copolyester formed by esterification of terephthalic acid with a dihydroxy compound component containing ethylene glycol and cyclohexanemethanol, (v) a copolyester formed by esterification of terephthalic acid with a dihydroxy compound containing ethylene glycol and neopentyl glycol, (vi) copolyesters formed by esterification of terephthalic acid with a dihydroxy compound component containing ethylene glycol and diethylene glycol, and (vii) a copolyester formed by esterification of dicarboxylic acid containing terephthalic acid and aliphatic dicarboxylic acid of 6-10 carbon atoms with ethylene glycol.

The polyethylene terephthalate resin [A] used herein is the same as used in the tooth blow molded articles of the invention.

The polyester resin [B] used, together with the above-mentioned polyethylene terephthalate resin [A], in the above-mentioned fourteenth blow molded articles of the invention is selected from the group consisting of the resins and copolyesters mentioned below.

(i) Polyethylene naphthalate resin

The polyethylene naphthalate resin used in the invention desirably contains not less than 60 mol %, preferably not less than 80 mol % and especially not less than 90 mol % of ethylene-2,6-naphthalate units derived from 2,6-naphthalenedicarboxylic acid and ethylene glycol, and may contain less than 40 mol % of structural units other than ethylene-2,6-naphthalate.

The structural units other than ethylene-2,6-naphthalate include those derived from aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, 2,7-naphthalene dicarboxylic acid, 2,5-naphthalenedicarboxylic acid, diphenyl-4,4'-dicarboxylic acid, 4,4'-diphenylethanedicarboxylic acid, 4,4'-diphenylsulfone-dicarboxylic acid, 4,4'-diphenoxyethanedicarboxylic acid and dibromoterephthalic acid; aliphatic dicarboxylic acids such as adipic acid, azelaic acid, sebacic acid and decanedicarboxylic acid; alicyclic dicarboxylic acids such as 1,4-cyclohexanedicarboxylic acid, cyclopropanedicarboxylic acid and hexahydroterephthalic acid; hydroxycarboxylic acids such as glycolic acid,

p-hydroxybenzoic acid and p-hydroxyethoxybenzoic acid; propylene glycol, trimethylene glycol, diethylene glycol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, decamethylene glycol, neopentyl glycol, p-xylene glycol, 1,4-cyclohexane dimethanol, bisphenol A, p,p'-diphenylsulfone, 1,4-bis(β -hydroxyethoxy)benzene, 2,2-bis(p- β -hydroxyethoxyphenyl)propane, polyalkylene glycol, p-phenylenebis(dimethylsiloxane) and glycerin.

Further, the polyethylene naphthalate resin used in the invention may contain small amounts, for example, not more than 2 mol % of structural units derived from polyfunctional compounds such as trimesic acid, trimethylolmethane, trimethylolpropane, trimethylolmethane and pentaerythritol.

Furthermore, the polyethylene naphthalate resin used in the invention may contain small amounts, for example, not more than 2 mol % of structural units derived from monofunctional compounds such as benzoylbenzoic acid, diphenylsulfonemonocarboxylic acid, stearic acid, methoxypolyethylene glycol and phenoxypolyethylene glycol.

The polyethylene naphthalate resin as illustrated above is substantially linear in structure, and this can be confirmed by the fact that said polyethylene naphthalate resin dissolves in o-chlorophenol.

The intrinsic viscosity $[\eta]$, as measured in o-chlorophenol at 25° C., of the polyethylene naphthalate is desirably 0.2-1.1 dl/g, preferably 0.3-0.9 dl/g and especially 0.4-0.8 dl/g.

The intrinsic viscosity $[\eta]$ of polyethylene naphthalate is determined by the following procedure. That is, polyethylene naphthalate is dissolved at a concentration of 1 g/100 ml in o-chlorophenol to measure the viscosity of the resulting solution by means of a Ubbelohde viscometer, then o-chlorophenol is gradually added to said solution to measure the viscosity of the resulting solution at a lower concentration side, and the two viscosities thus measured are extrapolated to 0% concentration to obtain an intrinsic viscosity ($[\eta]$).

The heat-up crystallizing temperature (T_c) of polyethylene naphthalate when heated at a rate of 10° C./min by means of a differential scanning calorimeter (DSC) is usually more than 150° C., preferably 160°-230° C. and especially 170°-220° C.

The heat-up crystallizing temperature (T_c) of polyethylene naphthalate is determined by the following procedure. That is, a polyethylene naphthalate chip is dried for not less than about 5 hours at about 140° C. and a pressure of about 5 mmHg using DSC-2 Model differential scanning calorimeter manufactured by Perkin Elmer Co., Ltd. A thin specimen of about 10 mg is taken out of the center portion of the dried chip, and the specimen is encapsulated in an aluminum pan for liquid in a nitrogen atmosphere to carry out the measurement. The aluminum pan is raised in temperature rapidly from room temperature, and the molten specimen is kept therein at 290° C. for 10 minutes. The aluminum pan is then cooled rapidly to room temperature, and thereafter the aluminum pan is heated at a rate of 10° C./min to obtain an apex temperature of exothermic peak detected at that time.

In the polyester resin compositions containing the above-mentioned polyethylene naphthalate resin and polyethylene terephthalate resin, the former resin is used in an amount of 0.5-20% by weight, preferably 0.5-15% by weight, and the latter is used in an amount of 80-99.5% by weight, preferably 85-99.5% by weight.

(II) Polyethylene isophthalate resin

The polyethylene isophthalate resin used in the invention is polyester containing ethylene isophthalate units as the main structural units.

The content of the ethylene isophthalate units in the polyethylene isophthalate resin is usually not less than 50 mol %, preferably not less than 70 mol %. The polyethylene isophthalate resin containing such ethylene isophthalate structural units as mentioned above is composed of diol component units and dicarboxylic acid component units. The dicarboxylic acid component units constituting the polyethylene isophthalate resin may contain small amounts of other aromatic dicarboxylic acid component units in addition to the isophthalic acid component units. Such aromatic dicarboxylic acid component units include, for example, component units derived from isophthalic acid, phthalic acid, naphthalenedicarboxylic acid and 2,6-naphthalenedicarboxylic acid.

In the ethylene isophthalate units which the polyethylene isophthalate resin comprises, there are present the isophthalic acid component units in an amount of usually 50-100 mol %, preferably 70-100 mol %, the aromatic dicarboxylic acid component units other than the isophthalic acid component units in an amount of usually 0-50 mol %, preferably 0-30 mol %, the ethylene glycol component units, i.e. the diol component units, in an amount of usually 50-100 mol %, preferably 70-100 mol %, the diol component units other than the ethylene glycol units in an amount of usually 0-50 mol %, preferably 0-30 mol %, and the polyfunctional compound component units in an amount of usually 1-2 mol %, preferably 0-1 mol %.

The above-mentioned polyethylene isophthalate resin desirably has an intrinsic viscosity $[\eta]$ (as measured in a mixed solvent (weight ratio 1/1) of phenol and tetrachloroethane) of usually 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g, a melting point of usually 210°-265° C., preferably 220°-260° C., and a glass transition temperature of usually 50°-120° C., preferably 60°-100° C.

In the polyester resin compositions containing the above-mentioned polyethylene isophthalate resin and polyethylene terephthalate resin, the latter resin is used in an amount of 85-99.5% by weight, preferably 90-99.5% by weight and the former is used in an amount of 0.5-15% by weight, preferably 0.5-10% by weight.

(III) Copolyester

The copolyester (III) is obtained by condensation reaction of dicarboxylic acid including terephthalic acid and 2,6-naphthalenedicarboxylic acid with ethylene glycol.

In preparing the above-mentioned copolyester, there may also be used, in addition to the above-mentioned terephthalic acid and 2,6-naphthalenedicarboxylic acid used as the dicarboxylic acid, other dicarboxylic acids in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dicarboxylic acids usable herein include isophthalic acid, phthalic acid, 2-methylterephthalic acid, etc.

In addition to ethylene glycol used as the dihydroxy compound component at the time of preparing the copolyester, there may also be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are dihydroxy compounds of 3-15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, cyclohexanedimethanol, 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4- β -hydroxyethoxyphenyl)propane and bis(4- β -hydroxyethoxyphenyl)sulfone.

The copolyester as illustrated above desirably has an intrinsic viscosity $[\eta]$, as measured in o-chlorophenol at 25° C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g.

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In the polyester resin composition obtained by blending of the above-mentioned copolyester and polyethylene terephthalate resin, it is desirable that said copolyester is formed by esterification of terephthalic acid and 2,6-naphthalenedicarboxylic acid with ethylene glycol in such amounts that the structural units derived from 2,6-naphthalenedicarboxylic acid becomes 0.5-20 mol %, preferably 0.5-10 mol % based on the structural units derived from all the dicarboxylic acid, and is blended with said polyethylene terephthalate resin.

(iv) Copolyester

The copolyester (iv) is obtained by the following cocondensation reaction of terephthalic acid with ethylene glycol and a dihydroxy compound component including cyclohexanedimethanol.

In preparing the above-mentioned copolyester, there may also be used, in addition to the above-mentioned terephthalic acid used as the dicarboxylic acid, other dicarboxylic acids in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dicarboxylic acids usable herein include isophthalic acid, phthalic acid, 2-methylterephthalic acid, 2,6-naphthalenedicarboxylic acid, etc.

In addition to ethylene glycol and cyclohexane dimethanol used as the dihydroxy compounds at the time of preparing the copolyester, there may also be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are dihydroxy compounds of 3-15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4- β -hydroxyethoxyphenyl)propane and bis(4- β -hydroxyethoxyphenyl)sulfone.

The above-mentioned copolyester used in the invention desirably has an intrinsic viscosity $[\eta]$, as measured in o-chlorophenol at 25° C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g.

In the polyester resin composition obtained by blending of the above-mentioned copolyester and polyethylene terephthalate resin, it is desirable that said copolyester is formed by esterification of terephthalic acid with the dihydroxy compounds including ethylene glycol and cyclohexane dimethanol in such amounts that the structural units derived from cyclohexanedimethanol becomes 0.5-15 mol %, preferably 0.5-10 mol % based on the structural units derived from all the dihydroxy compounds, and is blended with said polyethylene terephthalate resin.

(v) Copolyester

The copolyester (v) is obtained by cocondensation reaction of terephthalic acid with dihydroxy compounds including ethylene glycol and neopentyl glycol.

In preparing the above-mentioned copolyester, there may also be used, in addition to the above-mentioned terephthalic acid used as the dicarboxylic acid, other dicarboxylic acids in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dicarboxylic acids usable herein include isophthalic acid, phthalic acid, 2-methylterephthalic acid, 2,6-naphthalenedicarboxylic acid, etc.

In addition to ethylene glycol and neopentyl glycol used as the dihydroxy compounds at the time of preparing the copolyester, there may also be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are

dihydroxy compounds of 3-15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, cyclohexanediol, cyclohexanedimethanol, 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4- β -hydroxyethoxyphenyl)propane and bis(4- β -hydroxyethoxyphenyl)sulfone.

The above-mentioned copolyester desirably has an intrinsic viscosity $[\eta]$, as measured in o-chlorophenol at 25° C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g.

In the polyester resin composition obtained by blending the above-mentioned copolyester and polyethylene terephthalate resin, it is desirable that said copolyester is formed by esterification of terephthalic acid with the dihydroxy compounds including ethylene glycol and neopentyl glycol in such amounts that the structural units derived from neopentyl glycol becomes 0.5-15 mol %, preferably 0.5-10 mol % based on the structural units derived from all the dihydroxy compounds, and is blended with said polyethylene terephthalate resin.

(vi) Copolyester

The copolyester (vi) is obtained by cocondensation reaction of terephthalic acid with dihydroxy compounds including ethylene glycol and diethylene glycol.

In preparing the above-mentioned copolyester, there may also be used, in addition to terephthalic acid used as the dicarboxylic acid, other dicarboxylic acids in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dicarboxylic acids usable herein include isophthalic acid, phthalic acid, 2-methylterephthalic acid, 2,6-naphthalenedicarboxylic acid, etc.

In addition to ethylene glycol and diethylene glycol used as the dihydroxy compounds at the time of preparing the copolyester, there may also be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are marred, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are dihydroxy compounds of 3-15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, cyclohexanedimethanol, 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4- β -hydroxyethoxyphenyl)propane and bis(4- β -hydroxyethoxyphenyl)sulfone.

The above-mentioned copolyester desirably has an intrinsic viscosity $[\eta]$, as measured in o-chlorophenol at 25° C., of 0.5-1.5 dl/g, preferably 0.6-1.2 dl/g.

In the polyester resin composition obtained by blending of the above-mentioned copolyester and polyethylene terephthalate resin, it is desirable that said copolyester is formed by esterification of terephthalic acid with the dihydroxy compounds including ethylene glycol and diethylene glycol in such amounts that the structural units derived from diethylene glycol become 2-7 mol %, preferably 2-5 mol % based on the structural units derived from all the dihydroxy compounds, and is blended with said polyethylene terephthalate resin.

(vii) Copolyester

The copolyester (vii) is obtained by cocondensation reaction of dicarboxylic acid including terephthalic acid and aliphatic dicarboxylic acid of 6-10 carbon atoms with ethylene glycol.

The aliphatic dicarboxylic acid of 6-10 carbon atoms used herein includes concretely adipic acid, sebacic acid, etc.

These aliphatic dicarboxylic acids may be used as a mixture thereof.

Of these aliphatic dicarboxylic acids, particularly preferred is adipic acid or sebacic acid.

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In preparing the above-mentioned copolyester, there may also be used, in addition to the above-mentioned terephthalic acid and aliphatic dicarboxylic acid of 6-10 carbon atoms used as the dicarboxylic acids, other dicarboxylic acids in such an amount that no characteristics of the resulting copolymer are masked, for example, not more than 1 mol %. The other dicarboxylic acids usable herein include isophthalic acid, phthalic acid, 2-methylterephthalic acid, 2,6-naphthalenedicarboxylic acid, etc.

In addition to ethylene glycol used as the dihydroxy compound at the time of preparing the above-mentioned copolyester, there may also be used other dihydroxy compounds in such an amount that no characteristics of the resulting copolyester are masked, for example, not more than 1 mol %. The other dihydroxy compounds usable herein are dihydroxy compounds of 3-15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, cyclohexanedimethanol, 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4-β-hydroxyethoxyphenyl)propane and bis(4-β-hydroxyethoxyphenyl)sulfone.

In the polyester resin composition obtained by blending of the above-mentioned copolyester and polyethylene terephthalate resin, it is desirable that said copolyester is formed by esterification of dicarboxylic acid including terephthalic acid and aliphatic dicarboxylic acid of 6-10 carbon atoms with ethylene glycol in such amounts that the structural units derived from aliphatic dicarboxylic acid of 6-10 carbon atoms become 0.5-15 mol %, preferably 0.5-10 mol % based on the structural units derived from all the dicarboxylic acids, and is blended with said polyethylene terephthalate resin.

Blow molded article

The blow molded articles of the present invention are composed of the above-mentioned copolyester or polyester composition, and are highly oriented so that the stretch index as defined by the following equations becomes not less than 130 cm, preferably 140-220 cm and especially 150-200 cm.

$$\text{Stretch index} = \frac{\text{Internal volume (excluding stopper portion) of oriented bottle}}{\text{Internal volume (excluding stopper portion) of unoriented preform}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area (including stopper portion) of oriented bottle}}{\text{Internal volume (excluding stopper portion) of oriented bottle}} \quad (\text{cm}^{-2})$$

The stretch index of the blow molded article of the invention is illustrated below with reference to the accompanying FIG. 1. The blow molded article 1 of the invention is composed, as shown in FIG. 1, of a stopper portion 2, an upper shoulder portion 3, a body 4, a lower shoulder portion 5 and a bottom portion 6.

In preparing such blow molded article 1 as mentioned above, a preform 7 is used, and this preform 7 is shown in FIG. 1 by means of a dotted line.

The internal volume of such oriented blow molded article as mentioned above is an internal volume of the oriented blow molded article 1 excluding the stopper portion 2, particularly, an internal volume of a portion below a support ring 8 of the blow molded article 1, and more particularly, said internal volume means an internal volume of a portion below an imaginary straight line 9 of the blow molded article.

The internal volume of the unoriented preform is an internal volume of the preform 7 excluding the stopper

portion 2, particularly an internal volume of a portion below the support ring 8 of the preform 7, and more particularly said internal volume means an internal volume of a portion below the imaginary straight line 9 of the preform.

The internal surface area of the oriented blow molded article is an internal surface area including the stopper portion 2 of the oriented blow molded article 1, particularly an internal surface area of a portion below the support ring 8 of the oriented blow molded article 1, and more particularly said internal surface area means an internal surface area of a portion below the imaginary straight line 9 of the blow molded article.

The internal surface area S of the oriented blow molded article (excluding an internal surface area of the stopper portion) may be measured by the micro-division method wherein the blow molded article is divided, the profile of the internal surface area of the blow molded article is detected by means of the three-dimensional tester, and the blow molded article is divided into small portions, followed by integrating the surface area of the small portions thus divided. When the oriented blow molded article has a simple shape, the internal surface area thereof may also be obtained as an approximate value by assuming that the body of the blow molded article is a cylinder, and the lower and upper portions of the blow molded article are respectively a hemisphere.

The above-mentioned stretch index of the oriented blow molded article may be calculated on the basis of the internal surface area and internal volume (excluding the stopper portion) of the oriented blow molded article and the internal volume of the unoriented blow molded article (excluding the stopper portion) as obtained. The internal volume of the blow molded article may be easily measured by placing a liquid such as water therein. The units of f value and orientation index are cm^{-2} and cm, respectively.

In the blow molded article of the invention, the wall thickness of the body is similar to that of conventional blow molded articles, and is usually 0.1-0.5 mm, preferably 0.2-0.4 or thereabouts.

The process for preparing the blow molded article of the invention is illustrated below.

First, a preform is prepared from the above-mentioned copolyester, for example, by the methods, per se, known.

The preform used in the invention desirably has a length shorter than that of the prior art preform, because in the present process the portion to be oriented of the present preform is more highly oriented by far than the prior art preform. If necessary, the present preform may be molded shorter in diameter than the prior art preform.

In the process of the invention, the blow molded article is prepared by blow molding the preform for blow molded article as mentioned above.

In that case, the present preform is blow molded so that the resulting blow molded article has the stretch index as defined above of not less than 130 cm, preferably 140-220 cm and especially 150-200 cm.

The temperature employed at the time of blow molding the present preform is 80°-110° C., preferably 90°-105° C.

EFFECT OF THE INVENTION

The blow molded articles of the present invention are prepared by stretching specific copolyesters or polyester resin compositions both having a specific stretch ratio. Accordingly, they have excellent transparency and moldability as well as gas barrier properties, and they are also advantageous from the economical standpoint.

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The present invention is illustrated below with reference to examples, but it should be construed that the present invention is in no way limited to those examples.

EXAMPLE 1

A dicarboxylic acid component composed of 99 mol % of terephthalic acid and 1 mol % of 2,6-naphthalenedicarboxylic acid was esterified with ethylene glycol by the prior art method to obtain a copolyester having an intrinsic viscosity $[\eta]$ of 0.65 dl/g.

The thus obtained copolyester was molded by a molding machine (trade name of M-100A, manufactured by Melli Selsakusho K.K.) to obtain a preform for forming a bottle. The molding temperature was 270° to 290° C.

The thus obtained preform was molded by a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 100° to 130° C.

The internal volume (excluding the stopper part) of the unstretched preform was 19 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 1469 cm³.

The internal surface area (excluding the internal surface area of the stopper part) of the stretched bottle was 678 cm².

The stretch index is therefore calculated as follows:

$$\text{Stretch index} = 1469/19 \times 1/0.46 = 168.$$

The gas barrier properties were evaluated from the permeability coefficients of carbon dioxide gas and oxygen gas. The permeability coefficient of carbon dioxide gas was measured in accordance with Permatrian method on a specimen sectioned from the central part of the bottle body having a thickness of 300 to 450 μ m, at a temperature of 23° C. and relative humidity of 0% using a carbon dioxide gas permeability testing apparatus (trade name of Perm-Race-TV type, manufactured by Modern Control, Co., Ltd. (U.S.A.)). The permeability coefficient of oxygen gas was measured in accordance with Oxtran method on a specimen sectioned from the central part of the bottle body having a thickness of 300 to 400 μ m, at a temperature of 23° C. and relative humidity of 0% using a permeability testing apparatus (trade name of Oxtran 100 type, manufactured by Modern Control Co., Ltd. (U.S.A.)).

The transparency was measured by a method based on ASTM D 1003 by cutting a body part of the bottle and using a haze meter (trade name of NDH-20D, manufactured by Nippon Denshoku K.K.). The haze value was obtained by measuring the test piece three times, and averaging these three values.

Pressure-resistant strength was measured using a pipe hydraulic destruction testing apparatus, by placing the bottle in a constant temperature water bath held at 30° C., applying a hydraulic pressure at a water flow rate of 500 cm³/min, measuring the hydraulic pressure at which the bottle was broken, and determining the measured value as the strength. The measurement was conducted three times ($n=3$) on each sample, and the average value was taken as the strength.

The results are shown in Table 1.

EXAMPLE 2

A dicarboxylic acid component composed of 90 mol % of terephthalic acid and 10 mol % of 2,6-naphthalenedicarboxylic acid was esterified with ethylene glycol by the prior art method to obtain a copolyester having an intrinsic viscosity $[\eta]$ of 0.66 dl/g.

Example 1 was repeated except that the copolyester prepared in Example 2 was used to obtain at first a preform

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for a biaxially stretch molded article and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that of Example 1.

The results are shown in Table 1.

Comparative Example 1 and 2

The procedure of Example 1 and 2 was repeated except that the stretch index was set at 95 cm and that the total weight of the bottle (preform) was increased by 11% to obtain biaxially stretched bottles. The transparency and gas barrier properties of the bottles were evaluated.

The results are shown in Table 1.

EXAMPLE 3

A preform for forming a bottle was obtained by molding the copolyester used in Example 1 using a molding machine (trade name of ASB-50HT, manufactured by Nissel ASB K.K.). The molding temperature was 270° to 290° C.

The thus obtained preform was molded by a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 100° to 130° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

The stretch index is calculated as follows:

$$\text{Stretch index} = 519/4.9 \times 1/0.67 = 158$$

$$= 345/519 = 0.67.$$

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 1.

EXAMPLE 4

Example 3 was repeated except that the copolyester employed in Example 2 was used to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 1.

Comparative Example 3

Example 4 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% in Example 3 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 1.

Comparative Example 4

Example 4 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

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The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.
The results are shown in Table 1.

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The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.
The results are shown in Table 2.

TABLE 1

Item	Unit	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Amount of comonomer	mol %	1	10	1	10	1	10	1	10
Stretch index	cm	168	168	198	198	95	95	92	92
Total wt. of bottle	g	94	94	21	21	60	60	29	29
Thickness of bottle body (just at base measurement)	mm	0.40	0.37	0.30	0.28	0.39	0.35	0.29	0.27
Transparency									
Total haze	%	0.5	0.3	0.3	0.2	0.8	0.6	0.5	4.4
Internal haze	%	0.3	0.2	0.1	0.1	0.6	0.4	0.3	4.2
CO ₂ permeability coefficient 23° C., 0% RH (Permation method)	$\frac{cm^3 \cdot mm}{m^2 \cdot sec}$	7.1	6.2	9.8	6.7	7.5	6.6	10.5	7.3
O ₂ permeability coefficient 23° C., 0% RH (Ox-Tran method)	$\frac{cm^3 \cdot mm}{m^2 \cdot sec}$	1.7	1.5	1.9	1.1	1.7	1.5	2.2	1
Pressure resistance	kg/cm ²	17	15	16	14	15	13	14	12

EXAMPLE 5

A dicarboxylic acid component composed of 99 mol % of terephthalic acid and 1 mol % of isophthalic acid was esterified with ethylene glycol by the prior art method to obtain a copolyester having an intrinsic viscosity $[\eta]$ of 0.79 dl/g.

The thus obtained copolyester was molded by a procedure similar to that in Example 1 using a molding machine (trade name of M-100A, manufactured by Meiki Seisakusho K.K.) to obtain a preform for molding a bottle. The molding temperature was 250° to 270° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Coroplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 19 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 1469 cm³.

The internal surface area (excluding the internal surface area of the stopper part) of the stretched bottle was 678 cm².

The stretch index is therefore calculated as follows:

stretch index=1469/19×1/0.46=168.

The resulting biaxially stretched bottle was evaluated by a procedure similar to that in example 1.

The results are shown in Table 2.

EXAMPLE 6

A dicarboxylic acid component composed of 90 mol % of terephthalic acid and 10 mol % of isophthalic acid was esterified with ethylene glycol by the prior art method to obtain a copolyester having an intrinsic viscosity $[\eta]$ of 0.80 dl/g.

Example 5 was repeated except that the preform in Example 6 was used to obtain at first a preform for a biaxially stretch molded article was and then a biaxially stretched bottle from the preform.

Comparative Examples 5 and 6

The procedure of Example 5 and 6 was repeated except that the stretch index was set at 95 cm and that the total weight of the bottle (preform) was increased by 11% in Examples 5 and 6 to obtain biaxially stretched bottles. The transparency and gas barrier properties of the bottles were evaluated.

The results are shown in Table 2

EXAMPLE 7

A preform for forming a bottle was prepared by molding the copolyester used in Example 5 using a molding machine (trade name of ASB-50HT, manufactured by Nissei ASB K.K.). The molding temperature was 250° to 270° C.

The thus obtained preform was molded by a molding machine (trade name of LB-01, manufactured by Coroplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

The stretch index is therefore calculated as follows:

stretch index=519/4.9×1/0.67=158

$\bar{s}$ =345/519=0.67.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 2.

EXAMPLE 8

Example 7 was repeated except that the copolyester employed in Example 6 was used to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

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The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 2.

Comparative Example 7

Example 8 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% in Example 7 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 2.

Comparative Example 8

Example 8 was repeated except that the stretch index was set at 92 cm, and that the total weight of the bottle (preform) was increased by 11% to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle was prepared from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 2.

TABLE 2

Item	Unit	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Amount of monomer	mol %	1	10	1	10	1	10	1	10
Stretch index	cm	168	168	138	138	95	95	92	92
Total wt. of bottle	g	54	54	21	21	60	60	23	23
Thickness of bottle body (cut at knee measurement)	mm	0.39	0.38	0.28	0.27	0.41	0.39	0.29	0.28
Transparency									
Total haze	%	0.4	0.4	0.2	0.2	0.4	0.4	0.2	0.2
Internal haze	%	0.2	0.2	0.1	0	0.3	0.2	0.1	0.1
CO ₂ permeability coefficient (23° C., 0% RH) (Furukawa method)	$\frac{cm^3 \cdot mm}{m^2 \cdot D \cdot atm}$	7.0	7.1	10.0	7.5	7.2	7.1	11.0	7.8
O ₂ permeability coefficient (23° C., 0% RH) (Ox-Tran method)	$\frac{cm^3 \cdot mm}{m^2 \cdot D \cdot atm}$	1.6	1.6	2.3	2.1	1.7	1.7	2.3	2.3
Parsons modulus	kg/cm ²	18	17	21	19	16	15	20	18

EXAMPLE 9

A dicarboxylic acid component composed of 99 mol % of terephthalic acid and 1 mol % of adipic acid was esterified with ethylene glycol by the prior art method to obtain a copolyester having an intrinsic viscosity $[\eta]$ of 0.80 dl/g.

The thus obtained copolyester was molded by a procedure similar to that in Example 1 using a molding machine (trade name of M-100A, manufactured by Maki Seisakusho K.K.) to obtain a preform for molding a bottle. The molding temperature was 250° to 270° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 19 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 1469 cm³.

The internal surface area (excluding the internal surface area of the stopper part) of the stretched bottle was 678 cm².

The stretch index is therefore calculated as follows:

$$\text{stretch index} = 1469/19 \times 1/0.46 = 168.$$

The resulting biaxially stretched bottle was evaluated by a procedure similar to that in example 1.

The results are shown in Table 3.

EXAMPLE 10

A dicarboxylic acid component composed of 90 mol % of terephthalic acid and 10 mol % of adipic acid was esterified with ethylene glycol by the prior art method to obtain a copolyester having an intrinsic viscosity $[\eta]$ of 0.80 dl/g.

Example 9 was repeated except that the copolyester prepared in Example 10 was used to obtain at first a preform for a biaxially stretch molded article and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 3.

Comparative Examples 9 and 10

The procedure of Example 9 and 10 was repeated except that the stretch index was set at 95 cm and that the total

weight of the bottle (preform) was increased by 11% to obtain biaxially stretched bottles. The transparency and gas barrier properties of the resulting bottles were evaluated.

The results are shown in Table 3

EXAMPLE 11

A preform for forming a bottle was prepared by molding the copolyester used in Example 9 using a molding machine (trade name of ASB-SOHT, manufactured by Nissei ASB K.K.). The molding temperature was 250° to 270° C.

The thus obtained preform was molded by a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

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The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the resulting stretched bottle was 345 cm².

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The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 3.

TABLE 3

Item	Unit	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Comp. Ex. 9	Comp. Ex. 10	Comp. Ex. 11	Comp. Ex. 12
Amount of comonomer	mol %	1	10	1	10	1	10	1	10
Stretch index	cm	168	168	158	158	95	95	92	92
Total wt. of bottle	g	54	54	21	21	60	60	23	23
Thickness of bottle body (part at base measurement)	mm	0.39	0.38	0.28	0.27	0.41	0.38	0.29	0.27
Transparency									
Total haze	%	0.4	0.3	0.2	0.2	0.5	0.4	0.2	0.2
Internal haze	%	0.3	0.2	0	0	0.3	0.2	0.1	0.1
CO ₂ permeability coefficient 23° C., 0% RH (Permum method)	$\frac{cc \cdot mm}{day \cdot cm^2}$	7.1	7.1	10.2	7.5	7.3	7.4	12.1	8.1
O ₂ permeability coefficient 23° C., 0% RH (Oxum method)	$\frac{cc \cdot mm}{m^2 \cdot day \cdot atm}$	1.8	1.7	2.3	2.2	1.9	1.9	2.5	2.8
Pressure resistance	kg/cm ²	18	18	21	20	17	16	20	19

The stretch index is therefore calculated as follows:
stretch index=519/4.9x1/0.67=158
s=345/519=0.67.
The transparency and gas barrier properties of the resulting biaxially stretched bottle was evaluated by a procedure similar to that in Example 1.

The results are shown in Table 3.

EXAMPLE 12

Example 11 was repeated except that the polyester resin composition employed in Example 10 was used to obtain a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 3.

Comparative Example 11

Example 12 was repeated except that the stretch index was set at 92 cm, and that the total weight of the bottle (preform) was increased by 11% in Example 11 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 3.

Comparative Example 12

Example 12 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

EXAMPLE 13

Terephthalic acid was esterified with a dihydroxy compound component composed of 97 mol % of ethylene glycol and 3 mol % of neopentyl alcohol by the prior art method to obtain a copolyester having an intrinsic viscosity [η] of 0.78 dl/g.

The thus obtained copolyester was molded by a procedure similar to that in Example 1 using a molding machine (trade name of M-100A, manufactured by Meiki Seisakusho K.K.) to obtain a preform for forming a bottle. The molding temperature was 240° to 260° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 19 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 1469 cm³.

The internal surface area (excluding the internal surface area of the stopper part) of the stretched bottle was 678 cm².

The stretch index is therefore calculated as follows:

stretch index=1469/19x1/0.46=168.

The resulting biaxially stretched bottle was evaluated by a procedure similar to that in example 1.

The results are shown in Table 4.

EXAMPLE 14

Terephthalic acid was esterified with a dihydroxy compound component composed of 90 mol % of ethylene glycol and 10 mol % of neopentyl glycol by the prior art method to obtain a copolyester having an intrinsic viscosity [η] of 0.78 dl/g.

Example 13 was repeated except that the copolyester prepared in Example 14 was used to obtain at first a preform

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for a biaxially stretch molded article and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 4.

Comparative Examples 13 and 14

The procedure of Examples 13 and 14 was repeated except that the stretch index was set at 95 cm and that the total weight of the bottle (preform) was increased by 11% in Examples 13 and 14 to obtain biaxially stretched bottles. The transparency and gas barrier properties of the bottles were evaluated.

The results are shown in Table 4.

EXAMPLE 15

A preform for forming a bottle was prepared by molding the copolyester used in Example 13 using a molding machine (trade name of ASB-50HT, manufactured by Nissai ASB K.K.). The molding temperature was 240° to 260° C.

The thus obtained preform was molded by a molding machine (trade name of LB-01, manufactured by Carpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

The stretch index is therefore calculated as follows:

$$\text{stretch index} = 519/4.9 \times 1/0.67 = 158$$
$$f = 345/519 = 0.67.$$

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 4.

EXAMPLE 16

Example 15 was repeated except that the copolyester employed in Example 14 was used to obtain at first a

preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 4.

Comparative Example 15

Example 15 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% in Example 15 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 4.

Comparative Example 16

Example 16 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% in Example 16 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 4.

TABLE 4

Item	Unit	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Comp. Ex. 13	Comp. Ex. 14	Comp. Ex. 15	Comp. Ex. 16
Amount of comonomer	mol %	3	10	3	10	3	10	3	10
Stretch index	cm	168	168	158	158	95	95	92	92
Total wt. of bottle	g	54	54	21	21	60	60	23	23
Thickness of bottle body (part at base measurement)	mm	0.40	0.38	0.28	0.27	0.41	0.39	0.29	0.28
Transparency									
Total haze	%	0.5	0.5	0.4	0.3	0.5	0.5	0.4	0.4
Internal haze	%	0.3	0.3	0.2	0.2	0.3	0.4	0.2	0.3
CO ₂ permeability coefficient 23° C., 0% RH (Furukawa method)	$\frac{\text{cc} \cdot \text{cm}}{\text{m}^2 \cdot \text{cm} \cdot \text{atm}}$	7.0	7.1	10.8	7.6	7.3	7.2	11.4	8.2
O ₂ permeability coefficient 23° C., 0% RH (Otsuka method)	$\frac{\text{cc} \cdot \text{cm}}{\text{m}^2 \cdot \text{cm} \cdot \text{atm}}$	1.6	1.7	2.3	2.1	1.7	1.8	2.4	2.4
Pressure resistance	kg/cm ²	18	18	21	19	17	16	19	18

EXAMPLE 17

Terephthalic acid was esterified with a dihydroxy compound component composed of 97 mol % of ethylene glycol and 3 mol % of cyclohexanedimethanol by the prior art method to obtain a copolyester having an intrinsic viscosity $[\eta]$ of 0.80 dl/g.

The thus obtained copolyester was molded by a procedure similar to that in Example 1 using a molding machine (trade name of M-100A, manufactured by Maki Salsakishi K.K.)

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to obtain a preform for forming a bottle. The molding temperature was 250° to 270° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 19 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 1469 cm³.

The internal surface area (excluding the internal surface area of the stopper part) of the stretched bottle was 678 cm².

The stretch index is therefore calculated as follows:

stretch index=1469/19×1/0.46=168.

The resulting biaxially stretched bottle was evaluated by a procedure similar to that in example 1.

The results are shown in Table 5

EXAMPLE 18

Terephthalic acid was esterified with a dihydroxy compound component composed of 90 mol % of ethylene glycol and 10 mol % of cyclohexanedimethanol by the prior art method to obtain a copolyester having an intrinsic viscosity $[\eta]$ of 0.81 dl/g.

Example 17 was repeated except that the copolyester prepared in Example 18 was used to obtain at first a preform for a biaxially stretch molded article and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 5.

Comparative Examples 17 and 18

The procedure of Examples 17 and 18 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% in Examples 17 and 18 to obtain biaxially stretched bottles. The transparency and gas barrier properties of the resulting bottles were evaluated.

The results are shown in Table 5.

EXAMPLE 19

A preform for forming a bottle was prepared by molding the copolyester employed in Example 17 using a molding machine (trade name of ASB-50HT, manufactured by Nissai ASB K.K.). The molding temperature was 250° to 270° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade

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name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

The stretch index is therefore calculated as follows:

stretch index=519/4.9×1/0.67=158

1-345/519-0.67.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 5.

EXAMPLE 20

Example 19 was repeated except that the copolyester employed in Example 18 was used to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 5.

Comparative Example 19

Example 19 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% in Example 19 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 5.

Comparative Example 20

Example 20 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% in Example 20 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 5.

TABLE 5

Item	Unit	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Comp. Ex. 17	Comp. Ex. 18	Comp. Ex. 19	Comp. Ex. 20
Amount of comonomer	mol %	9	10	9	10	9	10	9	10
Stretch index	cm	168	168	158	158	92	92	92	92
Total wt. of bottle	g	94	94	21	21	60	60	23	23
Thickness of bottle body (part of base measurement)	mm	0.39	0.38	0.28	0.27	0.40	0.39	0.29	0.28
Transparency									
Total haze	%	0.3	0.3	0.2	0.1	0.3	0.3	0.2	0.3
Internal haze	%	0.1	0.1	0.1	0	0.2	0.1	0.1	0.1

TABLE 5-continued

Item	Unit	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Comp. Ex. 17	Comp. Ex. 18	Comp. Ex. 19	Comp. Ex. 20
CO ₂ permeability coefficient 23° C., 0% RH (Permation method)	$\frac{\text{cc} \cdot \text{cm}}{\text{m}^2 \cdot \text{cm} \cdot \text{atm}}$	7.1	7.1	10.5	8.1	7.5	7.2	11.2	8.5
O ₂ permeability coefficient 23° C., 0% RH (Ox-Tran method)	$\frac{\text{cc} \cdot \text{cm}}{\text{m}^2 \cdot \text{cm} \cdot \text{atm}}$	1.6	1.7	2.3	2.1	1.7	1.8	2.4	2.3
Residual monomer	kg/cm ²	18	17	19	18	17	17	18	17

EXAMPLE 21

Terephthalic acid was esterified with a dihydroxy compound component composed of 97 mol % of ethylene glycol and 3 mol % of diethylene glycol by the prior art method to obtain a copolyester having an intrinsic viscosity $[\eta]$ of 0.78 dl/g.

The thus obtained copolyester was molded by a procedure similar to that in Example 1 using a molding machine (trade name of M-100A, manufactured by Melki Seisakusho K.K.) to obtain a preform for forming a bottle. The molding temperature was 270° to 290° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 19 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 1469 cm³.

The internal surface area (excluding the internal surface area of the stopper part) of the stretched bottle was 678 cm².

The stretch index is therefore calculated as follows:

$$\text{stretch index} = 1469/19 \times 1/0.46 = 168.$$

The resulting biaxially stretched bottle was evaluated by a procedure similar to that in example 1.

The results are shown in Table 6

EXAMPLE 22

Terephthalic acid was esterified with a dihydroxy compound component composed of 95 mol % of ethylene glycol and 5 mol % of diethylene glycol by the prior art method to obtain a copolyester having an intrinsic viscosity $[\eta]$ of 0.76 dl/g.

The procedure of Example 21 was repeated except that the copolyester prepared in Example 22 was used to obtain at first a preform for a biaxially stretch molded article and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 6.

Comparative Examples 21 and 22

The procedure of Examples 21 and 22 was repeated except that the stretch index was set at 95 cm and that the total weight of the bottle (preform) was increased by 11% in Examples 21 and 22 to obtain biaxially stretched bottles.

The transparency and gas barrier properties of the bottles were evaluated.

The results are shown in Table 6.

EXAMPLE 23

A preform for forming a bottle was prepared by molding the copolyester employed in Example 21 using a molding machine (trade name of ASB-50HT, manufactured by Nissei ASB K.K.). The molding temperature was 260° to 270° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

The stretch index is therefore calculated as follows:

$$\text{stretch index} = 519/4.9 \times 1/0.67 = 158$$

$$= 345/519 \times 0.67.$$

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 6.

EXAMPLE 24

Example 23 was repeated except that a polyester resin composition employed in Example 22 was used to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 6.

Comparative Example 23

Example 24 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% in Example 23 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 6.

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Comparative Example 24

Example 24 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 6.

The internal surface area (excluding the internal surface area of the stopper part) of the stretched bottle was 678 cm². The stretch index is calculated as follows:
stretch index=1469/19×1/0.46=168
The resulting biaxially stretched bottle was evaluated by a procedure similar to that in Example 1.
The results are shown in Table 7.

EXAMPLE 26

Example 25 was repeated except that a copolyester resin described below was used and that a resin composition

TABLE 6

Item	Unit	Ex. 21	Ex. 22	Ex. 23	Ex. 24	Comp. Ex. 21	Comp. Ex. 22	Comp. Ex. 23	Comp. Ex. 24
Amount of container	mol %	9	5	3	5	3	5	3	5
Stretch index	cm	168	168	158	158	95	95	92	92
Total wt. of bottle	g	54	54	21	21	60	60	23	23
Thickness of bottle body (just at base measurement)	mm	0.39	0.36	0.28	0.27	0.40	0.37	0.29	0.28
Transparency									
Total haze	%	0.4	0.3	0.2	0.1	0.4	0.3	0.2	0.2
Internal haze	%	0.2	0.2	0	0	0.2	0.2	0.1	0.1
CO ₂ permeability coefficient 25° C., 0% RH (Permation method)	$\frac{\text{cc} \cdot \text{mm}}{\text{m}^2 \text{D} \cdot \text{atm}}$	7.1	7.0	11.8	13.6	7.4	7.9	12.9	13.9
O ₂ permeability coefficient 25° C., 0% RH (Ox-Tran method)	$\frac{\text{cc} \cdot \text{mm}}{\text{m}^2 \text{D} \cdot \text{atm}}$	1.6	1.6	2.2	2.1	1.8	1.8	2.4	2.3
Pressure resistance	kg/cm ²	19	17	20	19	17	16	18	17

EXAMPLE 25

The resins described below were used for preparing a polyester resin composition for high stretch molding.

Polyethylene terephthalate: a resin (trade name of J 135, manufactured by Mitsui PET Resins K.K.) having a relative viscosity (IV) of 0.85 dl/g measured in o-chlorophenol at 25° C.;

Copolyester: the dicarboxylic acid component thereof being composed of 90 mol % of isophthalic acid constituent units and 10 mol % of terephthalic acid constituent units, the dihydroxy compound component thereof being composed of 15 mol % of 1,3-bis(2-hydroxyethoxy)benzene constituent units and 85 mol % of ethylene glycol constituent units, the copolyester comprising 0.3 part by mol of trimethylolpropane constituent units based on 100 parts by mol of dicarboxylic acid constituent units and having a relative viscosity (IV) of 0.85 dl/g measured in o-chlorophenol at 25° C.

After mixing 1% by weight of the copolyester and 99% by weight of the polyethylene terephthalate mentioned above, the resulting polyester resin composition (I) was molded by a molding machine (trade name of M-100A, manufactured by Meiki Seisakusho K.K.) to obtain a preform for forming a bottle. The molding temperature was 270° to 290° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 19 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 1469 cm³.

composed of 4% by weight of the copolyester and 96% by weight of polyethylene terephthalate was employed to obtain at first a preform for biaxially stretch molded article and then a biaxially stretched bottle from the preform.

Copolyester: the dicarboxylic acid component thereof being composed of 90 mol % of isophthalic acid constituent units and 10 mol % of terephthalic acid constituent units, the dihydroxy compound component thereof being composed of 7.5 mol % of 1,3-bis(2-hydroxyethoxy)benzene constituent units and 92.5 mol % of ethylene glycol constituent units, the copolyester comprising 0.3 part by mol of trimethylolpropane constituent units based on 100 parts by mol of the dicarboxylic acid constituent units, and having a relative viscosity (IV) of 0.85 dl/g measured in o-chlorophenol at 25° C.

The transparency and gas barrier properties of the resulting biaxially stretched bottle was evaluated by a procedure similar to that in Example 1.

The results are shown in Table 7.

Comparative Examples 25 and 26

The procedure of Examples 25 and 26 was repeated except that the stretching index was set at 95 cm and that the total weight of the bottle (preform) was increased by 11% in Examples 25 and 26 to obtain a biaxially stretched bottle. The transparency and gas barrier properties of the bottle were evaluated.

The results are shown in Table 7.

Comparative Example 27

Comparative Example 25 was repeated except that only the polyethylene terephthalate was used without using the

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copolyester in Comparative Example 25 to obtain biaxially stretched bottles. The transparency and gas barrier properties of the bottles were evaluated.

The results are shown in Table 7.

Comparative Example 28

Example 25 was repeated except that only the polyethylene terephthalate was used without using the copolyester in Example 25 to obtain a biaxially stretched bottle. The transparency and gas barrier properties of the resulting bottle were evaluated.

The results are shown in Table 7.

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was used to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 8.

Comparative Example 29

Example 28 was repeated except that the stretch index was set at 92 cm and that the total weight of the preform was increased by 11% in Example 27 to obtain at first a preform and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting bottle were evaluated.

TABLE 7

Item	Unit	Example 25	Example 26	Comp. Ex. 25	Comp. Ex. 26	Comp. Ex. 27	Comp. Ex. 28
PET/copolyester (wt. ratio)	mol %	99/1	98/4	99/1	96/4	100/0	100/0
Stretch index	cm	168	168	95	95	95	168
Total wt. of bottle	g	54	54	60	60	60	60
Thickness of bottle body (part at base measurement)	mm	0.39	0.38	0.40	0.40	0.40	0.40
Transparency							
Total haze	%	0.1	0.1	0.1	0.1	0.1	4.2
Internal haze	%	0.1	0.1	0.1	0.1	0.1	4.0
CO ₂ permeability coefficient 23° C., 0% RH (Permatran method)	$\frac{cc \cdot mm}{m^2 \cdot atm}$	7.5	5.2	8.3	6.8	8.5	7.6
O ₂ permeability coefficient 23° C., 0% RH (Ox-Tran method)	$\frac{cc \cdot mm}{m^2 \cdot atm}$	1.7	1.6	1.9	1.8	2.0	1.8
Pressure resistance	kg/cm ²	20	18	16	16	16	12

EXAMPLE 27

A preform for forming a bottle was obtained by molding polyester resin composition [I] employed in Example 25 using a molding machine (trade name of ASB-50HT, manufactured by Nissai ASB K.K.). The molding temperature was 260° to 270° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

The stretch index is therefore calculated as follows:

$$\text{stretch index} = 519/4.9 \times 1/0.67 = 158$$

$$s = 345/519 = 0.67.$$

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated.

The results are shown in Table 8.

EXAMPLE 28

The procedure of Example 27 was repeated except that the polyester resin composition employed in Example 26

The results are shown in Table 8.

Comparative Example 30

Example 27 was repeated except that the stretch index was set at 92 cm and that the total weight of the preform was increased by 11% in Example 28 to obtain at first a preform and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 8.

Comparative Example 31

Comparative Example 29 was repeated except that only the polyethylene terephthalate was used, that a stretch index was set at 92 cm and that the total weight of the preform was increased by 11% to obtain a biaxially stretched bottle.

The transparency and gas barrier properties of the bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 8.

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copolyester in Comparative Example 25 to obtain biaxially stretched bottles. The transparency and gas barrier properties of the bottles were evaluated.

The results are shown in Table 7.

Comparative Example 28

Example 25 was repeated except that only the polyethylene terephthalate was used without using the copolyester in Example 25 to obtain a biaxially stretched bottle. The transparency and gas barrier properties of the resulting bottle were evaluated.

The results are shown in Table 7.

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was used to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 8.

Comparative Example 29

Example 28 was repeated except that the stretch index was set at 92 cm and that the total weight of the preform was increased by 11% in Example 27 to obtain at first a preform and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting bottle were evaluated.

TABLE 7

Item	Unit	Example 25	Example 26	Comp. Ex. 25	Comp. Ex. 26	Comp. Ex. 27	Comp. Ex. 28
PE/Copolyester (wt. ratio)	mol %	99/1	99/1	99/1	99/1	100/0	100/0
Stretch index	cm	168	168	95	95	95	168
Total wt. of bottle	g	54	54	60	60	60	60
Thickness of bottle body (part at knee measurement)	mm	0.39	0.38	0.40	0.40	0.40	0.40
Transparency							
Total haze	%	0.1	0.1	0.1	0.1	0.1	4.2
Internal haze	%	0.1	0.1	0.1	0.1	0.1	4.0
CO ₂ permeability coefficient 23° C., 0% RH (Permation method)	$\frac{cc \cdot mm}{m^2 \cdot D \cdot atm}$	7.5	5.2	8.3	6.8	8.5	7.6
O ₂ permeability coefficient 23° C., 0% RH (Ox-Tran method)	$\frac{cc \cdot mm}{m^2 \cdot D \cdot atm}$	1.7	1.6	1.9	1.8	2.0	1.8
Pressure resistance	kg/cm ²	20	18	16	16	16	12

EXAMPLE 27

A preform for forming a bottle was obtained by molding polyester resin composition [I] employed in Example 25 using a molding machine (trade name of ASB-SOBT, manufactured by Nissai ASB K.K.). The molding temperature was 260° to 270° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

The stretch index is therefore calculated as follows:

$$\text{stretch index} = 519/4.9 \times 1/0.67 = 158$$

$$I = 345/519 = 0.67.$$

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated.

The results are shown in Table 8.

EXAMPLE 28

The procedure of Example 27 was repeated except that the polyester resin composition employed in Example 26

The results are shown in Table 8.

Comparative Example 30

Example 27 was repeated except that the stretch index was set at 92 cm and that the total weight of the preform was increased by 11% in Example 28 to obtain at first a preform and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 8.

Comparative Example 31

Comparative Example 29 was repeated except that only the polyethylene terephthalate was used, that a stretch index was set at 92 cm and that the total weight of the preform was increased by 11% to obtain a biaxially stretched bottle.

The transparency and gas barrier properties of the bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 8.

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TABLE 8

Item	Unit	Example 27	Example 28	Comp. Ex. 29	Comp. Ex. 30	Comp. Ex. 31	Comp. Ex. 32
PET/Copolyester (wt. ratio)		99/1	99/1	99/1	99/1	100/0	100/0
Stretch index	cm	158	158	92	92	92	158
Total wt. of bottle	g	21	21	23	23	23	23
Thickness of bottle body (part at base measurement)	mm	0.26	0.27	0.26	0.26	0.26	0.31
Transparency							
Total haze	%	0.1	0.1	0.1	0.1	0.1	2.2
Internal haze	%	0	0	0	0	0	1.7
CO ₂ permeability coefficient 25° C., 0% RH (Permatran method)	$\frac{cc \cdot cm}{m^2 \cdot sec}$	9.5	6.8	11.2	7.9	11.3	10.1
O ₂ permeability coefficient 25° C., 0% RH (Ox-Tran method)	$\frac{cc \cdot cm}{m^2 \cdot sec}$	2.0	1.9	2.2	2.0	2.3	2.1
Pressure resistance	kg/cm ²	20	18	18	17	18	20

EXAMPLE 29

The resins described below were used for preparing a polyester resin composition for high stretch molding.

Polyethylene terephthalate: a resin (trade name of J 125, manufactured by Mitsui PET Resin K.K.) having a relative viscosity (IV) of 0.79 dl/g measured in o-chlorophenol at 25° C.;

Copolyester: a resin prepared by esterifying a dicarboxylic acid component composed of 30 mol % of terephthalic acid and 30 mol % of isophthalic acid with ethylene glycol by the prior art method, and having a relative viscosity (IV) of 0.85 dl/g.

After mixing 5% by weight of the copolyester and 95% by weight of the polyethylene terephthalate mentioned above, the resulting polyester resin composition (II) was molded by a molding machine (trade name of M-100A, manufactured by Meiki Seisakusho K.K.) to obtain a preform for forming a bottle. The molding temperature was 270° to 290° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 19 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 1469 cm³.

The internal surface area (excluding the internal surface area of the stopper part) of the stretched bottle was 678 cm².

The stretch index is therefore calculated as follows:

$$\text{stretch index} = 1469/19 \times 1/0.46 = 168$$

The resulting biaxially stretched bottle was evaluated by a procedure similar to that in Example 1.

The results are shown in Table 9.

EXAMPLE 30

Example 29 was repeated except that a resin composition composed of 10% by weight of the copolyester and 90% by

weight of the polyethylene terephthalate was used in Example 29 to obtain at first a preform for a biaxially stretch molded article and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 9.

Comparative Examples 33 and 34

The procedure of Examples 29 and 30 was repeated except that the stretching index was set at 95 cm and that the total weight of the bottle (preform) was increased by 11% in Examples 29 and 30 to obtain a biaxially stretched bottle.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated.

The results are shown in Table 9.

Comparative Example 35

Comparative Example 33 was repeated except that only the polyethylene terephthalate was used without using the copolyester and that the total weight of the preform was increased by 11% in Comparative Example 33 to obtain a biaxially stretched bottle.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated.

The results are shown in Table 9.

Comparative Example 36

Example 29 was repeated except that only the polyethylene terephthalate was used without using the copolyester and that the total weight of the preform was increased by 11% in Example 29 to obtain a biaxially stretched bottle.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated.

The results are shown in Table 9.

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TABLE 8

Item	Unit	Example 27	Example 28	Comp. Ex. 29	Comp. Ex. 30	Comp. Ex. 31	Comp. Ex. 32
PETD copolyester (wt. ratio)		99/1	94/4	99/1	94/4	100/0	100/0
Stretch index	cm	158	158	92	92	92	158
Total wt. of bottle	g	21	21	25	25	25	25
Thickness of bottle body (part of here measurement)	mm	0.28	0.37	0.28	0.28	0.28	0.31
Transparency							
Total haze	%	0.1	0.1	0.1	0.1	0.1	2.2
Internal haze	%	0	0	0	0	0	1.7
CO ₂ permeability coefficient	$\frac{cm^3 \cdot cm}{m^2 \cdot D \cdot atm}$	9.5	6.8	11.2	7.3	11.3	10.1
25° C., 0% RH (Pezerman method)							
O ₂ permeability coefficient	$\frac{cm^3 \cdot cm}{m^2 \cdot D \cdot atm}$	2.0	1.9	2.2	2.0	2.3	2.1
25° C., 0% RH (Ox-Tran method)							
Pressure resistance	kg/cm ²	20	18	18	17	18	20

EXAMPLE 29

The resins described below were used for preparing a polyester resin composition for high stretch molding.

Polyethylene terephthalate: a resin (trade name of J 125, manufactured by Mitsui PET Resin K.K.) having a relative viscosity (IV) of 0.79 dl/g measured in o-chlorophenol at 25° C;

Copolyester: a resin prepared by esterifying a dicarboxylic acid component composed of 50 mol % of terephthalic acid and 50 mol % of isophthalic acid with ethylene glycol by the prior art method, and having a relative viscosity (IV) of 0.85 dl/g.

After mixing 5% by weight of the copolyester and 95% by weight of the polyethylene terephthalate mentioned above, the resulting polyester resin composition (II) was molded by a molding machine (trade name of M-100A, manufactured by Meiki Seisakusho K.K.) to obtain a preform for forming a bottle. The molding temperature was 270° to 290° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 19 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 1469 cm³.

The internal surface area (excluding the internal surface area of the stopper part) of the stretched bottle was 678 cm².

The stretch index is therefore calculated as follows:

stretch index=1469/19×10.46=168

The resulting biaxially stretched bottle was evaluated by a procedure similar to that in Example 1.

The results are shown in Table 9.

EXAMPLE 30

Example 29 was repeated except that a resin composition composed of 10% by weight of the copolyester and 90% by

weight of the polyethylene terephthalate was used in Example 29 to obtain at first a preform for a biaxially stretch molded article and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 9.

Comparative Examples 33 and 34

The procedure of Examples 29 and 30 was repeated except that the stretching index was set at 95 cm and that the total weight of the bottle (preform) was increased by 11% in Examples 29 and 30 to obtain a biaxially stretched bottle.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated.

The results are shown in Table 9.

Comparative Examples 35

Comparative Example 33 was repeated except that only the polyethylene terephthalate was used without using the copolyester and that the total weight of the preform was increased by 11% in Comparative Example 33 to obtain a biaxially stretched bottle.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated.

The results are shown in Table 9.

Comparative Examples 36

Example 29 was repeated except that only the polyethylene terephthalate was used without using the copolyester and that the total weight of the preform was increased by 11% in Example 29 to obtain a biaxially stretched bottle.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated.

The results are shown in Table 9.

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TABLE 9

Item	Unit	Example 29	Example 30	Comp. Ex. 33	Comp. Ex. 34	Comp. Ex. 35	Comp. Ex. 36
PEI/polyester (wt. ratio)		95/5	90/10	95/5	90/10	100/0	100/0
Stretch index	cm	168	168	95	95	95	168
Total wt. of bottle	g	34	34	60	60	60	60
Thickness of bottle body (gast or laser measurement)	mm	0.98	0.97	0.98	0.98	0.99	0.40
Transparency							
Total haze	%	0.3	0.3	0.4	0.3	0.3	5.6
Internal haze	%	0.1	0	0.2	0.2	0.2	4.8
CO ₂ permeability coefficient (23° C., 0% RH (Permation method))	$\frac{cm^3 \cdot mm}{m^2 \cdot day \cdot atm}$	7.3	7.1	7.1	7.2	8.6	7.5
O ₂ permeability coefficient (23° C., 0% RH (Ox-Tran method))	$\frac{cm^3 \cdot mm}{m^2 \cdot day \cdot atm}$	1.6	1.6	1.7	1.8	2.1	1.9
Fluorescence substance	lighter ²	17	16	15	14	15	11

EXAMPLE 31

A preform for forming a bottle was obtained by molding the polyester resin composition employed in Example 29 using a molding machine (trade name of ASB-SOHT, manufactured by Nissei ASB K.K.). The molding temperature was 260° to 270° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

The stretch index is therefore calculated as follows:

stretch index=519/4.9×1/0.67=158
s=345/519=0.67.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 10.

EXAMPLE 32

Example 31 was repeated except that the polyester resin composition employed in Example 30 was used to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated.

The results are shown in Table 10.

Comparative Example 37

Example 31 was repeated except that the stretching index was set at 92 cm and that the total weight of the preform was increased by 10% in Example 31 to obtain at first a preform

for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 10.

Comparative Example 38

Example 32 was repeated except that the stretch index was set at 92 cm and that the total weight of the preform was increased by 10% in Example 32 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 10.

Comparative Example 39

Example 32 was repeated except that only the polyethylene terephthalate was used, that the stretch index was set at 92 cm and that the total weight of the preform was increased by 10% to obtain a biaxially stretched bottle.

The transparency and gas barrier properties of the resulting bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 10.

Comparative Example 40

Example 32 was repeated except that only the polyethylene terephthalate was used and that the weight of the bottle (preform) was increased by 10% to obtain at first a preform and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 10.

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TABLE 10

Item	Unit	Example 31	Example 32	Comp. Ex. 37	Comp. Ex. 38	Comp. Ex. 39	Comp. Ex. 40
PET/copolyester (wt. ratio)		99/1	90/10	99/1	90/10	100/0	100/0
Stretch Index	cm	138	138	92	92	92	138
Total wt. of bottle	g	21	21	23	23	23	23
Thickness of bottle body (just at base measurement)	mm	0.27	0.26	0.28	0.27	0.28	0.30
Transparency							
Total haze	%	0.3	0.1	0.3	0.3	0.3	2.5
Internal haze	%	0	0	0.2	0.1	0.1	1.8
CO ₂ permeability coefficient 23° C., 0% RH (Purvison method)	$\frac{cm^3 \cdot cm}{m^2 \cdot atm}$	7.5	7.6	7.7	7.8	12.0	11.6
O ₂ permeability coefficient 23° C., 0% RH (Ox-Tran method)	$\frac{cm^3 \cdot cm}{m^2 \cdot atm}$	2.2	2.3	2.4	2.3	2.5	2.2
Pressure resistance	kg/cm ²	19	18	17	16	18	20

EXAMPLE 33

The resins described below were used for preparing a polyester resin composition for high stretch molding.

Polyethylene terephthalate: a resin (trade name of J 125, manufactured by Mitsui PHT Resin K.K.) having a relative viscosity (IV) of 0.79 dl/g measured in o-chlorophenol at 25° C.;

Copolyester: a resin prepared by esterifying a dicarboxylic acid component composed of 90 mol % of terephthalic acid and 10 mol % of isophthalic acid with ethylene glycol by the prior art method, and having an intrinsic viscosity (η) of 0.80 dl/g.

A polyester resin composition was obtained by mixing 20% by weight of the copolyester and 80% by weight of the polyethylene terephthalate mentioned above. Example 29 was repeated except that the above-prepared polyester resin composition was used to obtain at first a preform for biaxially stretch molded article and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle was evaluated by a procedure similar to that in Example 1.

The results are shown in Table 11.

EXAMPLE 34

Example 33 was repeated except that a resin composition composed of 50% by weight of the copolyester and 50% by weight of the polyethylene terephthalate was used in Example 33 to obtain at first a preform for a biaxially stretch molded article and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 11.

Comparative Examples 41 and 42

The procedure of Examples 33 and 34 was repeated except that the stretch index was set at 95 cm and that the total weight of the bottle (preform) was increased by 11% to obtain biaxially stretched bottles.

The transparency and gas barrier properties of the resulting biaxially stretched bottles were evaluated.

The results are shown in Table 11.

Comparative Example 43

The procedure of Comparative Example 9 was repeated except that only the polyethylene terephthalate was used without using the copolyester in Comparative Example 41 and that the total weight of the preform was increased by 11% to obtain a biaxially stretched bottle. The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated.

The results are shown in Table 11.

Comparative Examples 44

The procedure of Example 5 was repeated except that only the polyethylene terephthalate was employed without using the copolyester in Example 33 and that the total weight of the preform was increased by 11% to obtain a biaxially stretched bottle. The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated.

The results are shown in Table 11.

TABLE 11

Item	Unit	Example 33	Example 34	Comp. Ex. 41	Comp. Ex. 42	Comp. Ex. 43	Comp. Ex. 44
PET/copolyester (wt. ratio)		80/20	50/50	80/20	50/50	100/0	100/0
Stretch Index	cm	168	168	95	95	95	168
Total wt. of bottle	g	34	34	60	60	60	60
Thickness of bottle body (just at base measurement)	mm	0.39	0.38	0.39	0.38	0.39	0.40

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TABLE 11-continued

Item	Unit	Example 33	Example 34	Comp. Ex. 41	Comp. Ex. 42	Comp. Ex. 43	Comp. Ex. 44
Transparency							
Total haze	%	0.1	0.1	0.4	0.3	0.3	5.6
Internal haze	%	0	0	0.1	0.2	0.2	4.8
CO ₂ permeability coefficient 23° C., 0% RH (Furukawa method)	$\frac{\text{cc} \cdot \text{mm}}{\text{m}^2 \cdot \text{D} \cdot \text{atm}}$	7.3	7.1	7.2	7.2	8.6	7.5
O ₂ permeability coefficient 23° C., 0% RH (Ox-Tran method)	$\frac{\text{cc} \cdot \text{mm}}{\text{m}^2 \cdot \text{D} \cdot \text{atm}}$	1.7	1.6	1.7	1.8	2.1	1.9
Pressure resistance	kg/cm ²	17	16	15	14	15	11

EXAMPLE 35

A preform for forming a bottle was obtained by molding the polyester resin composition employed in Example 33 using a molding machine (trade name of ASB-50HT, manufactured by Nissai ASB K.K.). The molding temperature was 260° to 270° C.

The thus obtained preform was molded by a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

The stretch index is therefore calculated as follows:

$$\text{stretch index} = 519/4.9 \times 1/0.67 = 158$$

$$s = 345/519 = 0.67.$$

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 12.

EXAMPLE 36

Example 35 was repeated by using the polyester resin composition employed in Example 35 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated.

The results are shown in Table 12.

Comparative Example 45

Example 35 was repeated except that the stretch index was set at 92 cm and that the total weight of the preform was increased by 10% to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 12.

Comparative Example 46

Example 36 was repeated except that the stretch index was set at 92 cm and that the total weight of the preform was increased by 10% in Example 36 to obtain a biaxially stretched bottle.

The transparency and gas barrier properties of the biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 12.

Comparative Example 47

Example 36 was repeated except that only the polyethylene terephthalate was used, that the stretch index was set at 92 cm and that the total weight of the preform was increased by 10% to obtain a biaxially stretched bottle.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 12.

Comparative Example 48

Example 36 was repeated except that only the polyethylene terephthalate was used and that the weight of the bottle (preform) was increased by 10% to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 12.

TABLE 12

Item	Unit	Example 35	Example 36	Comp. Ex. 45	Comp. Ex. 46	Comp. Ex. 47	Comp. Ex. 48
PET/epoxyresin (wt. ratio)		80/20	90/10	80/20	90/10	100/0	100/0
Stretch index	cm	158	158	92	92	92	158
Total wt. of bottle	g	21	21	23	23	23	23

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TABLE 12-continued

Item	Unit	Example 35	Example 36	Comp. Ex. 45	Comp. Ex. 46	Comp. Ex. 47	Comp. Ex. 48
Thickness of bottle body (part at least measurement)	mm	0.28	0.27	0.28	0.27	0.28	0.30
<u>Transparency</u>							
Total haze	%	0.1	0.1	0.3	0.3	0.2	2.5
Internal haze	%	0	0	0.2	0.1	0.1	1.8
CO ₂ permeability coefficient 23° C., 0% RH (Permastat method)	$\frac{\text{cc} \cdot \text{mm}}{\text{m}^2 \text{D} \cdot \text{atm}}$	7.6	7.6	7.7	7.8	12.0	11.6
O ₂ permeability coefficient 23° C., 0% RH (Ox-Tran method)	$\frac{\text{cc} \cdot \text{mm}}{\text{m}^2 \text{D} \cdot \text{atm}}$	2.3	2.3	2.4	2.3	2.5	2.2
Pressure resistance	kg/cm ²	19	18	17	16	18	20

EXAMPLE 37

The resins described below were used for preparing a polyester resin composition for high stretch molding.

Polyethylene terephthalate: a resin (trade name of J 125, manufactured by Mitsui PET Resin K.K.) having a relative viscosity (IV) of 0.79 dl/g measured in o-chlorophenol at 25° C.;

Copolyester: a resin prepared by esterifying a dicarboxylic acid component composed of 90 mol % of terephthalic acid and 10 mol % of isophthalic acid with ethylene glycol by the prior art method, and having a relative viscosity (IV) of 0.80 dl/g.

A polyester resin composition was prepared by mixing 30% by weight of the copolyester and 70% by weight of the polyethylene terephthalate mentioned above. Example 29 was repeated except that the above-prepared polyester resin composition was used to obtain at first a preform for biaxially stretch molded article and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 13.

EXAMPLE 38

A preform for forming a bottle was prepared by molding the polyester resin composition employed in Example 37 using a molding machine (trade name of ASB-50HT, manufactured by Nissei ASB K.K.). The molding temperature was 260° to 270° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Coroplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

The stretch index is therefore calculated as follows:

$$\text{stretch index} = 519/4.9 \times 1/0.67 = 158$$

$$= 345/519 = 0.67.$$

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 13.

TABLE 13

Item	Unit	Example 37	Example 38	Comp. Ex. 49	Comp. Ex. 50
PET/copolyester (wt. ratio)		70/30	70/30	70/30	70/30
Stretch index		168	158	95	92
Total wt. of bottle	g	34	21	60	29
Thickness of bottle body (part at least measurement)	mm	0.37	0.27	0.30	0.28
<u>Transparency</u>					
Total haze	%	0.1	0.1	0.3	0.3
Internal haze	%	0	0	0.2	0.1
CO ₂ permeability coefficient 23° C., 0% RH (Permastat method)	$\frac{\text{cc} \cdot \text{mm}}{\text{m}^2 \text{D} \cdot \text{atm}}$	6.8	7.4	7.1	7.6

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TABLE 13-continued

Item	Unit	Example 37	Example 38	Comp. Ex. 49	Comp. Ex. 50
O ₂ permeability coefficient 23° C., 0% RH (Ox-Tran method)	$\frac{\text{cc} \cdot \text{cm}}{\text{m}^2 \cdot \text{atm}}$	1.4	1.7	1.6	1.8
Pressure resistance	kg/cm ²	18	20	15	18

EXAMPLE 39

The resins described below were used for preparing a polyester resin composition for high stretch molding.

Polyethylene terephthalate: a resin (trade name of J 125, manufactured by Mitsui PET Resin K.K.) having a relative viscosity (IV) of 0.79 dl/g measured in o-chlorophenol at 25° C.;

Copolyester: a resin prepared by esterifying a dicarboxylic acid component composed of 93 mol % of terephthalic acid and 7 mol % of isophthalic acid with ethylene glycol by the prior art method, and having a relative viscosity (IV) of 0.80 dl/g.

A polyester resin composition was prepared by mixing 70% by weight of the copolyester and 30% by weight of the polyethylene terephthalate mentioned above. Example 29 was repeated except that the above-prepared polyester resin composition was used to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 14.

EXAMPLE 40

A preform for forming a bottle was prepared by molding the polyester resin composition employed in Example 39 using a molding machine (trade name of ASB-50HT, manufactured by Nissei ASB K.K.). The molding temperature was 260° to 270° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

The stretch index is therefore calculated as follows:
stretch index=519/4.9×1/0.67=158

1-345/519=0.67.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 14.

Comparative Example 49

Example 37 was repeated except that the stretching index was set at 95 cm and that the total weight of the preform was increased by 10% in Example 37 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 14.

Comparative Example 50

Example 38 was repeated except that the stretch index was set at 92 cm and that the total weight of the preform was increased by 10% in Example 38 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 14.

Comparative Example 51

Example 39 was repeated except that the stretch index was set at 95 cm and that the total weight of the preform was increased by 10% in Example 39 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 14.

Comparative Example 52

Example 39 was repeated except that the stretch index was set at 92 cm and that the total weight of the preform was increased by 10% in Example 39 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 14.

TABLE 14

Item	Unit	Example 39	Example 40	Comp. Ex. 51	Comp. Ex. 52
PET/copolyester (wt. ratio)		30/70	30/70	30/70	30/70
Stretch index	cm	168	158	95	92
Total wt. of bottle	g	34	21	60	25

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TABLE 14-continued

Item	Unit	Example 39	Example 40	Comp. Ex. 51	Comp. Ex. 52
Thickness of bottle body (part of lens measurement)	mm	0.35	0.25	0.36	0.26
Transparency					
Total lens	%	0.1	0.1	0.3	0.2
Internal lens	%	0	0	0.1	0.1
CO ₂ permeability coefficient 23° C., 0% RH (Purmaton method)	$\frac{\text{cc} \cdot \text{cm}}{\text{m}^2 \cdot \text{cm} \cdot \text{atm}}$	5.3	5.3	5.3	6.0
O ₂ permeability coefficient 23° C., 0% RH (Ox-Tran method)	$\frac{\text{cc} \cdot \text{cm}}{\text{m}^2 \cdot \text{cm} \cdot \text{atm}}$	1.3	1.4	1.6	1.8
Pressure resistance	kg/cm ²	17	29	15	17

EXAMPLE 41

The resins described below were used for preparing a polyester resin composition for high stretch molding.

Polyethylene terephthalate: a resin (trade name of J 133, manufactured by Mitsui PET Resin K.K.) having a relative viscosity (IV) of 0.85 dl/g measured in o-chlorophenol at 25° C.;

Copolyester: the dicarboxylic acid component thereof being composed of 90 mol % of isophthalic acid constituent units and 10 mol % of terephthalic acid constituent units, the dihydroxy compound component thereof being composed of 15 mol % of dihydroxy-ethoxyresorcinol constituent units and 85 mol % of ethylene glycol constituent units, the copolyester comprising 0.3 part by mol of trimethylolpropane constituent units based on 100 parts by mol of the dicarboxylic acid component and having a relative viscosity (IV) of 0.85 dl/g measured in o-chlorophenol at 25° C.

After mixing 5% by weight of the copolyester and 95% by weight of the polyethylene terephthalate mentioned above, the resulting polyester resin composition (III) was molded by a molding machine (trade name of M-100A, manufactured by Meiki Seisakusho K.K.) to obtain a preform for forming a bottle. The molding temperature was 270° to 290° C.

The preform obtained as described above was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 19 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 1469 cm³.

The internal surface area (excluding the internal surface area of the stopper part) of the stretched bottle was 678 cm².

The stretch index is therefore calculated as follows:

stretch index=1469/19×1/0.46=168

The resulting biaxially stretched bottle was evaluated by a procedure similar to that in Example 1.

The results are shown in Table 15.

EXAMPLE 42

Example 1 was repeated except that a copolyester as described below was used and that a resin composition composed of 10% by weight of the copolyester and 90% by

weight of the polyethylene terephthalate employed in Example 41 was used to obtain at first a preform for biaxially stretch molded article and then a biaxially stretched bottle from the preform.

Copolyester: the dicarboxylic acid component thereof being composed of 90 mol % of isophthalic acid constituent units and 10 mol % of terephthalic acid constituent units, the dihydroxy compound component thereof being composed of 7.5 mol % of dihydroxy-ethoxyresorcinol constituent units and 92.5 mol % of ethylene glycol constituent units, the copolyester comprising 0.3 part by mol of trimethylolpropane constituent units based on 100 parts by mol of the dicarboxylic acid constituent units, and having a relative viscosity (IV) of 0.85 dl/g measured in o-chlorophenol at 25° C.

The transparency and gas barrier properties of the resulting biaxially stretched bottle was evaluated by a procedure similar to that in Example 1.

The results are shown in Table 15.

EXAMPLE 43

Example 41 was repeated except that a copolyester described below was used and that a resin composition composed of 20% by weight of the copolyester and 80% by weight of the polyethylene terephthalate employed in Example 41 was used to obtain at first a preform for biaxially stretch molded article and then a biaxially stretched bottle from the preform.

Copolyester: the dicarboxylic acid component thereof being composed of 80 mol % of isophthalic acid constituent units and 20 mol % of terephthalic acid constituent units, the dihydroxy compound component thereof being composed of 15 mol % of dihydroxy-ethoxyresorcinol constituent units and 85 mol % of ethylene glycol constituent units, the copolyester comprising 0.3 part by mol of trimethylolpropane constituent units based on 100 parts by mol of the dicarboxylic acid component, and having a relative viscosity (IV) of 0.85 dl/g measured in o-chlorophenol at 25° C.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 15.

Comparative Examples 53, 54 and 55

The procedure of Examples 41, 42 and 43 was repeated except that the stretching index between the preform for the

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biaxially stretch molded article and the stretched bottle was set at 95 cm in Example 41, 42 and 43 to obtain biaxially stretched bottles. The transparency and gas barrier properties of the resulting bottles were evaluated.
The results are shown in Table 15.

Comparative Example 56

Comparative Example 53 was repeated except that only the polyethylene terephthalate was used without using the copolyester in Comparative Example 51 to obtain a biaxially stretched bottle. The transparency and gas barrier properties of the resulting bottle were evaluated.
The results are shown in Table 15.

Comparative Example 57

Example 41 was repeated except that only the polyethylene terephthalate was used without using the copolyester to obtain a biaxially stretched bottle. The transparency and gas barrier properties thereof were evaluated.
The results are shown in Table 15.

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1-345/519=0.67.
The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.
The results are shown in Table 16.

EXAMPLE 45

Example 44 was repeated except that the polyester resin composition employed in Example 42 was used to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.
The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.
The results are shown in Table 16.

EXAMPLE 46

Example 44 was repeated except that the polyester resin composition employed in Example 43 was used to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

TABLE 15

Item	Unit	Ex. 41	Ex. 42	Ex. 43	Comp. Ex. 53	Comp. Ex. 54	Comp. Ex. 55	Comp. Ex. 56	Comp. Ex. 57
PEI copolyester (wt. ratio)		95/5	90/10	80/20	95/5	90/10	80/20	100/0	100/0
Stretch index	cm	168	168	168	95	95	95	95	168
Thickness of bottle body (just at base measurement)	mm	0.44	0.38	0.37	0.41	0.34	0.30	0.40	0.40
Transparency									
Total haze	%	0.6	0.5	0.7	0.1	0.1	0.4	0.1	4.3
Internal haze	%	0.4	0.5	0.4	0.1	0	0.1	0.1	4.0
CO ₂ permeability coefficient	$\frac{\text{cc}}{\text{day} \cdot \text{cm}^2}$	5.17	4.49	3.98	6.83	6.65	6.06	8.39	7.61
O ₂ permeability coefficient	$\frac{\text{cc} \cdot \text{cm}^3}{\text{m}^2 \cdot \text{day} \cdot \text{atm}}$	1.80	1.33	1.15	1.79	1.34	1.27	1.98	1.79
Beckling strength v = 10 mm/min	kg	60	38	35	37	34	25	31	48
Dropping strength									
Min. destruction height	mm	5.5	5.0	3.5	4.5	2.5	2.0	3.5	5.0
Strength maintenance ratio	%	96	98	75	91	73	51	96	98
Density	g/cc	1.367	1.370	1.369	1.368	1.365	1.364	1.366	1.375

EXAMPLE 44

A preform for forming a bottle was prepared by molding polyester resin composition [IV] employed in Example 41 using a molding machine (trade name of ASB-50HT, manufactured by Nissei ASB K.K.). The molding temperature was 260° to 270° C.
The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.
The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.
The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².
The stretch index is therefore calculated as follows:
stretch index=519/4.9×1/0.67=158

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.
The results are shown in Table 16.
Comparative Example 58
Example 44 was repeated except that the stretch index was set at 92 cm in Example 44 to obtain at first a preform and then a biaxially stretched bottle from the preform.
The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.
The results are shown in Table 16.
Comparative Example 59
Example 44 was repeated except that the stretch index was set at 92 cm in Example 45 to obtain at first a preform and then a biaxially stretched bottle from the preform.

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The transparency and gas barrier properties of the resulting bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 16.

Comparative Example 60

Example 44 was repeated except that the stretch index was set at 92 cm in Example 46 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 16.

Comparative Example 61

Example 44 was repeated except that only the polyethylene terephthalate was used and that the stretch index was set at 92 cm to obtain a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 16.

Comparative Example 62

Example 44 was repeated except that only the polyethylene terephthalate was used to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 16.

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EXAMPLE 47

A polyester resin composition was prepared by blending 99% by weight of a polyethylene terephthalate with 1% of a polyethylene naphthalate having an intrinsic viscosity $[\eta]$ of 0.70 dl/g.

The thus obtained polyester resin composition was molded by a molding machine (trade name of M-100A, manufactured by Miki Seisakusho K.K.) to obtain a preform for molding a bottle. The molding temperature was 270° to 290° C.

The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 19 cm³, and that (including the stopper part) of the resulting stretched bottle was 1469 cm³.

The internal surface area (excluding the internal surface area of the stopper part) of the stretched bottle was 678 cm².

The stretch index is therefore calculated as follows:
stretch index=1469/19×1/0.46=168.

The resulting biaxially stretched bottle was evaluated by a procedure similar to that in Example 1.

The results are shown in Table 17.

EXAMPLE 48

Example 47 was repeated except that there was prepared a polyester resin composition composed of 90% by weight of the polyethylene terephthalate and 10% by weight of the polyethylene naphthalate to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle prepared from the preform.

TABLE 16

Item	Unit	Ex. 44	Ex. 45	Ex. 46	Comp. Ex. 58	Comp. Ex. 59	Comp. Ex. 60	Comp. Ex. 61	Comp. Ex. 62
PET/pepolyester (wt. ratio)		99/5	90/10	80/20	99/5	90/10	80/20	100/0	100/0
Stretch index	cm	198	198	198	92	92	92	92	198
Transparency									
Total loss	%	2.0	1.5	0.5	1.5	0.7	0.4	0.1	2.3
Internal loss	%	1.2	0.9	0.3	0.8	0.4	0.2	0	1.7
CO ₂ permeability coefficient 25° C., 0% RH (Poustun method)	$\frac{\text{cc}}{\text{day} \cdot \text{cm}^2}$	6.6	6.3	5.1	9.9	7.5	6.0	11.5	10.1
O ₂ permeability coefficient 25° C., 0% RH (Osten method)	$\frac{\text{cc} \cdot \text{mm}}{\text{m}^2 \cdot \text{day} \cdot \text{atm}}$	1.8	1.4	1.2	2.1	1.8	1.5	2.3	2.1
Buckling strength $v = 10 \text{ mm/min}$ Dropping strength	kg	48	42	40	32	30	28	30	49
Min. destruction height	m	>5.4	>5.4	>5.4	>5.4	5.0	5.0	>5.4	>5.4
Strength maintenance rate	%	100	100	100	100	96	76	100	100
Density	g/cc	1.375	1.371	1.367	1.363	1.360	1.357	1.365	1.370

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The transparency and gas barrier properties of the resulting biaxially stretched bottle was evaluated by a procedure similar to that in Example 1.

The results are shown in Table 17.

Comparative Examples 63 and 64

The procedure of Examples 47 and 48 was repeated except that the stretch index was set at 95 cm and that the total weight of the bottle (preform) was increased by 11% in Examples 47 and 48 to obtain biaxially stretched bottles. The transparency and gas barrier properties of the bottles were evaluated.

The results are shown in Table 17.

EXAMPLE 49

A preform for forming a bottle was prepared by molding the polyester resin composition employed in Example 47 using a molding machine (trade name of ASB-50HT, manufactured by Nissei ASB K.K.). The molding temperature was 270° to 290° C.

The thus obtained preform was molded by a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 110° to 130° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

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preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 17.

Comparative Example 65

Example 49 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% in Example 49 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 17.

Comparative Example 66

Example 49 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% in Example 50 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 17.

TABLE 17

Item	Unit	Ex. 47	Ex. 48	Ex. 49	Ex. 50	Comp. Ex. 63	Comp. Ex. 64	Comp. Ex. 65	Comp. Ex. 66
PC/PEN (wt. ratio)	99/1	99/10	99/1	99/10	99/1	99/10	99/1	99/10	
Stretch index	cm	168	168	158	158	95	95	92	92
Total wt. of bottle	g	54	54	21	21	60	60	23	23
Thickness of bottle body (part at base measurement)	mm	0.41	0.39	0.31	0.30	0.40	0.38	0.30	0.28
Transparency									
Total haze	%	0.6	0.3	0.3	0.2	0.8	0.7	0.5	0.4
Internal haze	%	0.3	0.2	0.1	0.1	0.6	0.4	0.3	0.2
CO ₂ permeability coefficient 23° C., 0% RH (Pomeron method)	$\frac{\text{cm}^3 \cdot \text{mm}}{\text{day} \cdot \text{cm}^2}$	7.0	6.1	9.6	6.6	7.5	6.7	11.0	7.4
O ₂ permeability coefficient 23° C., 0% RH (Gutman method)	$\frac{\text{cm}^3 \cdot \text{mm}}{\text{m}^2 \cdot \text{day}}$	1.7	1.3	1.8	1.1	1.7	1.5	2.1	1.3
Fracture resistance	kg/cm ²	18	17	17	15	15	13	14	12

The stretch index is therefore calculated as follows:

stretch index= $3194.9 \times 1/0.67=158$

$5-345/519=0.67$.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 17.

EXAMPLE 50

Example 49 was repeated except that the copolyester employed in Example 48 was used to obtain at first a

EXAMPLE 51

A dicarboxylic acid component composed of 99 mol % of terephthalic acid and 1 mol % of isophthalic acid was esterified with a dihydroxy compound component composed of 85 mol % of ethylene glycol and 15 mol % of 1,3-bis(2-hydroxyethoxy)benzene, said dihydroxy compound component comprising 0.05 part by mol of a polyfunctional hydroxy compound based on 100 parts by mol of the dicarboxylic acid component, by a conventional method to obtain a copolyester having an intrinsic viscosity $[\eta]$ of 0.84 dl/g.

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The thus obtained copolyester was molded by a molding machine (trade name of M-100A, manufactured by Meiki Seisakusho K.K.) to obtain a preform for molding a bottle. The molding temperature was 270° to 290° C.

The thus obtained preform was molded by a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 19 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 1469 cm³.

The internal surface area (excluding the internal surface area of the stopper part) of the stretched bottle was 678 cm².

The stretch index is therefore calculated as follows:
stretch index=1469/19×1/0.46=168.

The resulting biaxially stretched bottle was evaluated by a procedure similar to that in Example 1.

The results are shown in Table 18.

EXAMPLE 52

A dicarboxylic acid component composed of 96 mol % of terephthalic acid and 4 mol % of isophthalic acid was esterified with a dihydroxy compound component composed of 85 mol % of ethylene glycol and 15 mol % of 1,3-bis(2-hydroxyethoxy)benzene, said dihydroxy compound component comprising 0.05 part by mol of a polyfunctional hydroxy compound based on 100 parts by mol of the dicarboxylic acid component, by the prior art method to obtain a copolyester having an intrinsic viscosity $[\eta]$ of 0.85 dl/g.

Example 51 was repeated except that the copolyester prepared in Example 52 was used to obtain at first a preform for a biaxially stretch molded article and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 18.

Comparative Example 67 and 68

The procedure of Example 51 and 52 was repeated except that the stretch index was set at 95 cm and that the total weight of the bottle (preform) was increased by 11% in Example 51 and 52 to obtain a biaxially stretched bottle. The transparency and gas barrier properties of the bottle were evaluated.

The results are shown in Table 18.

EXAMPLE 53

A preform for forming a bottle was prepared by molding the copolyester employed in Example 51 using a molding machine (trade name of ASB-50HT, manufactured by Nissei ASB K.K.). The molding temperature was 260° to 270° C.

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The thus obtained preform was molded by a procedure similar to that in Example 1 using a molding machine (trade name of LB-01, manufactured by Corpoplast Co., Ltd.) to obtain a biaxially stretched bottle. The stretching temperature was 80° to 110° C.

The internal volume (excluding the stopper part) of the unstretched preform was 4.9 cm³, and that (excluding the stopper part) of the resulting stretched bottle was 519 cm³.

The internal surface area (excluding the stopper part) of the stretched bottle was 345 cm².

The stretch index is therefore calculated as follows:

stretch index=519/4.9×1/0.67=158

$\bar{s}=345/519=0.67$.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 18.

EXAMPLE 54

Example 53 was repeated except that there was used the polyester resin composition employed in Example 52 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle prepared from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 18.

Comparative Example 69

Example 53 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% in Example 53 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle prepared from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 18.

Comparative Example 70

Example 54 was repeated except that the stretch index was set at 92 cm and that the total weight of the bottle (preform) was increased by 11% in Example 54 to obtain at first a preform for biaxial stretching and then a biaxially stretched bottle from the preform.

The transparency and gas barrier properties of the resulting biaxially stretched bottle were evaluated by a procedure similar to that in Example 1.

The results are shown in Table 18.

TABLE 18

Item	Unit	Ex. 51				Comp.			
		Ex. 51	Ex. 52	Ex. 53	Ex. 54	Ex. 67	Ex. 68	Ex. 69	Ex. 70
Amount of comonomer	mol %	1	4	1	4	1	4	1	4
Stretch index	cm	168	168	158	158	95	95	92	92
Total wt. of bottle	g	54	54	21	21	60	60	23	23
Thickness of bottle body (part of lens measurement)	mm	0.39	0.38	0.28	0.28	0.40	0.40	0.29	0.28

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TABLE 18-continued

Item	Unit	Ex. 51	Ex. 52	Ex. 53	Ex. 54	Comp. Ex. 67	Comp. Ex. 68	Comp. Ex. 69	Comp. Ex. 70
Transparency									
Total haze	%	0.5	0.3	0.3	0.2	0.5	0.4	0.3	0.3
Internal haze	%	0.2	0.2	0.2	0.1	0.3	0.2	0.2	0.1
CO ₂ permeability coefficient	$\frac{\text{cc} \cdot \text{mm}}{\text{m}^2 \cdot \text{d} \cdot \text{atm}}$	8.0	5.4	9.8	7.0	8.7	7.1	11.8	7.7
CO ₂ permeability coefficient	$\frac{\text{cc} \cdot \text{mm}}{\text{m}^2 \cdot \text{d} \cdot \text{atm}}$	1.7	1.6	2.0	1.9	2.0	1.9	2.3	2.1
Pressure resistance	kg/cm ²	19	18	20	19	16	16	18	17

What is claimed:

1. A blow molded article having excellent transparency, moldability and gas barrier properties,

wherein the blow molded article is produced by blow molding at a temperature of 80°-110° C., and

the blow molded article is composed of a copolyester having an intrinsic viscosity (η) of 0.5-1.5 dl/g formed by esterification of monomers consisting essentially of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 0-80 mol % of terephthalic acid and 20-100 mol % of isophthalic acid, said dihydroxy compound component comprising 10-95 mol % of ethylene glycol and 5-90 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxy groups and being used in an amount of 0.05-1.0 mol by part based on 100 mol by part of the dicarboxylic acid, and is highly oriented so that the stretch index defined by the following equations becomes not less than 130 cm

$$\text{Stretch index} = \frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented preform (including stopper portion)}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area of oriented bottle (excluding stopper portion)}}{\text{Internal volume of oriented bottle (including stopper portion)}} \quad (\text{cm}^{-2})$$

2. The blow molded article of claim 1 wherein said dicarboxylic acid comprises 2-50 mol % of terephthalic acid and 50-90 mol % of isophthalic acid, said dihydroxy compound component comprises 15-90 mol % of ethylene glycol and 10-85 mol % of 1,3-bis(2-hydroxyethoxy)benzene and said polyfunctional hydroxy compound comprises 0.1 to 0.5 mol part based on 100 mol part of the dicarboxylic acid.

3. The blow molded article of claim 1 wherein said polyfunctional hydroxy compound is a member selected from the group consisting of trimethylolmethane, trimethylolmethane and trimethylolpropane.

4. The blow molded article of claim 1 wherein the stretch index is 150 to 200.

5. A blow molded article having excellent transparency, moldability and gas barrier properties, wherein the blow molded article is produced by blow molding at a temperature of 80°-110° C., and

the blow molded article is composed of a copolyester having an intrinsic viscosity (η) of 0.5-1.5 dl/g formed by esterification of monomers consisting essentially of dicarboxylic acid with a hydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 85-99 mol % of terephthalic acid and 1-15 mol % of isophthalic acid, said dihydroxy compound component comprising 80-99 mol % of ethylene glycol and 1-20 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxy groups and being used in an amount of 0.05-0.3 mol by part based on 100 mol by part of the dicarboxylic acid, and is highly oriented so that the stretch index defined by the following equations becomes not less than 130 cm

$$\text{Stretch index} = \frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented preform (including stopper portion)}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area of oriented bottle (excluding stopper portion)}}{\text{Internal volume of oriented bottle (including stopper portion)}} \quad (\text{cm}^{-2})$$

6. The blow molded article of claim 5 wherein said dicarboxylic acid comprises 90-99 mol % of terephthalic acid and 1-10 mol % of isophthalic acid, said dihydroxy compound component comprises 85-99 mol % of ethylene glycol and 1-15 mol % of 1,3-bis(2-hydroxyethoxy)benzene and said polyfunctional hydroxy compound comprises 0.05-0.2 parts by mol based on 100 parts by mol of the dicarboxylic acid.

7. The blow molded article of claim 5 wherein said polyfunctional hydroxy compound is a member selected from the group consisting of trimethylolmethane, trimethylolmethane and trimethylolpropane.

8. The blow molded article of claim 5 wherein the stretch index is 150 to 200.

9. A blow molded article having excellent transparency, moldability and gas barrier properties, wherein the blow molded article is produced by blow molding at a temperature of 80°-110° C., and the blow molded article is composed of a copolyester having an intrinsic viscosity (η) of 0.5-1.5 dl/g formed by esterification of monomers consisting essentially of dicarboxylic acid with a dihydroxy compound compo-

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ment and a polyfunctional hydroxy compound, said dicarboxylic acid consisting essentially of 2-50 mol % of terephthalic acid and 50-90 mol % of isophthalic acid, said dihydroxy compound component consisting essentially of 15-90 mol % of ethylene glycol and 10-85 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound is a member selected from the group consisting of trimethylolmethane, trimethylolpropane and trimethylolpropane and is used in an amount of 0.1-1.5 mol by part based on 100 mol by part of the dicarboxylic acid, and is highly oriented so that the stretch index defined by the following equations is 150 to 200 cm

$$\text{Stretch index} = \frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented product (excluding stopper portion)}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area of oriented bottle (excluding stopper portion)}}{\text{Internal volume of oriented bottle (excluding stopper portion)}} \text{ (cm}^{-2}\text{)}$$

10. A blow molded article having excellent transparency, moldability and gas barrier properties, wherein the blow molded article is produced by blow molding at a temperature of 80°-110° C., and the blow molded article is composed of a copolyester having an intrinsic viscosity (η) of 0.5-1.5 dl/g formed by esterification of monomers consisting essentially of dicarboxylic acid with a hydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid consisting essentially of 90-99 mol % of terephthalic acid and 1-10 mol % of isophthalic acid, said dihydroxy compound component consisting essentially of 85-99 mol % of ethylene glycol and 1-15 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound is a member selected from the group consisting of trimethylolmethane, trimethylolpropane and trimethylolpropane and is used in an amount of 0.05-0.2 mol by part based on 100 mol by part of the dicarboxylic acid, and is highly oriented so that the stretch index defined by the following equations is 150 to 200 cm

$$\text{Stretch index} = \frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented product (excluding stopper portion)}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area of oriented bottle (excluding stopper portion)}}{\text{Internal volume of oriented bottle (excluding stopper portion)}} \text{ (cm}^{-2}\text{)}$$

11. A blow molded article having excellent transparency, moldability and gas barrier properties, wherein the blow molded article is produced by blow molding at a temperature of 80°-110° C., and the blow molded article is composed of a copolyester having an intrinsic viscosity (η) of 0.5-1.5 dl/g formed by esterification of monomers consisting essentially of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 2-50 mol % of terephthalic acid and 50-90 mol % of isophthalic acid, said dihydroxy compound component comprising 15-90 mol % of ethylene glycol and 10-85 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional

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hydroxy compound having at least three hydroxy groups and being used in an amount of 0.1 to 0.5 mol by part based on 100 mol by part of the dicarboxylic acid, and is highly oriented so that the stretch index defined by the following equations is 150 to 200 cm

$$\text{Stretch index} = \frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented product (excluding stopper portion)}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area of oriented bottle (excluding stopper portion)}}{\text{Internal volume of oriented bottle (excluding stopper portion)}} \text{ (cm}^{-2}\text{)}$$

12. A blow molded article having excellent transparency, moldability and gas barrier properties, wherein the blow molded article is produced by blow molding at a temperature of 80°-110° C. and the blow molded article is composed of a copolyester having an intrinsic viscosity (η) of 0.5-1.5 dl/g formed by esterification of monomers consisting essentially of dicarboxylic acid with a hydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 90-99 mol % of terephthalic acid and 1-10 mol % of isophthalic acid, said dihydroxy compound component comprising 85-99 mol % of ethylene glycol and 1-15 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxyl groups and being used in an amount of 0.05-0.2 mol by part based on 100 mol by part of the dicarboxylic acid, and is highly oriented so that the stretch index defined by the following equations is 150 to 200 cm

$$\text{Stretch index} = \frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented product (excluding stopper portion)}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area of oriented bottle (excluding stopper portion)}}{\text{Internal volume of oriented bottle (excluding stopper portion)}} \text{ (cm}^{-2}\text{)}$$

13. A blow molded article wherein the blow molded article is composed of a polyester resin composition comprising (A) 30-99% by weight of a polyethylene terephthalate resin and (B) 1-70% by weight of a copolyester formed by esterification of dicarboxylic acid with ethylene glycol, said dicarboxylic acid comprising 10-92 mol % of terephthalic acid and 8-90 mol % of isophthalic acid, and is highly oriented so that the stretch index as defined above becomes not less than 130 cm.

14. A blow molded article wherein the blow molded article is composed of a polyester resin composition comprising (A) 80-95% by weight of a polyethylene terephthalate resin and (B) 5-20% by weight of a copolyester formed by esterification of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 0-80 mol % of terephthalic acid and 20-100 mol % of isophthalic acid, said dihydroxy compound component comprising 10-95 mol % of ethylene glycol and 5-90 mol % of dihydroxyethoxy resorcinol, and said polyfunctional hydroxy compound having at least three hydroxyl groups and being used in an amount of 0.05-1.0 part by mol based on 100 parts by mol of the dicarboxylic acid, and is highly oriented so that the stretch index as defined above becomes not less than 130 cm.

15. A blow molded article wherein the blow molded article is composed of a copolyester having an intrinsic viscosity (η) of 0.5–1.5 dl/g formed by esterification of dicarboxylic acid with ethylene glycol, said dicarboxylic acid comprising 85–99.5 mol % of terephthalic acid and 0.5–15 mol % of isophthalic acid, and is highly oriented so that the stretch index defined by the following equations becomes not less than 130 cm

$$\text{Stretch index} = \frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented preform (including stopper portion)}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area of oriented bottle (including stopper portion)}}{\text{Internal volume of oriented bottle (including stopper portion)}} \text{ (cm}^{-2}\text{)}$$

16. The blow molded article of claim 15 wherein said dicarboxylic acid comprises 90–99.5 mol % of terephthalic acid and 0.5–10 mol % of isophthalic acid.

17. The blow molded article of claim 15 wherein the stretch index is 150 to 200.

18. A blow molded article wherein the blow molded article is composed of a copolyester having an intrinsic viscosity (η) of 0.5–1.5 dl/g formed by esterification of terephthalic acid with a dihydroxy compound component comprising 93–98 mol % of ethylene glycol and 2–7 mol % of diethylene glycol, and is highly oriented so that the stretch index defined by the following equations becomes not less than 130 cm

$$\text{Stretch index} = \frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented preform (including stopper portion)}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area of oriented bottle (including stopper portion)}}{\text{Internal volume of oriented bottle (including stopper portion)}} \text{ (cm}^{-2}\text{)}$$

19. The blow molded article of claim 18 wherein said dihydroxy compound component comprises 95–98 mol % of ethylene glycol and 2–5 mol % of diethylene glycol.

20. The blow molded article of claim 18 wherein the stretch index is 150 to 200.

21. A process for preparing a blow molded article which process comprises

(a) forming a preform from a copolyester having an intrinsic viscosity (η) of 0.5–1.5 dl/g formed by esterification of monomers consisting essentially of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 0–80 mol % of terephthalic acid and 20–100 mol % of isophthalic acid, said dihydroxy compound component comprising 10–95 mol % of ethylene glycol and 5–90 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxy groups and being used in an amount of 0.05–1.0 mol by part based on 100 mol by part of the dicarboxylic acid, and

(b) blow-molding the preform at a temperature of 80°–110° C. such that the stretch index is not less than 130 cm, wherein the stretch index is defined by the following equations:

$$\text{Stretch index} = \frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented preform (including stopper portion)}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area of oriented bottle (including stopper portion)}}{\text{Internal volume of oriented bottle (including stopper portion)}} \text{ (cm}^{-2}\text{)}$$

22. The process as claimed in claim 21 wherein said dicarboxylic acid comprises 2–50 mol % of terephthalic acid and 50–90 mol % of isophthalic acid, said dihydroxy compound component comprises 15–90 mol % of ethylene glycol and 10–85 mol % of 1,3-bis(2-hydroxyethoxy)benzene and said polyfunctional hydroxy compound comprises 0.1 to 0.5 mol part based on 100 mol part of the dicarboxylic acid.

23. The process as claimed in claim 21 wherein said polyfunctional hydroxy compound is a member selected from the group consisting of trimethylolmethane, trimethylolthane and trimethylolpropane.

24. The process as claimed in claim 21 wherein the stretch index is 150 to 200 cm.

25. A process for preparing a blow molded article which process comprises

(a) forming a preform from a copolyester having an intrinsic viscosity (η) of 0.5–1.5 dl/g formed by esterification of monomers consisting essentially of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 85–99 mol % of terephthalic acid and 1–15 mol % of isophthalic acid, said dihydroxy compound component comprising 80–99 mol % of ethylene glycol and 1–20 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxy groups and being used in an amount of 0.05–0.3 mol by part based on 100 mol by part of the dicarboxylic acid, and

(b) blow-molding the preform at a temperature of 80°–110° C. such that the stretch index is not less than 130 cm, wherein the stretch index is defined by the following equations:

$$\text{Stretch index} = \frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented preform (including stopper portion)}} \times \frac{1}{f}$$

$$f = \frac{\text{Internal surface area of oriented bottle (including stopper portion)}}{\text{Internal volume of oriented bottle (including stopper portion)}} \text{ (cm}^{-2}\text{)}$$

26. The process as claimed in claim 25 wherein said dicarboxylic acid comprises 90–99 mol % of terephthalic acid and 1–10 mol % of isophthalic acid, said dihydroxy compound component comprises 85–99 mol % of ethylene glycol and 1–15 mol % of 1,3-bis(2-hydroxyethoxy)benzene and said polyfunctional hydroxy compound comprises 0.05 to 0.2 parts by mol based on 100 mol parts of the dicarboxylic acid.

27. The process as claimed in claim 25 wherein said polyfunctional hydroxy compound is a member selected from the group consisting of trimethylolmethane, trimethylolthane and trimethylolpropane.

28. The process as claimed in claim 25 wherein the stretch index is 150 to 200 cm.

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29. A process for preparing a blow molded article which process comprises

- (a) forming a preform from a copolyester having an intrinsic viscosity (η) of 0.5-1.5 dl/g formed by esterification of monomers consisting essentially of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid consisting essentially of 2-50 mol % of terephthalic acid and 50-90 mol % of isophthalic acid, said dihydroxy compound component consisting essentially of 15-90 mol % of ethylene glycol and 10-85 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound is selected from the group consisting of trimethylolmethane, trimethylolpropane and trimethylolpropene and is used in an amount of 0.1-1.5 mol by part based on 100 mol by part of the dicarboxylic acid, and
- (b) blow-molding the preform at a temperature of 80°-110° C. such that the stretch index is 150-200 cm, wherein the stretch index is defined by the following equations:

$$\text{Stretch index} = \frac{\frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented preform (excluding stopper portion)}} \times \frac{1}{f}}$$

$$f = \frac{\frac{\text{Internal surface area of oriented bottle (excluding stopper portion)}}{\text{Internal volume of oriented bottle (excluding stopper portion)}}}{\text{Internal volume of oriented bottle (excluding stopper portion)}} \quad (\text{cm}^{-2})$$

30. A process for preparing a blow molded article which process comprises

- (a) forming a preform from a copolyester having an intrinsic viscosity (η) of 0.5-1.5 dl/g formed by esterification of monomers consisting essentially of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid consisting essentially of 90-99 mol % of terephthalic acid and 1-10 mol % of isophthalic acid, said dihydroxy compound component consisting essentially of 85-99 mol % of ethylene glycol and 1-15 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound is selected from the group consisting of trimethylolmethane, trimethylolpropane and trimethylolpropene and is used in an amount of 0.05-0.2 mol by part based on 100 mol by part of the dicarboxylic acid, and
- (b) blow-molding the preform at a temperature of 80°-110° C. such that the stretch index is 150-200 cm, wherein the stretch index is defined by the following equations:

$$\text{Stretch index} = \frac{\frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented preform (excluding stopper portion)}} \times \frac{1}{f}}$$

$$f = \frac{\frac{\text{Internal surface area of oriented bottle (excluding stopper portion)}}{\text{Internal volume of oriented bottle (excluding stopper portion)}}}{\text{Internal volume of oriented bottle (excluding stopper portion)}} \quad (\text{cm}^{-2})$$

31. A process for preparing a blow molded article having excellent transparency, moldability and gas barrier properties, which process comprises

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- (a) forming a preform from a copolyester having an intrinsic viscosity (η) of 0.5-1.5 dl/g formed by esterification of monomers consisting essentially of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 2-50 mol % of terephthalic acid and 50-90 mol % of isophthalic acid, said dihydroxy compound component comprising 15-90 mol % of ethylene glycol and 10-85 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxy groups and being used in an amount of 0.1-0.5 mol by part based on 100 mol by part of the dicarboxylic acid, and
- (b) blow-molding the preform at a temperature of 80°-110° C. such that the stretch index is 150-200 cm, wherein the stretch index is defined by the following equations:

$$\text{Stretch index} = \frac{\frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented preform (excluding stopper portion)}} \times \frac{1}{f}}$$

$$f = \frac{\frac{\text{Internal surface area of oriented bottle (excluding stopper portion)}}{\text{Internal volume of oriented bottle (excluding stopper portion)}}}{\text{Internal volume of oriented bottle (excluding stopper portion)}} \quad (\text{cm}^{-2})$$

32. A process for preparing a blow molded article having excellent transparency, moldability and gas barrier properties, which process comprises

- (a) forming a preform from a copolyester having an intrinsic viscosity (η) of 0.5-1.5 dl/g formed by esterification of monomers consisting essentially of dicarboxylic acid with a dihydroxy compound component and a polyfunctional hydroxy compound, said dicarboxylic acid comprising 90-99 mol % of terephthalic acid and 1-10 mol % of isophthalic acid, said dihydroxy compound component comprising 85-99 mol % of ethylene glycol and 1-15 mol % of 1,3-bis(2-hydroxyethoxy)benzene, and said polyfunctional hydroxy compound having at least three hydroxy groups and being used in an amount of 0.05-0.2 mol by part based on 100 mol by part of the dicarboxylic acid, and
- (b) blow-molding the preform at a temperature of 80°-110° C. such that the stretch index is 150-200 cm, wherein the stretch index is defined by the following equations:

$$\text{Stretch index} = \frac{\frac{\text{Internal volume of oriented bottle (excluding stopper portion)}}{\text{Internal volume of unoriented preform (excluding stopper portion)}} \times \frac{1}{f}}$$

$$f = \frac{\frac{\text{Internal surface area of oriented bottle (excluding stopper portion)}}{\text{Internal volume of oriented bottle (excluding stopper portion)}}}{\text{Internal volume of oriented bottle (excluding stopper portion)}} \quad (\text{cm}^{-2})$$

* * * * *

United States Patent [19] Agrawal

[11] 4,254,080
[45] Mar. 3, 1981

[34] FORMING SUBSTANTIALLY
RECTANGULAR ARTICLES FROM
PREFORMS OF POLYALKYLENE
TEREPHTHALATE

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Conn.

[73] Assignee: Monsanto Company, St. Louis, Mo.

[21] Appl. No.: 23,941

[22] Filed: Mar. 27, 1979

[51] Int. Cl.² B29C 17/07

[52] U.S. Cl. 264/537; 264/532;
264/533

[58] Field of Search 264/520, 521, 523, 524,
264/525, 526, 529, 530, 535, 537, 538, 540, 541,
542, 543, 532; 215/1 C; 428/35

[36] References Cited

U.S. PATENT DOCUMENTS

3,632,713	1/1972	Seefelt	264/320
3,662,048	5/1972	Turner	264/320 X
3,733,309	5/1973	Wyeth et al.	264/340 X
3,775,524	11/1973	Seefelt	264/321
3,892,830	7/1975	Hudson et al.	264/520
3,900,120	8/1975	Stroock	215/1 C
3,917,095	11/1975	Seefelt	215/1 C
3,989,784	11/1976	Uhlir	264/320
4,117,030	9/1978	Appel et al.	264/320 X

4,131,666 12/1978 Agrawal et al. 264/321

FOREIGN PATENT DOCUMENTS

1267430 3/1972 United Kingdom .

1355287 6/1974 United Kingdom .

OTHER PUBLICATIONS

J. A. Antonopoulos and F. G. Hohmann, *Modern Plastics*, "Stretch-blow molding PVC and Nitriles", 9-1976.

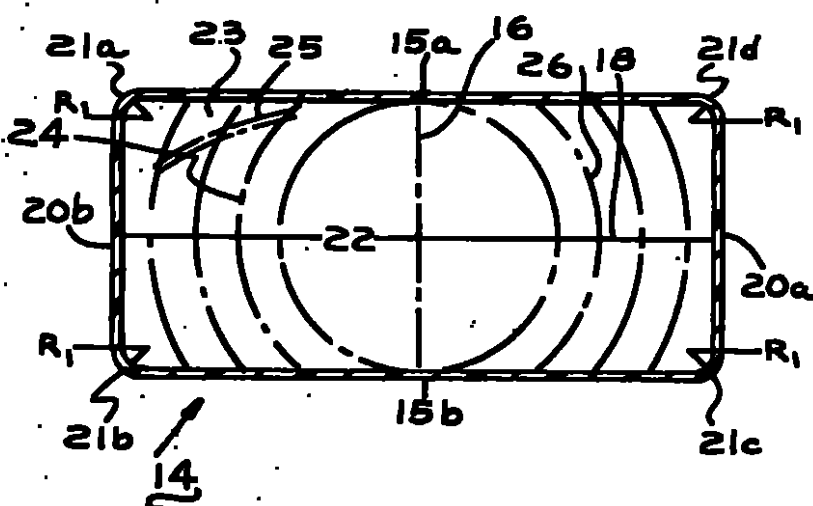
Primary Examiner—Jan H. Silbaugh

Attorney, Agent, or Firm—Michael J. Murphy

[57] ABSTRACT

In forming hollow, molecularly oriented articles having substantially rectangular cross sections from thermoplastic preforms by a method which includes distending the preforms in a mold while at molecular orientation temperature, the improvement providing improved material distribution in regions furthest from the central axes of the articles (e.g. in the corner areas) when the thermoplastic is moldable polyalkylene terephthalate having an inherent viscosity of at least 0.55 which involves limiting the corner definition ratio to between about 2 to about 14 and the circular deviation ratio to no greater than about 2.4 at the cross section during distension and controlling axial and maximum radial stretch of the preforms within predetermined limits.

9 Claims, 7 Drawing Figures



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Fig. 1

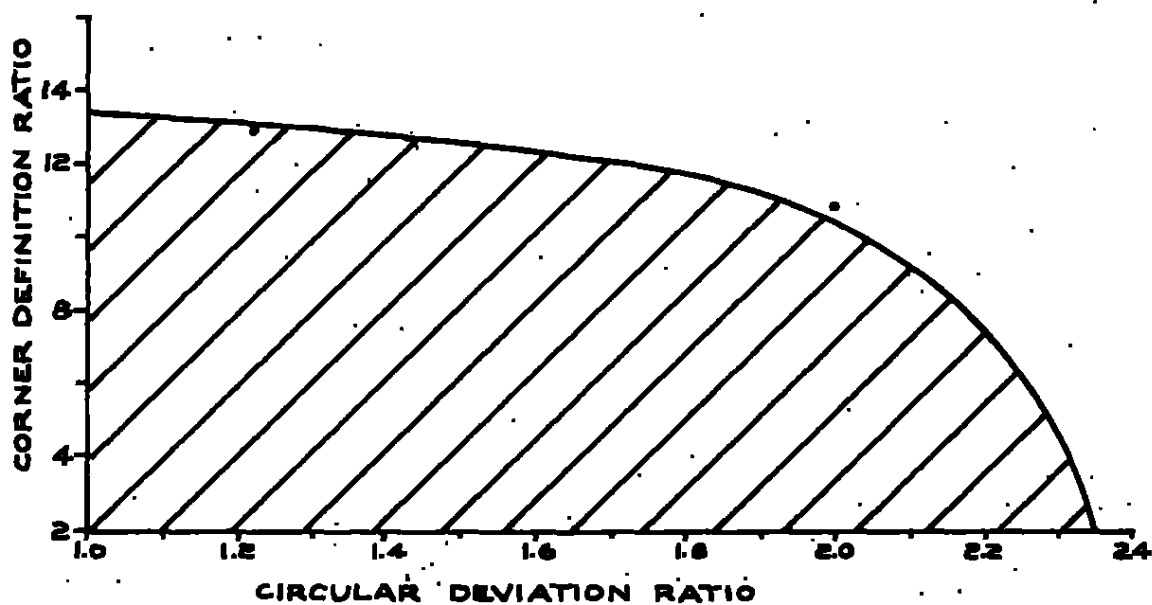
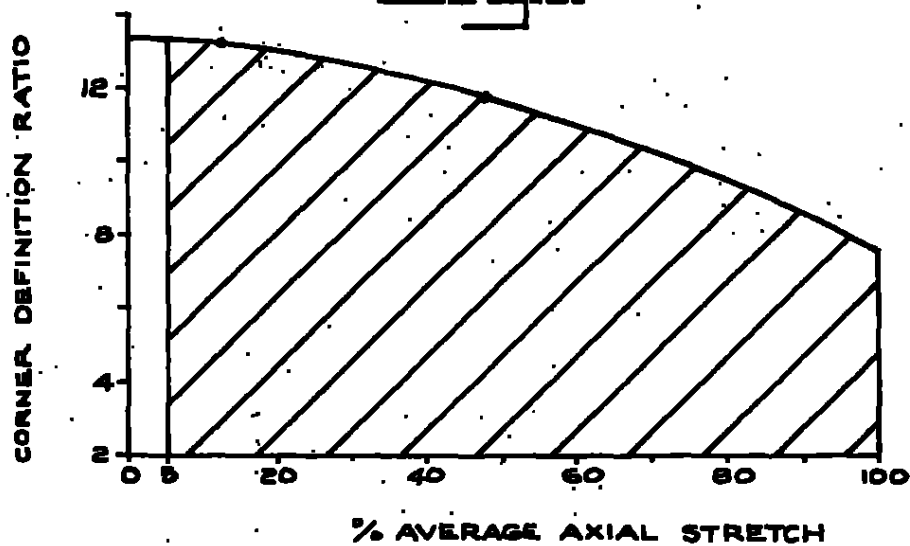


Fig. 2



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Fig. 2

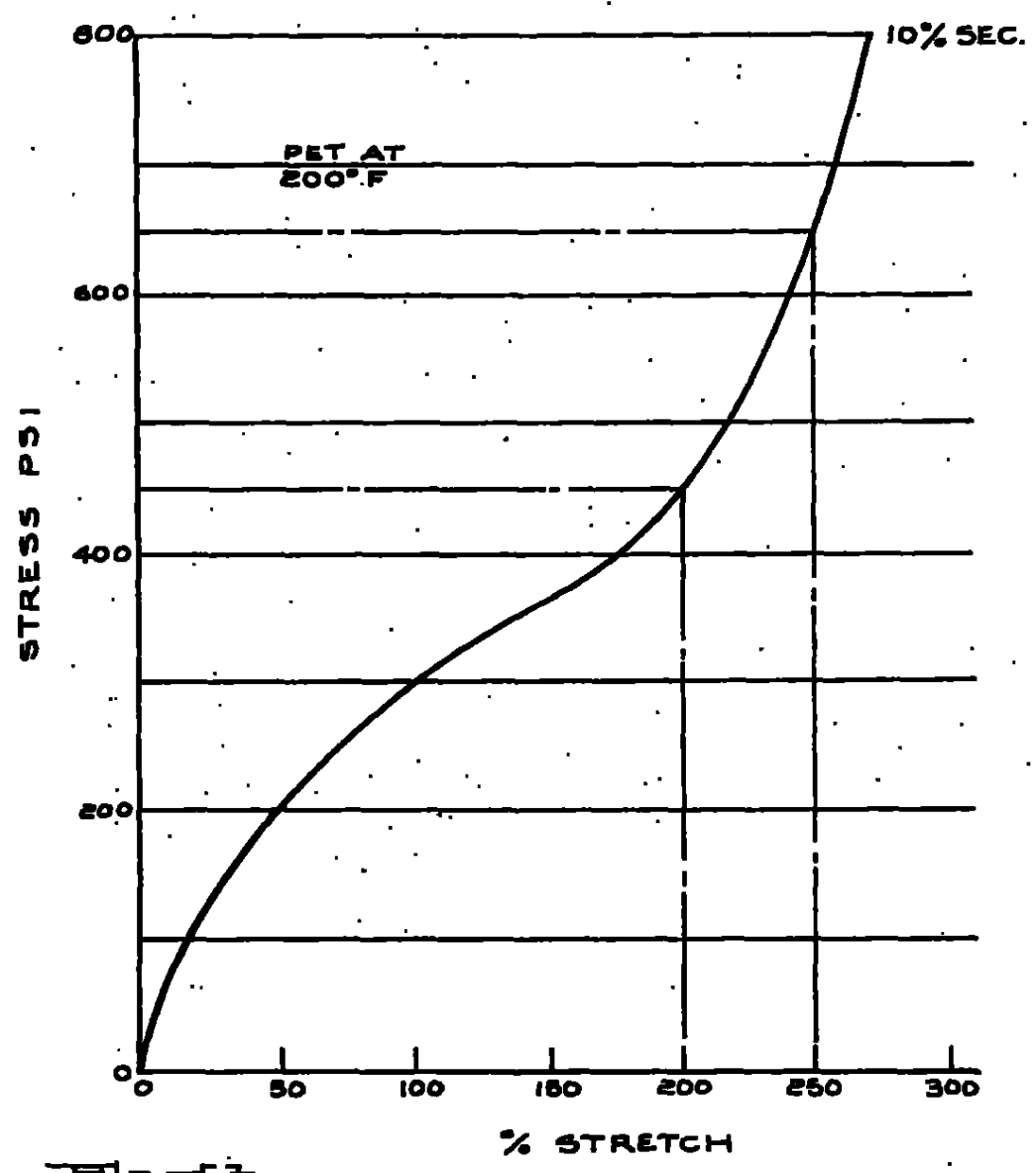
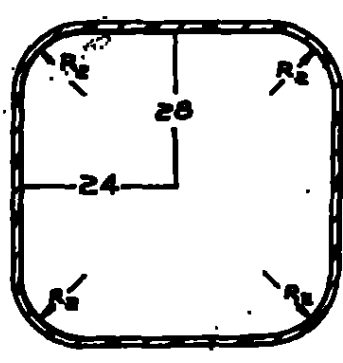


Fig. 3

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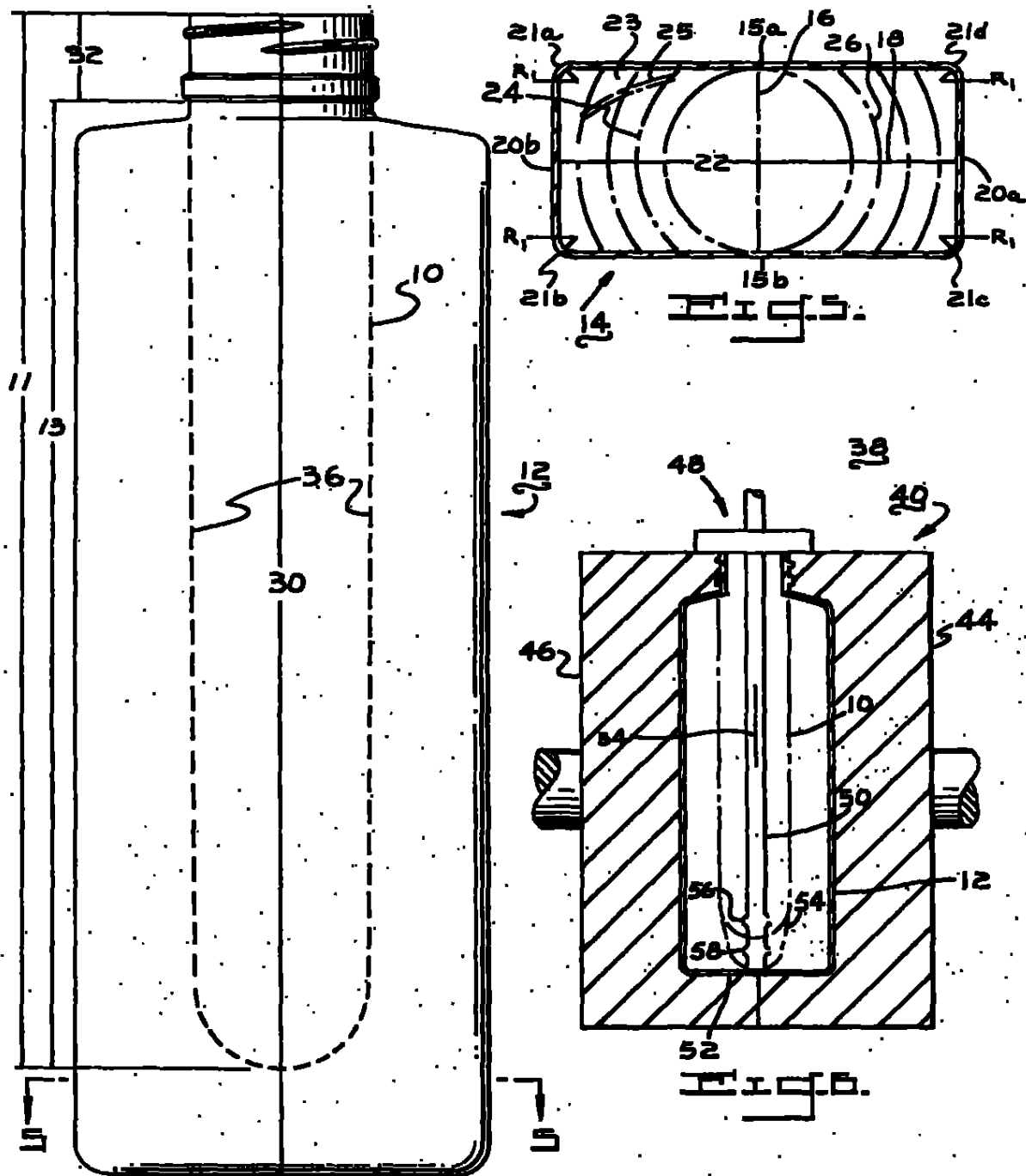


Fig. 4.

Fig. 6.

FORMING SUBSTANTIALLY RECTANGULAR ARTICLES FROM PREFORMS OF POLYALKYLENE TEREPHTHALATE

CROSS REFERENCE TO RELATED APPLICATION

Improvements In Forming Non-Cylindrical Articles From Preforms Of Polyalkylene Terephthalate, Pursu-
shottam D. Agrawal, U.S. Ser. No. 971,398, filed Dec. 20, 1978.

BACKGROUND OF THE INVENTION

This invention relates to forming hollow, molecularly oriented articles such as containers of polyalkylene terephthalate such as polyethylene terephthalate (PET), and more particularly to improvements in a preform process for forming articles of such material having certain non-round cross sections wherein material distribution is improved in the vicinity of the ends of the sides.

Containers of molecularly oriented PET are known and desirable for packaging because of superior clarity, impact strength and barrier properties. Prior to this invention, configurations of such containers have been largely limited to circular yet it is frequently desirable for aesthetics and functional reasons such as space conservation to be able to blow mold non-circular containers of rectangular, e.g. square, shape with good material thickness uniformity in the peripheral direction.

Attempts in the past to form non-round configurations from commodity thermoplastics such as polyethylene and polypropylene in a process wherein prior-shaped preforms are conditioned to molecular orientation temperature before distension in the blow mold entailed establishing special conditions to promote wall thickness uniformity between areas furthest from the lengthwise axis and areas close to the axis. As disclosed in U.S. Pat. No. 3,930,459, such systems usually involved establishing temperature differences in the circumferential direction of the preforms such that portions to expand less were cooler and therefore would stretch less than hotter portions which were to stretch more in the blow mold. If such temperature difference is not well established excessive thinning or even blow out at the extremities of the cross section could be expected to occur. Needless to say, consistent accurate provision of such a differential does not facilitate simplicity of the preform heat treating process.

SUMMARY OF THE INVENTION

Now, however, process improvements have been developed to facilitate fabrication of non-round hollow articles of polyalkylene (e.g. polyethylene) terephthalate.

Accordingly, it is a principal object of this invention to provide improvements in a process for forming non-round, molecularly oriented, hollow articles such as containers from polyalkylene terephthalate, e.g. PET, thermoplastic materials, which result in improved material thickness distribution in regions furthest from the lengthwise axis of non-round cross sections of the article.

Another object of this invention is to recognize and use the inherent mechanical properties of PET to advantage to promote such improved material distribution.

A specific object is to recognize and define relationships between forming parameters and the extent to which the cross sectional shape can be varied in blowing substantially rectangular molecularly oriented PET containers with good contour definition in the vicinity of the extremes of the container cross section, e.g. in the rounded corners.

Other objects of this invention will in part be obvious and will in part appear from the following description and claims.

These and other objects are provided in the method of forming a molecularly oriented hollow article having a substantially rectangular cross section from a preform of thermoplastic material, which includes distending the preform in a mold while at molecular orientation temperature, by providing the improvement wherein the thermoplastic material is moldable polyalkylene terephthalate having an inherent viscosity of at least about 0.55 and the forming operation comprises, in combination, the steps of limiting the corner definition ratio to between about 2 to about 14 and the circular deviation ratio to no greater than about 2.4 at the cross section during such distending and controlling such distending according to the relations:

$$\begin{aligned} \% \text{ total stretch } (A) &= \frac{\text{article length minus preform length times } 100}{\text{preform length minus preform neck finish length}} \\ \% \text{ maximum radial stretch } (B) &= \frac{\text{maximum container outside diameter minus minimum preform outside diameter times } 100}{\text{preform outside diameter}} \end{aligned}$$

wherein: A is between about 5 to about 100 and B is no greater than about 334.

BRIEF DESCRIPTION OF THE DRAWINGS

In describing the overall invention, reference will be made to the accompanying drawings wherein:

FIG. 1 is a graphical representation portraying dimensional limits of certain rectangular containers which can be effectively formed according to the invention;

FIG. 2 is a graphical representation of the relationship of the level of stretch which should be used according to the invention in forming rectangular containers having the dimensions shown on the ordinate of FIG. 1;

FIG. 3 is a stress/strain diagram at a stated strain rate for PET at a stated temperature;

FIG. 4 is a vertical elevational view of a container formable from a preform according to this invention;

FIG. 5 is a schematic sectional view along 5-5 of FIG. 4;

FIG. 6 is a schematic elevational view of a stretch-blow assembly capable of converting the preform outlined in FIG. 4 into the container therein shown; and

FIG. 7 is a view similar to FIG. 8 of an alternative container cross section.

DESCRIPTION OF ILLUSTRATED EMBODIMENTS

In forming containers of polyethylene terephthalate having non-round cross sections (such as substantially rectangular including square) either throughout most or all of the length or at least at one or more horizontal sections along such length, by distending circular preforms at molecular orientation temperature in a blow mold, such cross sections can be formed with good wall thickness uniformity because of the mechanical properties of the PET material without relying on a circumfer-

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ential temperature gradient in the material of the preform.

More particularly, preform 10, shown in outline in FIG. 4, is circular in cross section and is to be expanded in blow mold 40 (FIG. 6) having a cavity configuration conforming in outline to that of bottle 12 (FIG. 4) having maximum rectangular cross section 14 (FIG. 5) along its length lying in a plane perpendicular to its longitudinal axis. During blowing at molecular orientation temperature, preform 10 will initially distend radially until its outer surface first contacts the mold cavity wall in the vicinity of the ends of minor diameter or axis 16 (FIG. 5). Such initial expansion is illustrated schematically in FIG. 5 by the series of successively larger concentric circles shown in outline form with the initial contact just referred to occurring at 15a, 15b. Further expansion to complete formation of the rectangular shape stretches the free sides, schematically shown at 24, 26 in FIG. 5, of the partially expanded circular form which have not yet contacted the cavity surface outwardly toward the extremes of major axis 18 to eventually form short walls 20a, 20b at the ends of such axis. This further expansion draws plastic from the portions of the circumference of the circular shape which have already contacted the mold wall. The latter portions of the preform (i.e. the regions including 15a and 15b in FIG. 5) will be necessarily cooler than free, unrestrained portions 24, 26 at the ends of the developing rectangular shape, since the mold cavity walls are cooled in conventional manner by circulation of a heat transfer medium through channels in the mold just beneath the cavity surface. PET material by nature exhibits significant resistance to stretch at molecular orientation forming temperatures. Thus, as indicated in FIG. 3, at a temperature of 200° F. (93° C.), and a 10% per second strain rate, a stress of 450 psi is required to achieve 200 percent stretch. For an additional 50 percent increase in stretch (from 200 to 250 percent along the x axis in FIG. 5) a stress increase of 200 psi (14 kg./cm.²) (along the y axis) is required. At 200 percent stretch a stress of 450 psi (31.5 kg./cm.²) is needed while at 250 percent, a stress of 650 psi (45.5 kg./cm.²) is needed. This indicates a sharp increase in stress for relatively low percent stretch which has been found to cause a strain hardening effect at the 10 percent per second strain rate. Under actual container manufacturing conditions, however, strain rates on the order of 200 percent per second are more realistic in achieving economical blow molding cycle times. Compared to stress requirements at the 10 percent per second strain rate, at a 200 percent per second strain rate it is expected that PET will exhibit an even more severe rise in stress to achieve a relatively low percent stretch. This strain hardening characteristic of PET facilitates formation of rounded corners in rectangular sections of relatively uniform thickness in that after the polymer is stretched a given amount, the force required for further stretching substantially increases and at that point more material will be stretched out of areas not previously stretched much—i.e. the initially relatively thick portions in the vicinity of 15a and 15b in FIG. 5 which have stretched only to the ends of minor axis 16. This self-adjusting nature of PET which is reflected in a pulling of material out of regions 15a and 15b to provide material which eventually forms walls 20a, 20b and corners 21 results in an improved degree of wall thickness uniformity in a substantially rectangular configuration.

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In comparison, for comparable amounts of stretch and stretch rates with a thermoplastic material having a relatively flat stress/strain curve, for example a nitrile polymer such as a 70/30 weight percent acrylonitrile/butylene material, stress buildup will not increase sharply with strain. This means that material for walls forming sides at the ends of the major axis will not be pulled out of the already shaped and partially chilled plastic at the ends of the minor axis with the result that the thickness at the free expanding ends will continue to decrease as the plastic moves towards the ends of the major axis. This can lead to fracture in the vicinity of the extremes of the major axis if stretching is excessive or else substantial local thinning of the wall thickness versus that in the vicinity of the ends of the minor axis.

The tendency of PET to strain harden, however, imposes restrictions on the amount of definition achievable in highly stretched areas such as in the vicinity of and including rounded corners, 21a, 21b, 21c and 21d (FIG. 5) of a substantially rectangular cross section. In accordance with the invention, for containers having a substantially rectangular (including square) cross section a relationship has been established between (a) corner definition ratio (b) circular deviation ratio (c) percent axial stretch and (d) percent maximum radial stretch which, when followed, will provide excellent definition in highly stretched cornered areas of containers made of polyalkylene terephthalate such as PET thermoplastic materials. Such relationships are graphically depicted in FIGS. 1 and 2 and comprise limiting during stretching the corner definition ratio to between about 2 to about 14 and the circular deviation ratio to no greater than about 2.4. For purposes of the present invention, corner definition ratio is defined as two times the maximum distance between the lengthwise axis at the planar cross section of the finished rectangular configuration (or longitudinal axis 34 of the preform when mounted initially in the mold as at 10 in FIG. 6) and the mold cavity surface defining a planar side of the rectangular shape divided by the radius of the rounded corner. For the configuration of FIG. 5, such corner definition ratio is represented by two times distance 22 divided by R₁. For the symmetrical substantially square cross section of FIG. 7, such corner definition ratio is distance 24 plus distance 28 divided by R₂. The circular deviation ratio is defined as two times the maximum distance between the lengthwise axis at the planar cross section of the finished rectangular configuration (or longitudinal axis 34 of the preform when mounted initially in the mold as at 10 in FIG. 6) and the mold cavity defining a planar side of the rectangular shape divided by two times the minimum distance between the lengthwise axis at the planar cross section of the finished rectangular configuration (or longitudinal axis 34 of the preform when mounted initially in the mold as at 10 in FIG. 6) and the mold cavity defining a planar side of the rectangular shape. For the configuration of FIG. 5, such circular deviation ratio is major diameter 18 or two times distance 22 divided by minor diameter 16 whereas for the square configuration of FIG. 7 such ratio will always be one since distances 24 and 28 are equal.

With respect to blowing rectangular as compared with other cross sections such as oval, the corner definition to circular deviation ratio limits will be wider for rectangular shapes since the expanding portions of the preform after initial contact with the mold (i.e. the portions on either side of regions 15a and 15b in FIG. 6) will be able to stretch more before contacting the walls

of the rectangular cross section. For example, with respect to FIG. 3, the plastic will be able to freely extend through region 23 before contacting the mold surface whereas such additional expansion in an area equivalent to 23 could not occur if the cavity was oval as such oval cavity outline is schematically depicted by short phantom line 25 in FIG. 5. Because of this the previously described cooling effect associated with mold wall contact will be less pronounced with rectangular shapes thus facilitating formation of relatively shallow radii R_1 , R_2 in FIGS. 5 and 7 in rectangular configurations.

Further in accordance with the invention, preform distension in the mold is controlled according to the relations: percent axial stretch (A) equals article length (30 in FIG. 4) minus preform length (11 in FIG. 4) times 100 divided by preform length minus preform neck finish length (32 in FIG. 4); and percent maximum radial stretch (B) equals the maximum planar distance (22 in FIG. 5 and 24 in FIG. 7) to the mold surface defining a side of the rectangular shape from the preform axis (which in FIG. 6 is 34) when mounted in the mold minus the preform outside diameter (36 in FIG. 4) times 100 divided by the preform outside diameter wherein: A is between about 5 to about 100 and B is no greater than about 334. In situations where the finish is formed on the article during reshaping in the article blow mold, i.e. the preform does not have a molded finish, a length equivalent to the finish length on the formed article should be used in the foregoing equation for percent axial stretch, or if no finish is provided, a figure should be used for the length of plastic, if any, which is not axially stretched during final forming. With respect to the amount of axial stretch of the elongated preform being reshaped, this can vary along the length. For example, in the illustrated embodiment plastic close to the neck finish will stretch less than that adjacent the closed end whereas that in between will stretch an amount intermediate these extremes. Instead of using the simplified foregoing equation to determine axial stretch, the term "average" as it applies to axial stretch can be determined by considering the amount of axial stretch that occurs in incremental sections of the preform length and then calculating the arithmetic average of such individual stretch amounts. This is facilitated by forming spaced grid markings on the unstretched preform surface, e.g. 1 inch (2.54 cms.) apart, and computing individual stretch amounts by measuring the distance between immediately adjacent marks after axial stretching and before blowing.

Further with respect to the axial stretch parameter of FIG. 2, for a given amount of plastic in the preform adequate to produce a container of predetermined weight, if the initial preform is excessively long with respect to the lengthwise axis (30 in FIG. 4) of the container, which means the preform thickness is relatively small, the strain hardening effect because of the reduced thickness will be pronounced and this will tend against sharp formation of the desired corner radii since excessive thinning will occur as material approaches the areas of maximum stretch. In addition, when the preforms are injection molded, since PET is shear sensitive, lengthy movement of the material along a relatively elongated narrow injection mold cavity promotes formation of acetaldehyde which is a decomposition product which can cause taste problems when the containers are intended to package human-consumable substances. On the other hand, if the preform is made excessively

thick to offset the disadvantages just mentioned, different problems can be expected during injection molding. More specifically, if the thickness is too great even though sections of the thickness adjacent the outer and inner surfaces are chilled relatively quickly in the injection forming mold to below the crystalline freezing point of the material via chilling contact with the cooled preform injection mold and core rod to prevent formation of crystals and therefore cloudiness in the material, heat retained toward the middle of such relatively thick sections tends to cause the material to heat back up again after ejection from the mold to promote crystal formation and the cloudiness which it is desired to avoid.

FIG. 6 shows a stretch-blow assembly 38 for converting a preform 10 into molecularly oriented container 12 having the configuration of FIG. 4. This is accomplished by first enclosing each preform 10 while within the molecular orientation temperature range for the thermoplastic material of which it is formed within partible sections 44, 46 of conventional blow mold 40. Next, stretching mechanism 48 is moved over the open end of blow mold 40 and preform 10 whereupon telescopic stretch rod 50 is caused to move to extended position by a suitable mechanism, not shown, in order to force the hemispherical end of the preform 10 against base portion 52 of blow mold 40 thereby axially stretching the body portion of the preform (13 in FIG. 4) in the manner illustrated in phantom at 34 in FIG. 6. Simultaneously therewith or preferably immediately thereafter, a blowing medium such as compressed air is admitted to the interior of the preform through openings 54, 56 in rod 50 to stretch it radially outwardly against the mold cavity walls in the manner previously described into the shape of bottle 12. Under certain circumstances, for example those contemplating non-pressure applications for the finished container, it may not be necessary to provide a separate stretch rod in that the pressure of the blowing medium and the reduced length of the preform versus the container length may be adequate to provide the axial stretch desired.

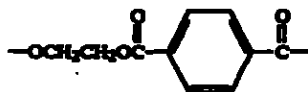
The nature of the surface of the mold cavity against which the thermoplastic is forced into shaping engagement can have an effect on the limits of formation along the major axis of the non-round container being formed. In this respect, coating such surface with a heat insulative material such as Teflon® in the area forming the panels of the container between its rounded corners can improve the ability to blow out into the short sides and into corners having relatively shallow radii— R_1 and R_2 in FIGS. 5 and 7. Such Teflon® coating apparently improves slippage of the material on the coated surface and retards excessive heat transfer from the plastic thereby preventing premature setting of the material. On the other hand, if cycle time is not of major concern the same effect can most likely be achieved by operating the molds at elevated temperature through use of a heat transfer medium circulating through channels in the mold providing a cavity surface temperature on the order of about 100° F. to 180° F. (38° to 82° C.).

Hollow articles such as containers formable according to the invention from preforms 10 may vary widely in size and are preferably characterized in terms of weight and volume as ranging from between about 0.03 to about 0.13 gms/cc of internal volume. The invention is applicable to non-round, substantially rectangular cross sectional configurations in container form wherein the latter have a volume of between about 170

to 3780 cc. and preferably between about 470 to 1890 cc. Though single layer articles are preferred, composite containers having plural layers of thermoplastic material in face-adhering contact are likewise within the scope of those formable according to this invention as long as at least one layer comprises a major proportion (e.g. at least about 50 weight percent) of a polyalkylene terephthalate.

The invention is applicable to the shaping of moldable polyalkylene terephthalates such as polyethylene and polybutylene terephthalate.

Polyethylene terephthalate useful in preparing the thermoplastic articles of this invention includes polymers wherein a major proportion such as about 50 and preferably up to about 97 weight % of the polymer contains repeating ethylene terephthalate units of the formula:



with the remainder being minor amounts of ester-forming components. It also includes copolymers of ethylene terephthalate wherein up to about 10 mole percent of the esterifying glycol units are derived from diethylene glycol; propane-1,3-diol; butane-1,4-diol; polytetramethylene glycol; polyethylene glycol; polypropylene glycol; 1,4-hydroxymethylcyclohexane and the like, and up to 10 mole percent of the acid component is derived from acids such as isophthalic; bibenzoic; naphthalene 1,4- or 2,6-dicarboxylic; adipic; sebacic; and decano-1,1-dicarboxylic acids and the like.

Polyethylene terephthalate should have an inherent viscosity (1% concentration of polymer in a 37.5/62.5 weight percent solution of tetrachloroethane/phenol, respectively, at 30° C.) of at least 0.55 to obtain the desired end properties in the formed articles. Preferably the inherent viscosity is at least about 0.7 to obtain an article having excellent toughness properties, i.e. resistance to impact loading. The inherent viscosity of the polymer solution is measured relative to that of the solvent alone and is defined as follows:

$$\text{inherent viscosity} = \frac{\text{natural logarithm} \frac{\text{viscosity of solution}}{\text{viscosity of solvent}}}{C}$$

where C is the concentration expressed in grams of polymer per 100 milliliters of solution.

Formation of containers with biaxial orientation according to this invention occurs when the outside surface temperature of the thermoplastic material of the preforms is between about 180° to about 230° F. (82.2° to 110° C.) and preferably about 37° F. (93.3° C.) above the glass transition temperature of the material, the latter being about 162° to about 165° F. (72.2° to 73.9° C.) for PET.

The following examples are given to illustrate the principles and practice of this invention and should not be construed as limitations thereof.

EXAMPLE 1

Containers of rectangular cross section throughout the entire length, identical in form to bottles 12 in FIG. 4, are formed from reheated, cylindrical, injection molded preforms. Such containers have 24 ounces (710

cc.) nominal capacity, a weight of 48 gms., a major diameter (18 in FIG. 5) of 3.3 inches (8.4 cms.), a minor diameter (16 in FIG. 5) of 2.7 inches (6.88 cms.), a total length of 7.88 inches (20.0 cms.), a circular deviation ratio (18 divided by 16 in FIG. 5) of 1.22 and a corner definition ratio (18 divided by R₁ in FIG. 5) of 13.2.

PET having an inherent viscosity of about 0.72 was injection molded in conventional equipment into preforms configured as shown at 10 in FIG. 4 having the following dimensions:

- total length=7.0 inches (17.7 cms.);
- finish length=0.57 inches (1.45 cms.);
- minimum outside diameter=1.131 inches (2.873 cms.); and
- average thickness=0.102 inches (0.259 cms.)

(Average thickness is defined as minimum thickness along the length of the preform below the finish plus maximum thickness along such length divided by two).

With cavity dimensions of a blow mold set to provide the above bottle configuration, the percentages of axial stretch and radial stretch were calculated at 13.3 and 192% respectively as follows:

$$\% \text{ axial stretch (A)} = \frac{\text{bottle length minus preform length (100)}}{\text{preform length minus preform neck finish length}}$$

$$A = \frac{7.88 - 7.0}{7.0 - 0.57} (100)$$

$$A = 13.3\%$$

$$\% \text{ maximum radial stretch (B)} =$$

$$\frac{[\text{maximum container outside diameter minus preform outside diameter}] (100)}{\text{preform outside diameter}}$$

$$B = \frac{(3.3 - 1.13)}{1.13} (100)$$

$$B = 192\%$$

While rotating about their lengthwise axes, the body portions of such preforms (13 in FIG. 4) are heated from substantially room temperature to about 200°-230° F. (93° to 110° C.) in accordance with a heating arrangement shown in FIG. 3 of U.S. Pat. No. 4,036,927, the content of col. 6, lines 29-53 of which is incorporated herein by reference.

The heated preforms are introduced to a stretch-blow assembly as illustrated in FIG. 6 which included a mold cavity having a surface corresponding in shape and extent to that of the desired end bottle configuration and which is conventionally cooled via circulating water at cooling water temperature on the order of 21° C. The preforms are then stretched axially against the base of such cavity and expanded along the major and minor axes into heat exchange contact with the side walls to form the bottle shape.

All of the bottles in the foregoing run completely conform to the mold surfaces in the corner areas of the rectangular shape.

EXAMPLE 2

The forming procedure of Example 1 is repeated except that the total preform length is reduced from 7.0 to 5.5 inches (14 cms.). Average axial stretch is 47% while maximum radial stretch along the major axis is 189%. Each of the bottles formed conformed to the mold surfaces fully in the corner areas of the rectangular shape.

EXAMPLE 3

The bottle mold of Example 1 is revised to provide a corner definition ratio of 17.6 and the forming proce-

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ture of Example 1 is then repeated. In each case the plastic in the corner areas of the rectangular cross sections failed to fully conform to the mold cavity surface.

Data from the foregoing Examples is used to form FIGS. 1 and 2.

The preceding Examples illustrate that when the circular deviation and corner definition ratios lie within the crosshatched area of FIG. 1 and the corner definition ratio to percentage axial stretch relationship is within the crosshatched portion of FIG. 2, good corner definition and material distribution is obtained at maximum percentage radial stretch levels no greater than about 334.

Though preforms forming the containers of this invention are preferably circular in cross section and are not purposely provided with a temperature differential in the circumferential direction prior to expansion in the blow mold in order to reduce the complexity of the preform heat treating process, it is within the scope of the invention to utilize non-cylindrical preforms heat treated to purposely develop a temperature gradient around the periphery prior to stretching in the blow mold. Preforms usable in the invention may be shaped by any well known plastic shaping technique such as injection or blow molding, thermoforming from sheet material with or without mechanical assist, compression molding and the like including combinations of the foregoing.

Various modifications and alterations will be readily suggested to persons skilled in the art. It is intended, therefore, that the foregoing be considered as exemplary only and the scope of the invention be ascertained from the following claims.

What is claimed is:

1. In the method of forming a molecularly oriented hollow article having a substantially rectangular cross section from a preform of thermoplastic material, which includes distending the preform in a mold while at molecular orientation temperature,

the improvements wherein the thermoplastic material is moldable polyalkylene terephthalate having an inherent viscosity of at least about 0.55, said preform region forming said cross section is not treated before said distending for the purpose of establishing a circumferential temperature difference therein, and the distending comprises, in combination, the steps of:

expanding first portions of said region against mold wall portions at the end of a minor axis of a cavity conforming to said substantially rectangular cross section to form relatively thick sections thereof while expanding other portions a greater extent than said first portions toward wall portions at the

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end of a major axis of said cavity thereby establishing a strain hardened pattern in the material wherein such expanded other portions are strain hardened greater than said thick sections; and

drawing material out of said thick sections as such expanded other portions of greater strain hardened level continue to expand toward the mold wall portions at the end of the major axis;

limiting the corner definition ratio to between about 2 to about 14 and the circular deviation ratio to no greater than about 2.4 at the cross section during said distending; and

controlling said distending according to the relations:

% axial stretch (A) =

$$\frac{\text{article length minus preform length times } 100}{\text{preform length minus preform neck length}}$$

% maximum radial stretch (B) =

$$\frac{\text{maximum container outside diameter minus minimum preform outside diameter times } 100}{\text{minimum preform outside diameter}}$$

wherein:

A is between about 5 to about 100; and

B is no greater than about 334; thereby forming said article having reduced wall thickness variability at the substantially rectangular cross section in comparison with an article having the same cross section formed of thermoplastic material which does not strain harden during distension.

2. The method of claim 1 wherein the preform comprises a major proportion of polyethylene terephthalate.

3. The method of claim 2 wherein the inherent viscosity of the PET is at least about 0.7.

4. The method of claim 1 or 2 wherein the preform is injection molded and is substantially circular in cross section.

5. The method of claim 4 wherein the preform is distended against surfaces of a mold cavity having a heat insulative coating thereon.

6. The method of claim 4 wherein the article is a container.

7. The method of claim 6 wherein the container has a square cross section.

8. The method of claim 7 wherein the container has a nominal capacity of between about 470 to about 1890 cc.

9. The method of claim 1 wherein the substantially rectangular cross section is rectangular and the article is a container.

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