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

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Radicación 0206654 0000006 Folios: 2
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Trámite 002 PATENTES D / REGISTRO/ 538 PETICION
Dependencia 2000 DIVISION DE NUEVAS CREACIONES

Trámite 002
Evento 538
Actuación 411

Referencia Expediente No 02 066 654
Solicitante NESTLE WATERS MANAGEMENT & TECHNOLOGY
SA ET TERGAL FIBRES SA
Asunto Solicitud de patente para POLIESTERES DE
REDUCIDA VI Y REDUCIDO TENOR DE
ACETALDEHÍDO, PREFORMADOS, Y
CONTENEDORES OBTENIDOS CON UN POLÍMERO
DE ESTE TIPO
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 efectue 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 -28 003 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 efectue 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

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MRE/MRM/
ID 000017/WPC13366

NIT 860.041 367-3

Colo 13366-801-001-9

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No 02- 66654

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 carga 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., 3 de Febrero de 2006

Doctor

EMILIO FERRERO

Representante **NESTLÉ WATERS MANAGEMENT & TECHNOLOGY S. A. Y
TERGAL FIBRES**

ASUNTO	Radicación No	02 - 66654
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	1419
	Folios	054

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 3 a 19 de la solicitud en estudio
- b) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 27 reivindicaciones en los folios 20 a 23 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 reclama prioridad de la primera solicitud FR 01 10279 presentada en Francia

2) Objeto de la Invención

- a) Las reivindicaciones 1 a 27 de la solicitud en estudio se refieren a
 - i) (1 -) Un poliéster, que comprende por lo menos el 92,5% en cantidad de unidades derivadas de un ácido tereftálico y de etilenglicol, caracterizado porque presenta una viscosidad intrínseca comprendida entre 0,45 dl/g y 0,70 dl/g, y un tenor en acetaldehído inferior a 3 ppm
 - ii) (10 -) Procedimiento para la manufactura de un poliéster de acuerdo con una cualquiera de las reivindicaciones precedentes, caracterizado porque consiste en llevar a cabo una polimerización en un medio fundido, de un poliéster que presenta una viscosidad intrínseca inferior a 0,80 dl/g, formar gránulos de dicho poliéster, hacer cristalizar dichos

gránulos, tratar térmicamente dichos gránulos mediante un calentamiento a una temperatura comprendida entre 130°C y 200°C a efectos de reducir la concentración de acetaldehído hasta un valor inferior a 3 ppm y obtener una viscosidad intrínseca de poliéster inferior a 0,70 dl/g

iii) (19) Procedimiento para la manufactura de preformas a partir de un poliéster de acuerdo con cualquiera de las reivindicaciones 1 a 9, caracterizado porque consiste en - Inyectar el poliéster fundido en por lo menos un molde de la preforma a ser obtenida, -enfriar la preforma rápidamente a efectos de evitar toda cristalización esferulítica

iv) (27 -) Contenedores huecos o botellas, caracterizados porque el poliéster que forma la pared del contenedor tiene una viscosidad intrínseca comprendida entre 0,45 y a 0,65 dl/g y porque el tenor del acetaldehído presente en el poliéster, es inferior a 6 ppm

b) Los anteriores productos y procedimientos buscan obtener un poliéster mejorado para aplicación en envases

c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 08 G 063/183

3) Evaluación de la Unidad de Invención

El artículo 25 de la Decisión 486 de la Comisión de la Comunidad Andina establece

"La solicitud de patente sólo podrá comprender una invención o un grupo de invenciones relacionadas entre sí, de manera que conformen un único concepto inventivo"

La presente solicitud carece de unidad de invención toda vez que configura dos productos diferentes y contempla dos procedimientos diferentes. La definición de la materia que caracteriza a cada una de las reivindicaciones independientes es muy diferente entre sí. Nótese como en la reivindicación 1 específicamente se refiere a un poliéster derivado de ácido tereftálico y de etilenglicol y la reivindicación 27 a cualquier poliéster. Esto permite afirmar que no se trata del mismo producto. De la misma forma, los procedimientos de las reivindicaciones 10 y 19 refieren etapas totalmente disímiles y no enlazadas. Todo el problema radica en configurar varias reivindicaciones independientes con materia diferente. El solicitante debe establecer una sola reivindicación independiente dirigida al producto en la forma más simple de la solicitud de invención, y/o una sola a la forma más simple de procedimiento, partiendo de allí establecer reivindicaciones dependientes que amplíen esa forma más simple hasta su forma más compleja.

De acuerdo a lo anterior, la presente solicitud no cumple con el requisito de unidad de invención de acuerdo al Art. 25 de la Decisión 486. De continuar con el impedimento, esta oficina procederá a estudiar solo el primer grupo de invenciones que conformen un único concepto inventivo.

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 este 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 C 08 G 063/163 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 poliésteres (especialmente PET) que tienen una viscosidad intrínseca reducida con una baja relación de acetaldehído

De acuerdo con o 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 0 041 035	Polyesters pour emballages à usage alimentaire et leur procédé d'obtention	1981 12 02
D2	WO 99 61505	Process to prepare a polyester resin	1999 12 02
D3	EP 0 661 326	Process for preparing polyester	1995 07 05

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 la novedad y el del Nivel Inventivo**

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 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"

El documento D1 específicamente habla de poliésteres basados en ácido tereftálico y en etilenglicol, que presentan una viscosidad intrínseca comprendida entre 0,65 dl/g y 1,05 dl/g, y con acetaldehído inferior a 1,25 ppm Para un técnico medio es evidente encontrar que un intervalo de la anterioridad coincide plenamente con intervalo de la presente solicitud Por demás, en los puntos que no coinciden, la diferencia entre los dos documento es muy pequeña, siendo para un técnico medio demasiado evidente considerar que se puede obtener lo que se quiere proteger en el presente documento basado en D1 En referencia al procedimiento objeto de la solicitud, el documento D1 revela que es ampliamente conocido en la técnica usual el manejo de las condiciones objeto de protección en la presente solicitud, y en general las etapas que pretende proteger En general, muchos apartes de la presente solicitud se encuentran contenidos totalmente en D1, y los que no se pueden derivar fácilmente de allí

Algo muy similar a lo que se describe en el párrafo anterior sucede entre los documentos D2 y/o D3 con la presente solicitud Nótese como el rango de viscosidades intrínsecas de D2 y/o D3 coincide en amplio grado con la presente solicitud Además, la esencia del procedimiento es la misma en cualquiera de los documentos, con las condiciones de proceso muy similares sino iguales en algunos casos

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 0 041 035	1 – 27	Novedad
			Nivel inventivo
D2	WO 99 61505	1 – 27	Novedad
			Nivel inventivo
D3	EP 0 661 326	1 – 27	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 N° 10 de 2001.



ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe División de Nuevas Creaciones

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

09 FEB 2006

Concepto Técnico N°	EXAMINADOR TÉCNICO Código No	EXAMINADOR JURÍDICO Código No
139	202003	



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② Polymères pour emballages à usage alimentaire et leur procédé d'obtention.

② **Poliesters saturés à base d'unités de tréthalène d'éthylène glycol.**

Les polyesters sont caractérisés par une teneur et une vitesse de reformation en acétylsalicyde réduites. Ils sont obtenus par copolymérisation avec un agent retardateur de cristallisation dans des conditions de polycondensation définies.

Les polyesters sont particulièrement utiles pour le moulage de bouteilles destinées au conditionnement des eaux minérales.

041 035 Af

ACCEPTED MANUSCRIPT

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POLYESTERS POUR EMBALLAGES A USAGE ALIMENTAIRE
ET LEUR PROCÉDE D'OBTENTION

5 La présente invention concerne un polyester saturé à base d'unités de téréphtalate d'éthylène glycol pour récipients à usage alimentaire. L'invention se rapporte également à son procédé d'ob-

10 On sait que les polyesters thermoplastiques constitués de motifs de téréphtalate d'éthylène glycol constituant des matières premières intéressantes pour le conditionnement de denrées alimentaires sous forme de films, feuilles, récipients et notamment de bouteilles destinées à la conservation de liquides plats ou de boissons gazeuses.

15 L'une des qualités essentielles à laquelle doit répondre un emballage et plus particulièrement une bouteille est sa transparence et sa brillance. Par étirage à partir de l'état amorphe dans des conditions de biorientation, le polytéréphtalate d'éthylène glycol conserve une bonne transparence tout en bénéficiant d'une

20 phase cristalline orientée qui renforce considérablement ses propriétés mécaniques et permet une réduction de la perméabilité aux gaz. La transparence et la brillance peuvent cependant être affectées par la formation de spherulites cristallines notamment dans le cas de récipients à parois relativement épaisses. La réalisation de

25 bouteilles par injection et/ou extrusion-soufflage passe nécessairement par la réalisation d'une préforme à parois épaisses obtenue par trempe à partir de l'état fondu et la formation de spherulites cristallines au stade de la préforme affecte la transparence de l'objet fini. Il s'est donc révélé avantageux de proposer des

30 grades de polyester ayant une faible vitesse de cristallisation

Une autre qualité à laquelle doit répondre un emballage en matière polymère est l'absence de tout composé susceptible de migrer dans la denrée alimentaire ou la boisson et d'en altérer le goût ou l'odeur. On sait que les résines polyesters libèrent par

35 dégradation de l'acétaldéhyde qui présente une forte odeur et un goût caractéristique et qui se manifeste à des teneurs extrêmement faibles

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Ce problème est particulièrement important pour le conditionnement des eaux minérales. Ainsi les bouteilles en polyester destinées à contenir des eaux minérales gazeuses doivent avoir une teneur en acétaldéhyde dans leur paroi inférieure à 5 ppm (parties par million de polyester en poids/poids) pour un volume compris entre 1 litre et 2 litres si l'on veut s'assurer que dans les conditions de stockage, à des températures pouvant atteindre 45°C, la quantité d'acétaldéhyde susceptible de migrer dans la liquide reste inférieure au seuil organoleptique détectable, soit 40-50 ppb (parties par milliard en poids/poids de liquide). L'origine de l'acétaldéhyde dans les objets finis dépend à la fois de la quantité résiduelle présente dans la granulé de polyester, avant sa transformation, et de la quantité formée au cours de la transformation à l'état fondu par suite d'une dégradation dans les conditions de cisaillement et de températures requises pour le moulage.

On a déjà proposé divers procédés pour diminuer la teneur et/ou la reformation d'acétaldéhyde des résines de polytéréphtalate d'éthylène glycol. D'une manière générale ces procédés décrivent des conditions opératoires au cours des phases de séchage, cristallisation ou post-condensation du précurseur telles qu'elles sont appliquées couramment pour l'obtention de résines de haute viscosité.

Ainsi selon la demande de brevet français publiée 78 23635 le séchage des copeaux de polyester est effectué à 180-230°C pendant 4 à 12 heures en atmosphère inerte pour abaisser la teneur en acétaldéhyde dans les copeaux à moins de 2,5 ppm. D'après la demande de brevet français 79.10061 on obtient une diminution de la vitesse de formation d'acétaldéhyde par traitement à l'état fondu sous atmosphère inerte du polyester complètement polymérisé.

Selon la demande de brevet français 79 11981 on cristallise le polymère par chauffage à 180-220°C et la post-condensation est réalisée à une température supérieure à la température de cristallisation.

Le brevet américain 4 154.920 décrit un procédé en deux étapes à partir d'un prépolymère de viscosité intrinsèque 0,1 à 0,3 dl/g selon lequel le prépolymère est d'abord condensé à l'état

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fondue en couche mince puis post-condensée à l'état solide

Enfin d'après la demande de brevet français 79 12337 les pastilles de polyester sont post-condensées et stabilisées par chauffage à 180-220°C durant 2 à 20 heures dans l'air, augmentant la viscosité intrinsèque jusqu'à une valeur comprise entre 0,60 et 0,97 dl/g

La demanderesse a trouvé que la quantité d'acétaldéhyde présente dans les parois d'un article moulé, et susceptible de migrer, c'est-à-dire la quantité résiduelle présente dans les granules additionnée à la quantité réformée lors de la transformation à l'état fondu en article moulé ne dépendait pas seulement des conditions de traitement du précurseur (séchage cristallisation et post-condensation) mais était liée d'une part à la qualité intrinsèque du précurseur, obtenu dans la phase initiale de la polycondensation à l'état fondu, et d'autre part à la caractéristique de recristallisation du polymère lors de l'opération de trappe à l'état fondu.

Le précurseur doit en effet contenir le plus petit nombre possible de sites initiateurs d'une dégradation ultérieure vinylique, carboxylique. Pour un même système catalytique, en fonction des conditions de la polycondensation, les qualités intrinsèques de la résine peuvent être très différentes. La stabilité thermique du précurseur peut se mesurer indirectement par la mesure de la vitesse de reformation d'acétaldéhyde du polymère porté à haute température. Par ailleurs la quantité d'acétaldéhyde réformée est directement liée à la température de mise en œuvre du matériau et celle-ci sera d'autant plus élevée que la vitesse de recristallisation sera plus grande lors de la trappe.

La présente invention a donc pour objet un polytétraphthalate d'éthylène glycol ayant des caractéristiques utiles pour le moulage par injection ou extrusion-soufflage d'articles transparents, ainsi qu'un procédé pour l'obtention dudit polytétraphthalate

La polytétraphthalate d'éthylène glycol selon l'invention, de viscosité intrinsèque comprise entre 0,65 et 1,05 dl/g et de densité $> 1,38$, est constitué de 92,5 à 98,5 % de motifs tétraphthalate d'éthylène et de 1,5 à 7,5 % en moles de motifs d'un agent retardateur de cristallisation choisi parmi un ou plusieurs poly-

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acides et/ou polyalcools, la quantité de di- et/ou tri-éthylène glycol étant limitée à une valeur inférieure à environ 3,5 % (moles par moles de restes diacides présents dans la chaîne) et est caractérisé par les propriétés suivantes prises en combinaison :

- teneur résiduelle en acétaldéhyde inférieure à 1,25 ppm
- vitesse de réformation d'acétaldéhyde à 220°C inférieure à 5 ppm/heure,
- absence de cristallisation visible dans une plaque d'épaisseur au moins égale à 4 mm obtenue par injection du matériau fondu à 280°C dans un moule dont les parois sont maintenues à une température égale à 37°C

On entend par motifs téréphtalate d'éthylène également la faible quantité de téréphtalate de di- et tri-éthylène glycol inévitablement formés lors de la polycondensation.

La fabrication des polyesters à partir d'acides dicarboxyliques aromatiques ou de leurs dérivés fonctionnels et de diols aliphatiques par estérification directe ou transestérification puis polycondensation en présence de catalyseurs est un procédé connu. Dans une première étape de réaction l'acide dicarboxylique est estérifié ou son ester diméthylique est transestérifié par le glycol. Dans une seconde étape on procède à la polycondensation de l'ester diglycolique formé. On obtient un polyester de bas poids moléculaire que l'on désignera ci-après par la terme "précurseur". Pour obtenir des polyesters de poids moléculaire élevé le précurseur est séché, cristallisé puis soumis à une post-condensation à l'état solide ou fondu jusqu'à l'obtention de la viscosité finale désirée.

Pour l'obtention du polytéréphtalate d'éthylène glycol selon l'invention, le procédé est caractérisé en ce que pour la formation du précurseur d'une viscosité intrinsèque comprise entre 0,55 et 0,70 dl/g, la polycondensation est réalisée en présence d'au moins un modifiant copolymérisable retardateur de cristallisation en quantité comprise entre 1,5 et 7,5 % en moles par rapport à l'ensemble diacide ou diester + retardateur, à une température inférieure à 290°C et est limitée à un degré compris entre 75 et 90 % du degré de polycondensation maximal accessible évalué d'après la viscosité intrinsèque du polymère

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Les modifiants copolymérisables retardateurs de cristallisation peuvent être des polyacides carboxyliques aromatiques et/ou aliphatiques et/ou des polyalcools. On peut utiliser par exemple les acides isophtalique, naphthalène dicarboxylique, adipique, sébacique ou leurs dérivés fonctionnels pouvant former des polyesters. Des exemples de diols sont le néopentyl glycol, 1'hexane diol-1,6, le bis-hydroxyéthyl-1,4 cyclohexane, le diéthylène glycol, le triéthylène glycol. S'agissant du di- et/ou tri-éthylène glycol il est essentiel que la quantité totale qui peut soit être ajoutée, soit résulter de sa formation in situ par déshydratation de 1'éthylène glycol en excès reste inférieure à 3,5% en moles par moles de restes diacides engagés dans la chaîne. L'emploi de très faibles quantités de composés trifonctionnels acides ou alcools est possible dans la mesure où cette addition n'augmente pas la vitesse de cristallisation du polymère. L'acide isophtalique a été trouvé particulièrement favorable.

Le système catalytique utilisé peut avoir une influence sur la formation de l'acétaldéhyde. Il est déconseillé d'utiliser les catalyseurs en quantité excessive. Les composés de l'antimoine comme catalyseur de polycondensation à des teneurs inférieures à 250 ppm (exprimé en poids de métal par rapport à la quantité de tous les constituants) a été trouvé particulièrement favorable.

Le degré de polycondensation du précurseur dépend de facteurs tels que la nature et la teneur du système catalytique, les performances de l'appareillage, la température et la pression de la polycondensation. Ce degré de polycondensation peut être déterminé par la mesure de la viscosité intrinsèque du polymère. Dans des conditions opératoires données il existe un seuil de polycondensation maximum, au-delà duquel la viscosité ne peut plus être augmentée, les réactions de dégradation prenant une importance prépondérante sur la réaction de polycondensation.

Selon l'un des moyens particuliers essentiel de l'invention la viscosité intrinsèque du précurseur VI_p est limitée à une valeur comprise entre 0,75 et 0,90 de la viscosité maximale possible VI_{max} , c'est-à-dire à la relation

$$0,75 VI_{max} < VI_p < 0,90 VI_{max}$$

Si la viscosité atteinte est limitée en-dessous de 0,75

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VI_{0.90}, le procédé n'est pas performant. Si la polycondensation est poursuivie au-delà de la valeur 0,90 VI_{0.90}, on observe une augmentation de la vitesse de reformation en acétaldéhyde.

3 Après cristallisation et séchage du précurseur obtenu selon le procédé de l'invention, la post-condensation peut être réalisée par tout procédé connu pour obtenir une viscosité intrinsèque finale comprise entre environ 0,65 et 1,05. La post-condensation est de préférence réalisée à l'état solide sous vide poussé
10 ou sous gaz inerte entre 190 et 230°C pendant une durée pouvant varier de 5 à 25 heures. Le produit obtenu peut être transformé en copeaux, granulés ou pastilles par des moyens connus.

15 Les polytéréphthalates obtenus selon l'invention peuvent être moulés en récipients par tous procédés. Ils peuvent être moulés par injection, extrusion, injection-soufflage ou extrusion-soufflage soit directement en un produit fini, soit indirectement en un tube ou préforme qui sera ultérieurement moulé à la forme du récipient souhaité.

20 Du fait de leur vitesse de recristallisation réduite lors de la trempe, ils permettent de mouler des articles transparents à parois relativement épaisses tels que des préformes pour bouteilles avec une dégradation minimale de la résine. Ils présentent un intérêt tout particulier pour la réalisation de bouteilles destinées au conditionnement des eaux minérales qui peuvent être
25 stockées pendant une durée prolongée sans altération sensible de goût.

30 Les exemples qui suivent illustrent l'invention. Il doit être bien entendu qu'ils ne sont pas donnés à titre limitatif et que toutes variantes ou modifications peuvent être apportées sans pour autant sortir du cadre général de la présente invention.

 Les méthodes de mesure suivantes ont été utilisées pour caractériser le produit selon l'invention.

35 - Taux résiduel en acétaldéhyde : AA résiduel. On broie l'échantillon refroidi sous de l'azote liquide en une poudre fine, inférieure à 800 microns. La poudre est chauffée 1h30 à 160°C en ballon fermé sous azote et la quantité d'acétaldéhyde libérée est dosée par chromatographie en phase vapeur (CPV).

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- Vitesse de reformation d'acétaldéhyde à 220°C Cette mesure est effectuée sur la poudre broyée comme précédemment. La poudre est chauffée 30 minutes jusqu'à 220°C de manière à éliminer l'acétaldéhyde résiduel initialement présent. Le ballon est purgé à l'azote et fermé. On prélève un échantillon de gaz après 1, 2, 3 heures de chauffage et on dose l'acétaldéhyde sur chaque échantillon par CPV. La quantité totale est divisée par le temps (3 heures) pour donner le nombre de parties en poids d'acétaldéhyde par million en poids de polyester par heure.

- Viscosité intrinsèque VI en dl/g : la mesure est effectuée à 25°C en solution à 1 % (poids/volume) dans un mélange phénol/ orthochlorophénol 47/53.

- Cristallisation On plastifie le polymère sec à 290°C de manière à détruire tout germe de cristallisation.

On injecte le produit fondu dans une série de moules dont l'épaisseur varie progressivement pour obtenir des plaques d'épaisseur comprise entre 2 et 5 mm. La température des parois du moule est conditionnée à 37°C. On note à quelle épaisseur apparaît un léger trouble correspondant à un début de cristallisation. Plus l'épaisseur des pièces amorphes, totalement transparentes, est grande, plus la vitesse de recristallisation est faible.

- Teneur en diéthylène glycol (DEG %) : L'échantillon est broyé et saponifié par la potasse en solution éthanolique. L'analyse est effectuée par chromatographie gaz en présence d'un étalon interne. Les résultats sont exprimés en moles par rapport aux restes diacides.

EXEMPLE 1 :

On prépare un précurseur par transestérification à partir d'un mélange de diméthyltétraphthalate, éthylène glycol et polycondensation en présence de 3 % d'acide isophthalique (en moles). On utilise un système catalytique à base de manganèse phosphate, antimoine contenant 200 ppm d'antimoine.

On arrête la polycondensation quand la viscosité intrinsèque du précurseur VI_p atteint 0,61 dl/g, la viscosité limite VI_{∞} pouvant être amenée jusqu'à une valeur de 0,72 dl/g. Après séchage et cristallisation les granules sont post-condensés à l'état solide.

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sous 66,66 Pa pendant 12 heures à 217°C pour obtenir une VI de 0,81 dl/g

	AA résiduel	0,9 ppm
5	AA reformation à 220°C	: 4 ppm/heure
	e moulage amorphe	: 5 mm
	DEG X	: 1,4

EXEMPLE 2

10 On renouvelle l'exemple 1 à la différence que l'on ajoute 2 % d'acide isophtalique.

On arrête la polycondensation à une valeur VI_p de 0,63 dl/g. La VI_{∞} est de 0,75 dl/g

15 Après post-condensation à l'état solide jusqu'à obtention d'une VI de 0,81 dl/g les granulés présentant les caractéristiques suivantes

	AA résiduel	: 1,2 ppm
	AA reformation à 220°C	: 4,6 ppm/heure
	e moulage amorphe	4,5 mm
20	DEG X	: 1,6

EXEMPLES COMPARATIFS :EXEMPLE 3 :

25 On prépare un homopolymère par transestérification de diméthyltétraphthalate et d'éthylène glycol, puis polycondensation en utilisant le même système catalytique que dans l'exemple précédent. On arrête la polycondensation à une valeur VI_p égale à 0,60, la VI_{∞} étant de 0,72. Le précurseur est traité dans les conditions de l'exemple 1 jusqu'à l'obtention d'une viscosité finale de 30 0,75 dl/g. On obtient les caractéristiques suivantes :

	AA résiduel	: 1,1 ppm
	AA reformation à 220°C	: 4,2 ppm/heure
	e moulage amorphe	: 3 mm
35	DEG X	1,3

EXEMPLE 4 :

On répète l'opération de l'exemple 1 (addition de 3 % d'acide isophtalique) mais la viscosité VI_p est poussée au maximum

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possible soit 0,72 Après post-condensation dans les mêmes conditions, on obtient les résultats suivants

5	AA résiduel	: 3 ppm
	AA reformation à 220°C	20 ppm/heure
	e moulage amorphe	5 mm

EXEMPLE 5 :

On reproduit l'exemple 1 en ajoutant 4 % en moles de diéthylène glycol aux produits réactionnels On arrête la polycondensation à une valeur de VI_p à 0,60 dl/g - VI_{∞} est de 0,70 dl/g Après séchage, cristallisation et post-condensations dans les conditions décrites on obtient les résultats suivants :

15	AA résiduel	: 1,9 ppm
	AA reformation à 220°C	9 ppm/heure
	e moulage amorphe	: 4,5 mm
	DEC %	3,72

Les polyesters obtenus selon les exemples 1 à 5 sont utilisés pour la fabrication de bouteilles biorientées.

A cet effet les granules sont séchés à moins de 50 ppm d'humidité et injectés à l'état fondu à l'aide d'une presse à injection au travers d'un moule de préforme à canaux chauds de manière à obtenir des préformes amorphes de 47 g, d'une épaisseur de parois de 3,8 mm. On mesure la teneur en acétaldéhyde sur un échantillon prélevé sur la paroi de la préforme Pour chacun des essais on note la température d'injection du matériau et le % d'AA mesuré sur la préforme (poids/poids polyester).

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Exemples		T° injection : en °C	AA en ppm
1		285	3,5
2		290	4,5
3		310	8
4		285	6
5		300	9,1

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Les préformes sont soufflées à la température de biorien-
tation en bouteilles de 1,5 litre de capacité. Les bouteilles sont
remplies d'eau minérale gazeuse et stockées à 45°C. Un test organo-
leptique effectué comparativement à une eau minérale stockée en
bouteille de verre ne révèle aucune modification de goût pouvant
résulter d'une migration de l'acétaldéhyde après un mois de
stockage pour la bouteille obtenue à partir du polytétraphthalate
selon les exemples 1 et 2. Dans tous les autres cas, on détecte une
altération sensible du goût à partir de 8 jours de stockage, ce qui
rend l'eau minérale impropre à la consommation.

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REVENDICATIONS

- 1 Polytéréphtalate d'éthylène glycol ayant une viscosité
 5 intrinsèque comprise entre 0,65 et 1,05 dl/g et une densité supérieure à 1,38, constitué de 92,5 à 98,5 % de motifs téréphtalate d'éthylène et de 1,5 à 7,5 % en moles de motifs d'un agent retardateur de cristallisation choisi parmi un ou plusieurs polyacides et/ou polyalcools, la quantité de di- et/ou tri- éthylène glycol
 10 étant limitée à une valeur inférieure à environ 3,5 % (moles par moles de restes diacides présents dans la chaîne), caractérisé par les propriétés suivantes prises en combinaison
- teneur résiduelle en acétaldéhyde inférieure à 1,25 ppm
 - vitesse de reformation d'acétaldéhyde à 220°C inférieure à 5 ppm/heure
 - absence de cristallisation visible dans une plaque d'épaisseur au moins égale à 4 mm obtenue par injection du matériau fondu à 280°C dans un moule dont les parois sont maintenues à une température égale à 37°C.
- 20 2. Polytéréphtalate d'éthylène glycol selon la revendication 1, caractérisé en ce que les motifs de l'agent retardateur de cristallisation sont dérivés de l'acide isophtalique.
- 3 Procédé de préparation de polytéréphtalate d'éthylène glycol par estérification ou transestérification de l'acide téréphtalique ou de ses dérivés fonctionnels par l'éthylène glycol et
 25 polycondensation en présence de catalyseurs, jusqu'à obtention d'un précurseur puis post-condensation du précurseur jusqu'à une viscosité intrinsèque comprise entre 0,65 et 1,05 dl/g, caractérisé en ce que pour la formation du précurseur d'une viscosité intrinsèque comprise entre environ 0,55 et environ 0,70 dl/g la polycondensation est réalisée en présence d'au moins un modifiant copolymérisable retardateur de cristallisation en quantité comprise entre 1,5 et 7,5 % (en moles par rapport à l'ensemble diacide ou diester + retardant)
 30 à une température inférieure à 290°C et est limitée à un degré compris entre 75 et 90 % du degré de polycondensation maximal accessible évalué d'après la viscosité intrinsèque
4. Procédé selon la revendication 3, caractérisé en ce que l'on utilise un catalyseur de polycondensation à base d'anti-

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moins à des teneurs inférieures à 250 ppm

5 5. Emploi du polytéréphtalate selon l'une quelconque des revendications 1 à 4 pour le moulage d'articles d'emballages destinés au conditionnement de denrées alimentaires

6. Emploi du polytéréphtalate selon l'une quelconque des revendications 1 à 4 pour la fabrication de bouteilles biorientées destinées au conditionnement des eaux minérales plates ou gazeuses.

AUTRICHE
0041035REVENDICATIONS

- 1 Procédé de préparation de polytéréphtalate d'éthylène glycol par estérification ou transestérification de l'acide téréphtalique ou de ses dérivés fonctionnels par l'éthylène glycol et polycondensation en présence de catalyseurs, jusqu'à obtention d'un précurseur puis post-condensation du précurseur jusqu'à une viscosité intrinsèque comprise entre 0,65 et 1,05 dl/g, caractérisé en ce que pour la formation du précurseur d'une viscosité intrinsèque comprises entre 0,55 et environ 0,70 dl/g la polycondensation est réalisée en présence d'au moins un modifiant copolymérisable retardateur de cristallisation en quantité comprise entre 1,5 et 7,5 % (en moles par rapport à l'ensemble diacide ou diester + retardateur) à une température inférieure à 290°C et est limitée à un degré compris entre 75 et 90 % du degré de polycondensation maximal accessible évalué d'après la viscosité intrinsèque
- 2 Procédé selon la revendication 1, caractérisé en ce que le modifiant copolymérisable retardateur de cristallisation est l'acide isophtalique, l'acide naphthalène dicarboxylique, l'acide adipique, l'acide sébacique, le néopentylglycol, l'hexanediol-1,6, le bis-hydroxyméthyl-1,4 cyclohexane, le diéthylèneglycol, le triéthylèneglycol ou un mélange de ces composés
- 3 Procédé selon l'une quelconque des revendications 1 et 2, caractérisé en ce que l'on utilise un catalyseur de polycondensation à base d'antimoine à des teneurs inférieures à 250 ppm.
- 4 Emploi du polytéréphtalate obtenu selon le procédé décrit dans l'une quelconque des revendications 1 à 3 pour le moulage d'articles d'emballages destinés au conditionnement de denrées alimentaires
- 5 Emploi du polytéréphtalate obtenu selon le procédé décrit dans l'une quelconque des revendications 1 à 3 pour la fabrication de bouteilles biorientées destinées au conditionnement des eaux minérales plates ou gazeuses

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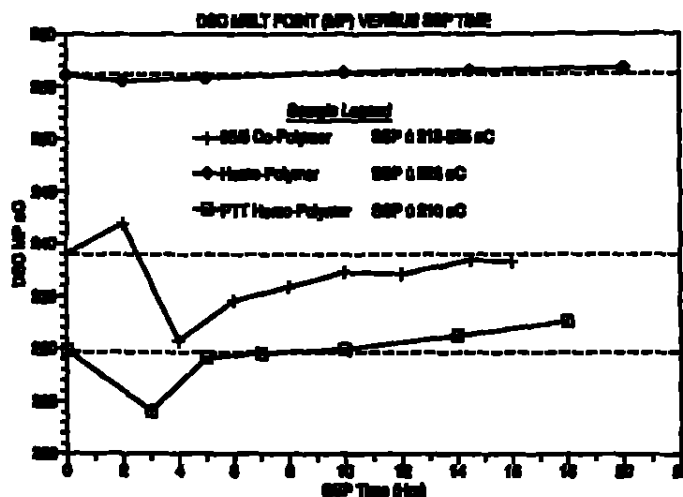
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(54) Title PROCESS TO PREPARE A POLYESTER RESIN



(57) Abstract

Accordingly, the invention provides a process to prepare a polyester resin having an acetaldehyde concentration of no more than about 1 ppm, which process comprises the steps of: a) reacting ethylene glycol with terephthalic acid or an ester thereof, and isophthalic acid or an ester thereof under constrained reaction conditions effective to prepare a melt phase polymer having an IV in the range of 0.38 dl/g to 0.52 dl/g and a diethylene glycol content of no more than 5 mole% (based on the diol content of the resin); b) recovering the melt phase polymer from step a) as the pre-polymer used in step c); and c) subjecting at least a portion of the pre-polymer recovered in step b) to elevated temperatures over a period of time to elevate the IV to a range of 0.60 dl/g to 0.90 dl/g. The resultant resin can be transformed into a bottle preform, which, when blown, forms a bottle suitable for packaging of mineral water.

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PROCESS TO PREPARE A POLYESTER RESIN

FIELD OF THE INVENTION

This invention relates to process for preparing a polyester resin having a low acetaldehyde (AA) content. The resin is useful in packaging of mineral water or other beverages where AA content must be kept below certain predetermined levels.

BACKGROUND OF THE INVENTION

The background of this invention recognizes that AA content in polyester resins is an important factor when the end-use of the resin is concerned. Generally, resin manufacturers wish to produce a resin with as low an AA content as possible within the economics of a continuous commercial process.

Bottle grade polyester resins are typically prepared by melt phase polymerization, wherein the monomers are linked to form a "prepolymer" or "melt phase polymer", followed by the preparation of pellets of the melt phase polymer, and by solid state polymerization (SSP) of these pellets until a polyester resin of sufficiently high viscosity index (IV) is obtained.

However, traditional melt-phase polymerization entrains undesirable products and unreacted monomer components. AA, a noxious by-product of the melt polymerization process, can spoil the flavor and aroma of contained beverages, especially mineral water. Producers of containers for drinking water and soft-drink containers desire an AA content of no more than 1 µg/l, (i.e., ≤ 1 parts per billion), evolved into the headspace of an empty container. To achieve such a low AA content container, the SSP-ed resin AA content should not exceed 1 part per million (ppm).

Multi-layer containers can also be used to avoid the problem of by-product AA contamination of drinking water and beverages. Each layer is composed of polymers with specific properties. Such containers are more expensive to make and raise concern with recycle of post consumer containers.

In U S Patent 4,340,721, a polyester is disclosed having a low AA content. The intrinsic viscosity of the melt condensate is limited to 0.75 to 0.90 of the maximum possible IV, i.e. of about 0.6 dl/g. A further reduction in the AA content, however, remains desirable.

Finally, in U S Patent 4,154,920 a pre-polymer is maintained at 0.1 to 0.3 dl/g prior to SSP. When one starts at this level of IV as the feed material to the SSP process, the resin becomes difficult to pelletize.

SUMMARY OF THE INVENTION

This invention provides a process for preparing in commercial quantities polyester resins having unique properties that allow for low melt temperature processing and concomitant slow rate of acetaldehyde reformation. Accordingly, the invention provides a process to prepare a polyester resin having an acetaldehyde concentration of no more than about 1 ppm, which process comprises the steps of

- a) reacting ethylene glycol with terephthalic acid or an ester thereof, and isophthalic acid or an ester thereof under constrained reaction conditions effective to prepare a melt phase polymer having an IV in the range of 0.38 dl/g to 0.52 dl/g and a diethylene glycol content of no more than 5 mole% (based on the diol content of the resin),
- b) recovering the melt phase polymer from step a) as the pre-polymer used in step c), and
- c) subjecting at least a portion of the pre-polymer recovered in step b) to elevated temperatures over a

period of time to elevate the IV to a range of 0.60 dl/g to 0.90 dl/g

This results in a resin (and preform and bottle made therefrom) having a desirable advantageous AA content. The resin from the SSP process also has a more favorable melt point (MP) for making bottle preforms and an unexpectedly lower rate of AA reformation rate when measured at 280 °C. This reformation rate is equal to 70 ppm to 190 ppm AA per hour measured at 280 °C based on ASTM D-4509 at 10, 20, and 30 minutes, respectively, and extrapolated to a one hour time interval. Polyester resins according to the present invention indeed achieve a reformation rate that is equal to 100 ppm to 160 ppm AA per hour measured at 280 °C based on the same analytical procedure.

DETAILED DESCRIPTION OF THE INVENTION

The resin is prepared by a combined melt polymerization/solid state polymerization process. This process captures a melt phase polyester resin having a relatively low intrinsic viscosity which is then solid state polymerized (SSP-ed) to a finished IV. This process results in low incipient AA content in the resin bottle preform and its bottle. Such low intrinsic viscosity can be achieved by selecting proper melt phase polymerization conditions in combination with the incorporation of glycols and/or acid co-monomers, with isophthalic acid being the preferred co-monomer. Lower temperature melt extrusion-preform injection molding and reduced shear rate effects combine to reduce AA generation. The resin has properties which combine a low incipient AA content (no more than 1.0 ppm), preferably lower than 0.50 ppm and more preferably lower than 0.24 ppm, and lower melt processing temperature (≤ 252 °C) to produce a bottle having a maximum AA content of 1 µg/l.

In a preferred embodiment, the monomers that may be used in the production of the polyester resin consist of terephthalic acid (TPA) or an ester thereof, and isophthalic acid (IPA) or an ester thereof, and ethylene glycol (EG) and/or diethylene glycol (DEG)
5 Copolymerization of these comonomers (optionally with other comonomers) results in the preparation of a poly(ethylene terephthalate/isophthalate) (PETI) polyester

10 The amount of IPA used in the preparation of the polyester resin is preferably in the range of 1-10 mole% IPA (based on the total acid component of the resin), while 1.5 to 6.6 mole%, better still 3.0 mole% to 5.5 mole% IPA is even more preferred and about 5 mole% is
15 most preferred. The preferred concentrations of EG and DEG are respectively 99-95 mole% and 1-5 mole%, with 96.7-97.5 mole% and 2.5-3.3 mole% being more preferred, based on the total diol component of the resin. This composition lowers the initial DSC melting point (MP) of
20 the polyester resin to a maximum of 245 °C. Other co-monomers, such as naphthalene dicarboxylic acid and/or propylene glycol may also be incorporated into the polyester resin.

Melt extrusion-injection molding of the SSP-ed resin
25 can be accomplished using an antimony triacetate catalyst followed by a phosphoric acid stabilizer and appropriate color toners. Alternatively, the process may employ a phosphoric acid stabilizer followed by cobalt acetate tetra-hydrate color toner and antimony ethylene glycolate
30 catalyst. Instead of cobalt acetate tetra-hydrate, color toning dyes can be added during the melt polymerization or in the melt extrusion-injection molding step.

This process allows melt extrusion-injection molding processing at temperatures up to 252 °C, low enough to
35 reduce AA generation for the production of polyester.

preforms, yielding containers with AA concentrations of no more than 10 µg/l. This process also allows the resin to maintain properties required for satisfactory container performance.

5 The melt phase polymer so produced and captured herein has properties that make it uniquely useful for preparation of low AA content containers employing melt processing steps. Figure 1 shows how resin produced from a 95/5 PETI formulation described herein yields a lower
10 initial DSC melting point after SSP than other resin compositions.

 The DSC melting point behavior of a normal PET resin shows a drop in the melting point after initial melting. Thereafter, the melting point increases. Eventually, the
15 measured DSC melting point exceeds the melting point at the beginning of SSP. The resin of the present invention shows a drop in the DSC melting point after the initial SSP sample. While the melting point increases thereafter, the melting point of the resin does not rise above the
20 initial melting point on prolonged heating.

 The effect of the lower temperature melt point is not present in homopolymers (comparison is made with PET and PTT). Without a co-monomer present, the melting point rapidly exceeds the initial melting point raising the
25 melt process temperature requirement. Thus, addition of the co-monomer suppresses the melt point increases over the initial melt point, resulting in lower melt process temperature requirements. The resulting resin has a lower AA generation rate and produces lower AA content in the
30 bottle preform and bottle.

 The constrained reaction conditions referred herein before include a temperature of from 260 °C to 290 °C, a pressure of from 480 kPa (initial pressure) to full vacuum (typical final pressure of about 0.1 kPa) and a
35 time of reaction of from 5 to 6 hours.

It is significant to constrain the melt polymerization reaction so that the IV range of the melt phase polymer is held between 0.38 dl/g to 0.52 dl/g, and preferably 0.40 dl/g to 0.50 dl/g, and most preferably at 0.46 dl/g $\pm$ 0.02 dl/g. It is also important that the amount of diethylene glycol content in the copolymer be 5 mole% or less. The diethylene glycol (DEG) may be prepared in-situ or it may be added, but it is significant that the content be 5 mole% or less regardless of how the DEG is generated. The melt phase polymer (pre-polymer) will have an AA content of from 15 ppm to 45 ppm.

The molecular weight of the melt phase polymer is not suitable for such uses as the manufacture of beverage bottles. Thus, the melt phase polymer must be SSP-ed to achieve the IV necessary for bottle grade manufacture, such as an IV of 0.60 dl/g to 0.90 dl/g, typically 0.65 to 0.80 dl/g, or preferably about 0.74 dl/g.

The SSP process of this invention can include a crystallization step followed by a solid phase polymerization step to elevate the IV of the resin. The crystallization conditions include a temperature of from 100 °C to 150 °C. The solid phase polymerization reactor (polycondensation) may be operated at temperatures between 200 °C and 232 °C for a period of time sufficient to raise the IV to the desired level. The time may range from about 15 to 21 hours. The preferred polycondensation temperatures include a temperature of from 215 °C to 232 °C. It is significant in this invention that when starting with an IV of 0.38 dl/g to 0.52 dl/g, in the melt phase, the solid phase polymerization reaction can transpire over a longer period of time, thereby reducing resin incipient AA content.

The crystallization and polymerization phase can be performed in a tumbler dryer reaction in a batch-type system or they can comprise one or more vessels in a

continuous solid state process whereby the polymer flows from vessel to vessel after its predetermined treatment in those vessels

5 The resins produced in this invention by the SSP process may then be converted to a preform of a bottle, which may be subjected to heat over a period of time, and stretch-blown or blown into a bottle for ultimate consumer use. The AA content in the preform will be higher than that in the polyester resin it is made of.
10 Using the polyester resin according to the present invention, preforms are achievable having an AA content of no more than about 2.5 ppm. Preform production is conducted at a temperature of from about 245 °C to about 280 °C. The bottle will possess an AA content of less
15 than 1 µg/l. The expression IV used in this specification refers to the intrinsic viscosity as determined by measuring the viscosity of a dilute solution of the polymer using a 60/40 (w/w) phenol/ tetra-chloroethane or suitable solvent system and using the Billmeyer equation
20 to calculate the IV. This procedure is based on ASTM D-4603.

The following Examples are illustrative of the invention herein claimed and are not presented as a limitation upon the scope of the claims.

25 Examples 1-5

The following Examples demonstrate the fact that different resin formulations result in different manufactured resin. Five resins were prepared using the mole percent of monomers as follows

Example No	Composition (mole %)		
	EG + DEG	IPA	TPA
1 Resin A	96.2 + 3.8	0	100
2 Resin B	98.0 + 2.0	2	98
3 Resin C	97.4 + 2.6	2.6	97.4
4 Resin D	95.5 + 4.5	5	95
5. Resin E	95.1 + 4.9	5	95

In Examples 4 and 5, the resins were compared to commercially available resins (Examples 1-3). The following quantities of EG (24.9 kg), PTA (55.8 kg) and IPA (3.0 kg), were loaded in a batch reactor and heated for a period of 5 to 6 hours at temperature conditions of 265 °C to 283 °C. A modified heel process was used in an effort to produce as low a DEG content as possible. Resins A, B, and C, were conventionally prepared using standard melt phase polymerization techniques to obtain an IV of 0.60 ± 0.02 dl/g, resulting in a melt point of 252-253 °C. For Resin D, the melt phase reaction was constrained to an IV of 0.46 ± 0.02 dl/g and the IPA was adjusted to arrive at a melt point no greater than 245 °C. For Resin E, the IV was 0.60 ± 0.02 dl/g. Resin E was incorporated to show the effect of IV on AA content if the IV was not constrained to 0.46 dl/g, but conventionally prepared to 0.60 dl/g. The AA content in these melt phase products were as follows:

Resin No	AA (ppm)
Resin A	40-60
Resin B	40-60
Resin C	40-50
Resin D	26
Resin E	49

Examples 6-10

In Examples 6-8, the melt phase Resins of Example 1-3 were SSP-ed at temperatures around 230-235 °C for a sufficient period of time to arrive at an IV of 0 72-0 74 dl/g In Example 9, Resin D, was SSP-ed at 225-228 °C for 21 hours to reach 0 74 dl/g IV In Example 10, Resin E was SSP-ed at 225 °C to 227 °C for 9 hours to reach a 0 747 dl/g IV The resins were tested for AA content at 200 °C based on the ASTM D-4509 The Resins were observed to have the following AA content

Resin No	AA (ppm)
Resin A	1 10
Resin B	0 48
Resin C	0 75
Resin D	0 24
Resin E	1 15

The data supports the fact that by constraining Resin D IV to 0 46 dl/g versus Resin E IV of 0 60 dl/g yields a substantially lower AA content after SSP

Examples 11-15

The Resins of Examples 1-5, SSP-ed in Examples 6-10, were converted to bottle preforms and bottles by the following sequence

- 1 Dry applicable Resin at 150-170°C for 8-16 hours
- 2 Extrusion processing of applicable Resin for injection molding of the respective preforms
- 3 Preform to bottle conversion by stretch-blow molding operation using Infra-Red (IR) re-heating

The preform temperatures and resultant AA content, as determined in Examples 11-15, were as follows

- 10 -

Preform from Resin No	Temp (°C)	AA (ppm)
Resin A	266	7 5
Resin B	270	7 5
Resin C	269	8 8
Resin D	250	2 0
Resin E	245	2 3

Examples 16-20

The bottle preforms made in Examples 11-15 were made into 0.6 L (20 oz) bottles at temperature and blowing conditions as follows

Preform from Resin No	Temp (°C)	Bottle AA, µg/l
Resin A	280	3 2
Resin B	250	2 4
Resin C	280	3 3
Resin D	250	0 8
Resin E	245	1 1

5 Even though all attempts were made, including using the lowest preform processing temperature, to suppress AA generation Resin E exceeded the 1 µg/l maximum AA limit. Resin D, prepared from 0.46 dl/g IV melt feed resin, even when processed at 5 °C higher preform process temperature yielded a lower AA content than the 1 µg/l AA limit.

10 The results of Examples 1-20 can be summarized in chart form as set out in the Table

Examples 21-24

15 Resins were prepared in these Examples to show the relationship of DEG content in the TPA/IPA copolymer to acceptable levels of AA in a blown bottle. Four series of resins were prepared using melt polymerization where the melt reactor was constrained to produce an IV of 0.46 dl/g. The Series of Resins were made under the following formulations.

20

Resin

- F 100-97 5/2 5 EG-TPA/IPA Copolymer The DEG level generated is in-situ 2.2 mole% (or as low as possible) IPA content increased as necessary to achieve a maximum MP of 245 °C Added additives comprised 0.210 parts per thousand (ppt) antimony triacetate, followed by phosphoric acid (0.015 ppt P) and appropriate color toners (0.001 ppt ESTOFIL blue, 0.0005 ppt ESTOFIL red)
- G 100-96/4 EG-TPA/IPA Copolymer modified with the appropriate amount of IPA to achieve a maximum MP of 245 °C MP A polyester resin was produced having a yellow color index value b* of -2 (determined on a HunterLab Color Spectrophotometer) The process employed a phosphoric acid stabilizer (0.045 ppt P) followed by cobalt acetate tetra-hydrate (0.050 ppt Co) and antimony oxide (0.210 ppt)
- H EG/DEG -TPA/IPA Copolymer modified with one half the amount of IPA determined in Series G and the DEG is varied to achieve a maximum MP of 245 °C and a target b* color of -2 using cobalt All the other ingredients were the same as used Resin G
- I EG/DEG - TPA Copolymer modified with the appropriate amount of DEG to achieve a target 245 °C MP The b* color was adjusted via cobalt

Examples 25-29

Resins F-I were prepared in the melt phase to a melt point of 245 °C and an IV of 0.46 dl/g as performed with Resin D in the former set of Examples The SSP of Resins F, G, H and I was terminated when an IV of 0.74 dl/g was

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TABLE
Resin Composition and Properties versus Bottle AA content

Experimental Resin ID	Composition				Feed Resin				Preform		Bottle
	(Mole%)				(Amorphous)		SSP Resin		Process		(0 6 L)
Series No	EG	DEG	IPA	TPA	IV, dl/g	DSC MP, °C	IV, dl/g	AA, ppm	Temp °C	AA, ppm	AA, µg/l
A	96 2	3 8	0 0	100	0 60	252	0 73	1 10	266	7 5	3 2
B	98 0	2 0	2 0	98 0	0 60	252	0 74	0 48	270	7 5	2 4
C	97 4	2 6	2 0	98 0	0 60	253	0 72	0 75	269	8 8	3 3
D	95 5	4 5	5 0	95 0	0 46	243	0 74	0 24	250	2 0	0 8
E	95 1	4 9	5 0	95 0	0 60	242	0 74	1 15	245	2 3	1 1
F	97 5	2 5	5 5	94 5	0 46	245	0 74	0 21	250	2 3	1 0
G	96 7	3 3	4 8	95 2	0 46	245	0 74	0 24	252	2 3	1 0
H	94 1	5 9	2 3	97 7	0 46	245	0 74	0 22	250	2 5	1 2
I	92 0	8 0	0.2	99.8	0.46	245	0 74	0 21	252	3 9	1 9

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Surprisingly, due to the high level of DEG content in Resins H and I, these resins could not be processed into bottles having an AA content of 10 µg/l or less. It is postulated that the reduced thermal stability caused by the DEG levels of greater than 5 mole% resulted in the elevated AA content in the blown preform.

C L A I M S

- 1 A process to prepare a polyester resin having an acetaldehyde concentration of no more than about 1 ppm, which process comprises the steps of
- 5 a) reacting ethylene glycol with terephthalic acid or an ester thereof, and isophthalic acid or an ester thereof under constrained reaction conditions effective to prepare a melt phase polymer having an IV in the range of 0.38 dl/g to 0.52 dl/g and a diethylene glycol content of no more than 5 mole% (based on the diol content of the
- 10 resin),
- b) recovering the melt phase polymer from step a) as the pre-polymer used in step c); and
- c) subjecting at least a portion of the pre-polymer recovered in step b) to elevated temperatures over a
- 15 period of time to elevate the IV to a range of 0.60 dl/g to 0.90 dl/g
- 2 The process of claim 1 wherein the terephthalic acid or the ester thereof, is present in an amount of 99 mole% to 90 mole% and the isophthalic acid or the ester thereof, is present in an amount of 1 mole% to 10 mole%,
- 20 based on total acid component of the resin
- 3 The process of claim 2, where the terephthalic acid or the ester thereof, is present in an amount of about 95 mole% and the isophthalic acid or the ester thereof,
- 25 is present in an amount of about 5 mole%
- 4 The process of claim 1 where the constrained reaction conditions include a temperature of from 260 °C to 290 °C, a pressure of from 480 kPa to full vacuum (0.1 kPa) and a time of reaction of from 5 to 6 hours
- 30 5 The process of claim 4, wherein the temperature, pressure and time are maintained to constrain the IV of

the melt phase polymer to a range of 0.40 dl/g to 0.50 dl/g

6 The process of claim 5, wherein the melt phase polymer contains from 15 ppm AA to 45 ppm AA

5 7 The process of claim 1 wherein the pre-polymer treatment in step c) comprises a temperature of 200 °C to 232 °C over a period of time of from 15 to 21 hours

8 The process of claim 7, wherein the conditions include a crystallization temperature of from 100 °C to 150 °C and a subsequent SSP temperature of 215 °C to 232 °C

9 A process to prepare a beverage container having an AA content of no more than 1 µg/l which comprises

15 a) reacting ethylene glycol with terephthalic acid or an ester thereof, and isophthalic acid or an ester thereof under constrained reaction conditions effective to prepare a melt phase polymer having an IV in the range of 0.38 dl/g to 0.52 dl/g and a diethylene glycol content of no more than 5 mole% (based on the diol content of the resin),

20 b) recovering the melt phase polymer from step a) as the pre-polymer used in step c),

25 c) subjecting at least a portion of the pre-polymer recovered in step b) to elevated temperatures over a period of time to prepare a polyester resin having an IV in the range of 0.60 dl/g to 0.90 dl/g,

d) forming a beverage container preform from at least a portion of said resin, and

30 e) heating and blowing said preform of step d) at conditions to form said beverage container having an AA of no more than 1 µg/l

10 A bottle preform and/or beverage container made from said polyester resin made by the process of claim 1

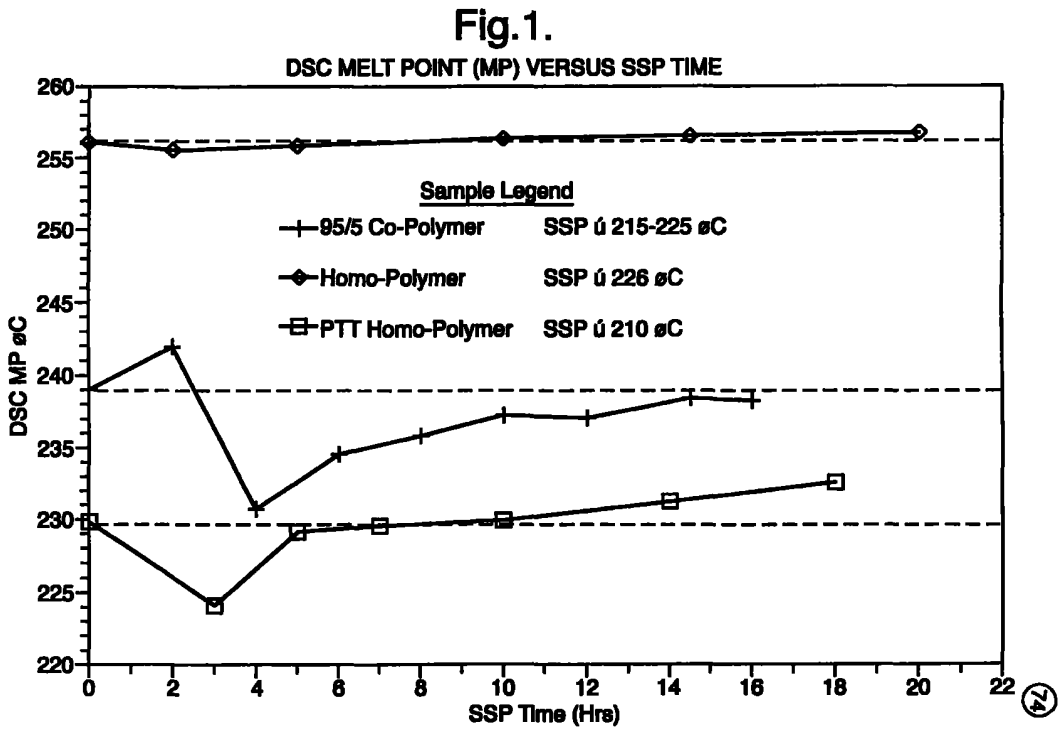
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FIG. 1

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⑩ Process for preparing polyester

⑪ The invention provides a process for preparing a polyester comprising [A] a liquid phase polycondensation step in which a dicarboxylic acid including terephthalic acid or its ester derivative and a diol including ethylene glycol or its ester derivative are subjected to polycondensation reaction in liquid phase and molten state under heating in the presence of a polycondensation catalyst to produce a polyester (a) having an intrinsic viscosity as measured in o-chlorophenol of 0.7 to 1.5 dl/g, [C] a hot water treatment step in which the polyester (a) is contacted with hot water of 80 to 130 °C for 30 minutes to 10 hours [D-1] a drying step in which the polyester after the hot water treatment step is dried at a temperature of 110 to 150 °C for 30 minutes to 6 hours, and [D-2] a heat treatment step in which the polyester after the drying treatment step is heated at a temperature of 180 to 200 °C for 1 to 10 hours; wherein the finally obtained polyester has an acetaldehyde content of not more than 10 ppm

The polyester (a) obtained in the step [A] can be precrystallized in [B] a precrystallization step by keeping it in an atmosphere of a heat-up crystallization temperature (T_{cr}) to 200 °C for 1 minute to 4 hours, prior to the drying step [D-1] and the heat treatment step [D-2]

Further when the precrystallization step [B] is carried out, the polyester obtained in the step [B] can also be subjected to the heat treatment step [D-2] and then the hot water treatment step [C].

The process of the invention has advantages that a solid phase polycondensation step can be omitted, and the process can provide a polyester having a low acetaldehyde content as well as reduced tendency to increase acetaldehyde during the molding process. Thus the polyester obtained by the process of the invention is particularly suited as a material for preform and beverage bottles formed from the preform. These bottles do not alter the tastes of the contents therein.

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FIELD OF THE INVENTION

The present invention relates to a process for preparing a polyester and more particularly to a process which is capable of providing a polyester having a low acetaldehyde content and hardly causing increase in acetaldehyde during molding thereof by means of simplified steps

BACKGROUND OF THE INVENTION

Bottles obtained by biaxially stretching a saturated polyester such as polyethylene terephthalate (PET bottles) have excellent transparency, mechanical strength, heat resistance and gas barrier properties and hence they have been widely used as containers for beverages such as juices, soft drinks and carbonated beverages.

For manufacturing bottles from such polyester, the polyester is generally injection molded into preforms which are then biaxially stretched by, for example, blow molding to be shaped into bottles.

If acetaldehyde remains in the bottles thus obtained from the polyester, tastes of the contents filled in the bottles are markedly deteriorated. For this reason, the acetaldehyde content in the bottle-forming polyester is desired to be as low as possible. In order to reduce the amount of acetaldehyde contained in the bottle-forming polyester, it is required that the polyester not only has a low acetaldehyde content before molding but also hardly causes increase in acetaldehyde during molding.

Polyesters have conventionally been prepared by esterification reaction of a dicarboxylic acid such as terephthalic acid or its ester derivative and a diol such as ethylene glycol or its ester derivative and then polycondensation reaction of the resulting esterified products in the presence of a polycondensation catalyst. The polycondensation reaction comprises liquid phase and solid phase polycondensation steps wherein a polyester from the liquid phase polycondensation step undergoes the solid phase polycondensation step to obtain a polyester having a high intrinsic viscosity and a low content of acetaldehyde.

Thus, conventional processes for preparing polyesters need both the liquid phase and solid phase polycondensation steps, the latter step taking a long period of time whereby leading to increased production costs.

If a polyester obtained by liquid phase polycondensation without solid phase polycondensation is directly molded into an article such as a bottle, there is involved a problem that acetaldehyde is produced in the molding process, which may remain in the polyester molded article.

Accordingly, it has been desired to develop a process for preparing a polyester in which a polyester having a low acetaldehyde content and hardly causing increase in acetaldehyde during molding into articles such as bottles can be prepared and the solid phase polycondensation step can be omitted.

OBJECT OF THE INVENTION

The present invention has been made in order to improve the prior art technique as mentioned above. An object of the invention is to provide a process for preparing a polyester which can provide a polyester having a low acetaldehyde content as well as hardly causing increase in acetaldehyde during molding into articles such as bottles, and in which the solid phase polycondensation step can be omitted.

SUMMARY OF THE INVENTION

The first process for preparing a polyester according to the invention comprises

[A] a liquid phase polycondensation step in which a dicarboxylic acid including terephthalic acid or its ester derivative and a diol including ethylene glycol or its derivative are subjected to polycondensation reaction in liquid phase and molten state under heating in the presence of a polycondensation catalyst to produce a polyester (a) having an intrinsic viscosity as measured in o-chlorophenol of 0.7 to 1.5 dl/g.

[C] a hot water treatment step in which the polyester (a) is contacted with hot water of 60 to 130 °C for 5 minutes to 10 hours,

[D-1] a drying step in which the polyester (c-1) having passed the hot water treatment step is dried at a temperature of 110 to 150 °C for 30 minutes to 6 hours, and

[D-2] a heat treatment step in which the polyester (c-1) having passed the drying step is heated at a temperature of 160 to 200 °C for 1 to 10 hours, wherein

the finally obtained polyester (d-1) has an acetaldehyde content of not more than 10 ppm.

In the first process for preparing a polyester according to the invention, the polyester (a) obtained in the liquid phase polycondensation step [A] may be subjected to [B] a precrystallization step in which the

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polyester (a) is kept in an atmosphere having a temperature of a heat-up crystallization temperature (T_{G1}) to 200 °C for 1 minute to 4 hours prior to the hot water treatment step [C].

The polyester (a) obtained in the step [A] of the first process preferably has an intrinsic viscosity, as measured in o-chlorophenol, of 0.8 to 1.2 dl/g

5 The second process for preparing a polyester according to the invention comprises

[A] a liquid phase polycondensation step in which a dicarboxylic acid including terephthalic acid or its ester derivative and a diol including ethylene glycol or its ester derivative are subjected to polycondensation reaction in liquid phase and molten state under heating in the presence of a polycondensation catalyst to produce a polyester (a) having an intrinsic viscosity as measured in o-chlorophenol, of 0.7 to 1.5 dl/g

10 [B] a precrystallization step in which the polyester (a) is kept in an atmosphere having a temperature a heat-up crystallization temperature (T_{G1}) to 200 °C for 1 minute to 4 hours,

[D-2] a heat treatment step in which the polyester (b) having passed the precrystallization step is heated at a temperature of 180 to 200 °C for 1 to 10 hours, and

15 [C] a hot water treatment step in which the polyester (c-2) having passed the heat treatment step is contacted with hot water of 80 to 130 °C for 5 minutes to 10 hours wherein

(i) the intrinsic viscosity of the polyester does not substantially increase in the steps [B] and [D-2], and

(ii) the finally obtained polyester (d-2) has an acetaldehyde content of not more than 10 ppm

20 The polyester (a) obtained in the step [A] of the second process preferably has an intrinsic viscosity as measured in o-chlorophenol of 0.8 to 1.2 dl/g

According to the first and second processes for preparing a polyester the solid phase polycondensation step required in the conventional processes for preparing polyesters can be omitted. Moreover, a polyester having a low acetaldehyde content and hardly causing increase in acetaldehyde in the molding process can be prepared

25 The polyester obtained by the processes of the invention is suitably used as a material for forming preforms and bottles for beverages

BRIEF DESCRIPTION OF THE DRAWING

30 Fig. 1 is a flow chart of the first process for preparing a polyester according to the invention

Fig. 2 is a flow chart of the second process for preparing a polyester according to the invention

Fig. 3 is a perspective view of a stepped square plate formed in the Examples

DETAILED DESCRIPTION OF THE INVENTION

35

The first and second processes for preparing a polyester according to the invention will be described in detail hereinafter with reference to the processing flow charts shown in Fig. 1 and Fig. 2.

To begin with, the first process for preparing a polyester according to the invention is explained

40 As shown in Fig. 1, the first process for preparing a polyester according to the invention comprises

[A] a liquid phase polycondensation step in which a dicarboxylic acid including terephthalic acid or its ester derivative and a diol including ethylene glycol or its ester derivative are subjected to polycondensation reaction in liquid phase and molten state under heating in the presence of a polycondensation catalyst to produce a polyester (a) having an intrinsic viscosity as measured in o-chlorophenol of 0.7 to 1.5 dl/g

45 [C] a hot water treatment step in which the polyester (a) is contacted with hot water of 80 to 130 °C for 5 minutes to 10 hours

[D-1] a drying step in which the polyester (c-1) having passed the hot water treatment step is dried at a temperature of 110 to 150 °C for 30 minutes to 8 hours and

50 [D-2] a heat treatment step in which the polyester (c-1) having passed the hot water treatment step is heated at a temperature of 180 to 200 °C for 1 to 10 hours; wherein

the finally obtained polyester (d-1) has an acetaldehyde content of not more than 10 ppm

In this invention the polyester (a) obtained in the liquid phase polycondensation step [A] may be subjected to [B] a precrystallization step in which the polyester (a) is kept in an atmosphere having a temperature of a heat-up crystallization temperature (T_{G1}) to 200 °C for 1 minute to 4 hours, prior to the hot water treatment step [C].

55 The steps of the above process are described below in more detail

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[A] Liquid phase polycondensation step

In the liquid phase polycondensation step according to the invention, the dicarboxylic acid including terephthalic acid or its ester derivative (e.g., a lower alkyl ester and a phenyl ester) and the diol including ethylene glycol or its ester derivative (e.g., a monocarboxylic ester) are subjected to polycondensation reaction in liquid phase and molten state under heating in the presence of a polycondensation catalyst to produce a polyester (a).

In the present invention, homopolyethylene terephthalate may be prepared by the use of terephthalic acid and ethylene glycol. Otherwise a copolymerized polyester may be prepared by using in addition to the terephthalic acid and ethylene glycol other dicarboxylic acid than terephthalic acid (or its derivative) in an amount of not more than 20 % by mol and/or other diol than ethylene glycol (or its derivative) in an amount of not more than 20 % by mol.

Examples of other dicarboxylic acids than terephthalic acid used for preparing the copolymerized polyester include aromatic dicarboxylic acids such as phthalic acid (orthophthalic acid), isophthalic acid, naphthalenedicarboxylic acid, diphenyldicarboxylic acids and diphenoxyethanedicarboxylic acids; aliphatic dicarboxylic acids such as adipic acid, sebacic acid, azelaic acid and decanedicarboxylic acids; alicyclic dicarboxylic acids such as cyclohexanedicarboxylic acids and ester derivatives thereof. They may be used in combination of two or more kinds.

Examples of other diols than ethylene glycol include aliphatic glycols such as trimethylene glycol (propylene glycol), tetramethylene glycol, neopentyl glycol, hexamethylene glycol, dodecamethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol and polyethylene glycols, alicyclic glycols such as cyclohexanedimethanols, aromatic diols such as bisphenols, hydroquinone and 2,2-bis(4- β -hydroethoxyphenyl)propane and ester derivatives thereof. They may be used in combination of two or more kinds.

In the present invention, polycarboxylic and polyhydric compounds such as trimesic acid, pyromellitic acid, trimethylolpropane trimethylolpropane trimethylolmethane and pentaerythritol can also be used in small amounts, e.g., not more than 2 % by mol.

The process of the invention may be carried out batchwise and continuously and by way of example a continuous procedure will be described below.

The liquid phase polycondensation step [A] in which the dicarboxylic acid or its ester derivative (also referred to as "dicarboxylic acid") and the diol or its ester derivative (also referred to as "diol") are polycondensed to prepare a polyester generally comprises an esterification reaction step [A-1] of the dicarboxylic acid and the diol and a subsequent liquid phase polycondensation reaction step [A-2].

More specifically in the step [A], a slurry containing the dicarboxylic acid and the diol is first prepared. The slurry may contain the diol in an amount of 1.02 to 2.0 mol, preferably 1.03 to 1.5 mol based on 1 mol of the dicarboxylic acid. The slurry is continuously fed to the esterification reaction step [A-1].

The esterification reaction is generally conducted in an apparatus comprising for example two esterification reactors in line connected under the conditions of refluxing the diol while removing water or alcohol produced by the reaction out of the system by means of a fractionating column.

When the esterification reaction step [A-1] is conducted in two stages as mentioned above, the esterification reaction of the first stage may be carried out at a temperature of usually 240 to 270 °C, preferably 245 to 265 °C, under a pressure of usually 0.2 to 3 kg/cm²-G, preferably 0.5 to 2 kg/cm²-G and the esterification reaction of the second stage may be carried out at a temperature of usually 250 to 280 °C, preferably 255 to 275 °C, under a pressure of usually 0 to 1.5 kg/cm²-G, preferably 0 to 1.3 kg/cm²-G.

Although there is no specific limitation on the esterification conversion in each stage, it is preferred that the conversion increases smoothly (gradually) from stage to stage and particularly reaches usually not less than 80 % preferably not less than 93 % in the last stage.

Through the esterification reaction step [A-1], an esterified product (low condensate) having a number-average molecular weight of usually 500 to 5,000 is obtained.

The esterification reaction may be carried out without adding any substance other than the dicarboxylic acid and the diol or in the presence of a polycondensation catalyst described later. It is also possible to carry out the reaction in the presence of a small amount of tertiary amines such as trimethylamine, tri-n-butylamine and benzyldimethylamine; quaternary ammoniums such as tetraethylammonium hydroxide, tetra-n-butylammonium hydroxide and trimethylbenzylammonium hydroxide; and basic compounds such as lithium carbonate, sodium carbonate, potassium carbonate and sodium acetate. These basic compounds may be added to all the esterification reactors or to any one or more reactors of the first to the last stages.

Subsequently the esterified product thus obtained is continuously fed to the liquid phase polycondensation reactor where the polycondensation reaction is carried out at a temperature not lower than the melting point of the resulting polyester under a reduced pressure in the presence of a polycondensation

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catalyst while distilling off the produced glycol from the system

In the present invention, the next step, the polycondensation reaction step [A-2], may be conducted either in one or more stages

When the polycondensation reaction step [A-2] is conducted in plural stages the polycondensation reaction of the first stage may be carried out at a temperature of usually 250 to 290 °C preferably 260 to 280 °C under a pressure of usually 500 to 20 Torr preferably 200 to 30 Torr and the polycondensation reaction of the last stage is carried out at a temperature of usually 265 to 300 °C, preferably 270 to 295 °C under a pressure of usually 10 to 0.1 Torr preferably 5 to 0.1 Torr particularly preferably 2 to 0.1 Torr

When the polycondensation reaction step [A-2] is conducted in three or more stages, the polycondensation reactions from the second stage to the last stage but one may be carried out under the conditions between those of the first and the last stages. For instance in the polycondensation reaction step comprising three stages, the polycondensation reaction of the second stage may be carried out at a temperature of usually 260 to 285 °C, preferably 270 to 285 °C under a pressure of usually 50 to 2 Torr preferably 40 to 5 Torr

Through the liquid phase polycondensation step [A] stated above a polyester (a) having an intrinsic viscosity, as measured in o-chlorophenol at 25 °C, of 0.7 to 1.5 dl/g, preferably 0.8 to 1.2 dl/g is prepared. Although there is no specific limitation on the intrinsic viscosity of the polyester reached in each of the stages excluding the last stage in the polycondensation reaction step [A-2] it is preferred that the intrinsic viscosity increases smoothly and gradually from stage to stage

For preparing the polyester (a) having the above-mentioned intrinsic viscosity in the liquid phase polycondensation step [A], the polycondensation reaction step [A-2] is desired to be carried out in three or more stages preferably in three stages and the polyester subjected to the polycondensation reaction of the last stage (the third stage) desirably has an intrinsic viscosity of 0.4 to 0.7 dl/g preferably 0.5 to 0.65 dl/g

Further for obtaining the polyester (a) having the above-defined intrinsic viscosity by the multi-stage polycondensation reaction conventionally known liquid phase polycondensation reactors can be used in combination. For instance, the first stage reaction can be carried out in a vertical reactor the second stage reaction in a horizontal reactor equipped with a monoxal stirrer and the third stage reaction in a horizontal reactor equipped with a blade stirrer. In this specification the intrinsic viscosity is calculated from a solution viscosity of a polyester solution which is obtained by measuring at 25 °C on a cooled solution of 1.2 g of polyester heated and dissolved in 5 ml of o-chlorophenol

The liquid phase polycondensation reaction is carried out in the presence of a catalyst

Examples of the catalysts used herein include germanium compounds such as germanium dioxide, germanium tetrachloride, germanium tetra-n-butoxide; antimony catalysts such as antimony trioxide and antimony acetate; and titanium catalysts such as titanium tetrabutoxide

Of these catalysts germanium dioxide is preferably employed because a polyester having good hue and high transparency can be obtained

The polycondensation reaction is preferably carried out in the presence of a stabilizer. Examples of the stabilizers include phosphoric esters such as trimethyl phosphate, triethyl phosphate, tri-n-butyl phosphate, trioctyl phosphate, triphenyl phosphate and tricresyl phosphate; phosphorous esters such as triphenyl phosphite, tris(dodecyl) phosphite and tris(nonylphenyl) phosphite; acid phosphoric esters such as methyl acid phosphate, isopropyl acid phosphate, butyl acid phosphate, dibutyl phosphate, monobutyl phosphate and dioctyl phosphate; phosphorus compounds such as phosphoric acid and polyphosphoric acid

The catalyst is desirably used in an amount of 0.0005 to 0.2 % by weight preferably 0.001 to 0.05 % by weight, in terms of metal atom in the catalyst, based on the total weight of the dicarboxylic acid and the diol

The stabilizer is desirably used in an amount of 0.001 to 0.1 % by weight preferably 0.002 to 0.02 % by weight, in terms of phosphorus atom in the stabilizer, based on the total weight of the dicarboxylic acid and the diol

These catalysts and stabilizers may be added in the esterification reaction step [A-1] or to the reactor of the first stage in the polycondensation reaction step [A-2]

The polyester (a) prepared in the last polycondensation reactor as described above is generally molded into particles (chips) by a melt extrusion molding method

[B] Precrystallization step

In the present invention the particulate polyester (a) obtained in the liquid phase polycondensation step may be subjected to a precrystallization step

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The precrystallization step is carried out by keeping the particulate polyester (a) in a dry state at a temperature of a heat-up crystallization temperature (T_{C1}) to 200 °C preferably at a temperature of T_{C1} to 180 °C for 1 minute to 4 hours.

It is preferred that the precrystallization step is conducted in air or an inert atmosphere

5 The polyester (b) after the precrystallization desirably has a crystallinity of 20 to 50 %

In this precrystallization step so-called solid polycondensation reaction of polyester does not proceed and therefore the intrinsic viscosity of the polyester (b) after the precrystallization is almost equal to that of the polyester (a) obtained in the liquid phase polycondensation step [A]

10 By subjecting the polyester to the precrystallization step as described above the amount of acetaldehyde contained in the polyester can be decreased and the polyester particles (chips) can be prevented from being fusion bonded with each other in the subsequent hot water treatment step or drying step

[C] Hot water treatment step

15 In the first process for preparing a polyester according to the invention the polyester (a) or the precrystallized polyester (b) is subjected to hot water treatment.

This hot water treatment is carried out by bringing the particulate polyester (a) or the particulate polyester (b) having passed the precrystallization step into contact with hot water water vapor water vapor-containing inert gas water vapor-containing air or the like

20 The contact between the particulate polyester (a) or (b) and hot water is desirably carried out by immersing the polyester in hot water heated to a temperature of usually 80 to 130 °C preferably 80 to 100 °C for usually 5 minutes to 10 hours, preferably 30 minutes to 5 hours

When the particulate polyester (a) or (b) is brought into contact with water vapor the contact therebetween may be carried out by feeding water vapor (or water vapor-containing inert gas or water vapor-containing air) of usually 80 to 130 °C, preferably 80 to 100 °C in an amount of not less than 0.5 kg per 1 kg of the particulate polyester (a) or (b) The contact between the particulate polyester and water vapor is conducted for usually 5 minutes to 10 hours preferably 1 to 8 hours

The particulate polyester (c-1) obtained immediately after the hot water treatment generally has a water content of 5,000 to 10,000 ppm

30 By subjecting the polyester (a) or (b) to the hot water treatment as described above increase of acetaldehyde in the molding process can be inhibited

The reason why increase of acetaldehyde in the molding process can be inhibited is presumed that the hot water treatment of polyester deactivates the polycondensation catalyst, e.g. germanium catalyst, contained in the polyester whereby decomposition reaction or ester interchange reaction hardly proceeds 35 even if the polyester is heated in the molding process, resulting in reduction of acetaldehyde produced

[D-1] Low-temperature drying step

40 In the first process for preparing a polyester according to the invention the polyester (c-1) having undergone the hot water treatment as described above is then subjected to low-temperature drying

More specifically the polyester (c-1) having undergone the hot water treatment is desirably dried at a temperature of 110 to 150 °C, preferably 120 to 140 °C for 30 minutes to 6 hours, preferably 1 to 4 hours.

The polyester (c-1) from which water is removed by the low-temperature drying as described above is preferred because this polyester is prevented from being hydrolyzed

[D-2] Heat treatment step

50 In the first process for preparing a polyester according to the invention the polyester (c-1) obtained after the hot water treatment and the subsequent low-temperature drying is then heated at a high temperature

More specifically the polyester (c-1) is desirably heated at a temperature of 180 to 200 °C preferably 170 to 190 °C for 1 to 10 hours preferably 2 to 6 hours The heat treatment can be carried out by bringing the polyester (c-1) into contact with a flowing gas (e.g. air or nitrogen gas) heated to 180 to 200 °C preferably 170 to 190 °C.

55 Through the heating under the above conditions acetaldehyde contained in the polyester is removed so that a polyester (d-1) having a reduced acetaldehyde content can be obtained

In the heat treatment step [D-2] the polycondensation reaction of the polyester hardly proceeds, and the polyester (d-1) obtained after the heat treatment step has almost the equal intrinsic viscosity to that of

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the polyester (a) obtained in the liquid phase polycondensation step

As described above in the first process for preparing a polyester according to the invention not only the precrystallization step [B], the low-temperature drying step [D-1] and the heat treatment step [D-2] are carried out at temperatures lower than those employed in the so-called solid phase polycondensation step, but also the catalyst is deactivated in the low-temperature drying step [D-1] and the heat treatment step [D-2]. Therefore the polycondensation reaction does not substantially proceed in these steps so that the intrinsic viscosity of the polyester does not substantially increase, and also the acetaldehyde content of the resulting polyester can be reduced effectively.

The polyester (d-1) prepared by the first process of the invention has

- (i) an acetaldehyde content of not more than 10 ppm preferably not more than 5 ppm and
- (ii) an intrinsic viscosity as measured in o-chlorophenol of usually 0.7 to 1.5 dl/g preferably 0.8 to 1.1 dl/g particularly preferably 0.8 to 1.0 dl/g

Further the polyester (d-1) prepared by the first process of the invention desirably has a crystallinity of 30 to 50 %

As described above the polyester (d-1) obtained by the first process of the invention has not only the low acetaldehyde content, but also reduced tendency to increase acetaldehyde in the molding process. For instance, a molded article such as a preform obtained from the polyester (d-1) by injection molding hereof at a molding temperature of 270 to 310 °C e.g. 290 °C, has an acetaldehyde content of usually not more than 20 ppm preferably not more than 15 ppm.

Next, the second process for preparing a polyester according to the invention is explained.

As shown in Fig. 2 the second process for preparing a polyester according to the invention comprises [A] a liquid phase polycondensation step in which a dicarboxylic acid including terephthalic acid or its ester derivative and a diol including ethylene glycol or its ester derivative are subjected to polycondensation reaction in liquid phase and molten state under heating in the presence of a polycondensation catalyst to produce a polyester (a) having an intrinsic viscosity as measured in o-chlorophenol of 0.7 to 1.5 dl/g.

[B] a precrystallization step in which the polyester (a) is kept in an atmosphere having a temperature a heat-up crystallization temperature (T_{C1}) to 200 °C for 1 minute to 4 hours.

[D-2] a heat treatment step in which the polyester (b) having passed the precrystallization step is heated at a temperature of not lower than 180 to 200 °C for 1 to 10 hours and

[C] a hot water treatment step in which the polyester (c-2) having passed the heat treatment step is contacted with hot water of 80 to 130 °C for 5 minutes to 10 hours wherein

- (i) the intrinsic viscosity of the polyester does not substantially increase in the steps [B] and [D-2] and
- (ii) the finally obtained polyester (d-2) has an acetaldehyde content of not more than 10 ppm.

In the second process for preparing a polyester according to the invention the liquid phase polycondensation step [A] and the precrystallization step [B] can be conducted under those conditions described for the corresponding steps in the first process of the invention respectively.

In the second process for preparing a polyester according to the invention the polyester (b) having been precrystallized as above is subjected firstly to the heat treatment step [D-2] and then the hot water treatment step [C].

The heat treatment [D-2] and the hot water treatment [C] in the second process of the invention can also be conducted under those conditions described for the corresponding steps in the first process of the invention respectively.

It can be seen from the comparison between the first and second processes of the invention that in the second process the low-temperature drying step [D-1] in the first process can be omitted (but preferably be carried out) and the steps after the precrystallization step [B] are carried out in different order in the first process. However, the polyester (d-2) obtained by the second process has also excellent properties, i.e. a low acetaldehyde content as well as reduced tendency to increase of acetaldehyde in the molding process.

In the heat treatment step [D-2], the polycondensation reaction of the polyester also hardly proceeds, and the polyester (c-2) obtained after the heat treatment step has almost the equal intrinsic viscosity to that of the polyester (a) obtained in the liquid phase polycondensation step.

The particulate polyester obtained immediately after the hot water treatment [C] generally has a water content of 5,000 to 10,000 ppm.

By subjecting the polyester (c-2) to the hot water treatment as described above increase of acetaldehyde in the molding process can be inhibited.

The reason why increase of acetaldehyde in the molding process can be inhibited is presumed that the hot water treatment of polyester deactivates the polycondensation catalyst, e.g., germanium catalyst, contained in the polyester whereby decomposition reaction or ester interchange reaction hardly proceeds.

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even if the polyester is heated in the molding process, resulting in reduction of acetaldehyde produced

The polyester (d-2) having been treated with hot water as described above is then preferably subjected to low-temperature drying. More specifically, the polyester is desirably dried at a temperature of 110 to 150 °C, preferably 120 to 140 °C, for 30 minutes to 6 hours, preferably 1 to 4 hours.

8 The polyester (d-2) from which water is removed by the low-temperature drying as described above is preferred because this polyester is prevented from being hydrolyzed.

In the second process for preparing a polyester according to the invention, the precrystallization step [B] and the heat treatment step [D-2] are carried out at temperatures lower than those employed in the so-called solid phase polycondensation step so that in these steps the polycondensation reaction does not substantially proceed and the intrinsic viscosity of the polyester does not substantially increase.

10 The polyester (d-2) prepared by the second process of the invention has

(i) an intrinsic viscosity as measured in o-chlorophenol of 0.7 to 1.5 dl/g, preferably 0.8 to 1.1 dl/g, particularly preferably 0.8 to 1.0 dl/g and

(ii) an acetaldehyde content of not more than 10 ppm, preferably not more than 5 ppm.

15 Further, the polyester (d-2) prepared by the second process of the invention desirably has a crystallinity of 30 to 50 %.

As described above, the polyester (d-2) obtained by the second process of the invention has not only the low acetaldehyde content but also reduced tendency to increase acetaldehyde in the molding process. For instance, a molded article such as a preform obtained from the polyester (d-2) by injection molding thereof at a molding temperature of 270 to 310 °C, e.g. 290 °C, has an acetaldehyde content of usually not more than 20 ppm, preferably not more than 15 ppm.

20 The polyesters prepared by the first and second processes of the invention can be used for any purpose of conventionally known polyesters, and are particularly suited for manufacturing hollow molded articles. For example, these polyesters can be fed to a molding machine such as an injection molding machine to form preforms for hollow articles which is then placed in a mold of predetermined shape and blow molded into hollow containers. The hollow containers thus obtained hardly alter the tastes of the contents.

The polyesters prepared according to the invention can be suitably used as a material for forming preforms for beverage bottles.

30

EFFECT OF THE INVENTION

The polyesters obtained by the processes according to the invention have not only a low acetaldehyde content, but also tendency to hardly increase amount of acetaldehyde produced in the molding process. Therefore, hollow containers such as bottles manufactured from the polyesters do not alter the tastes of the contents.

Further, the processes for preparing polyesters according to the invention do not need a solid phase polycondensation step so that the processes have the advantages of productivity and economy.

40 The polyesters according to the invention can be suitably used as a material for forming preforms for beverage bottles.

EXAMPLE

45 The present invention will be further described with reference to the following examples, but it should be construed that the invention is in no way limited to those examples.

In this specification, acetaldehyde content or concentration (ppm) is measured with respect to a stepped square plate molded article as shown in Fig. 3, which is obtained by injection molding of polyester chips in the manner described below.

50 The stepped square plate in Fig. 3 comprises six parts A to F wherein the part A is 2 mm in thick, the part B is 4 mm, the part C is 6 mm, the part D is 3 mm, the part E is 5 mm and the part F is 7 mm. The acetaldehyde concentration is measured on the part E of the stepped square plate.

Preparation of stepped square plate

55 2 kg of dried polyester chips are injection molded into a stepped square plate as shown in Fig. 3 by means of an injection molding machine of M-70A produced by Meiki Seisakusho K.K., in which nitrogen having a dew point of -70 °C is fed to an upper part of a hopper and to a screw feeder shooting part at a rate of 5 Nm³/hr, respectively, at a barrel temperature of 290 °C at C1, C2, C3 and nozzle tip temperatures

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of 280 °C 280 °C 280 °C and 300 °C, respectively and at a mold-cooling temperature of 15 °C

The injection molding to obtain the stepped square plate is carried out by feeding the dried polyester chips to the injection molding machine in such a manner that the metering time and the injection time are 12 seconds and 60 seconds respectively. The residence time of the molten resin in the molding machine is about 72 seconds. The weight of one stepped square plate is about 75 g

Measurement of acetaldehyde concentration

The acetaldehyde concentration of the stepped square plate molded article was determined as follows. A sample from the part E of the stepped square plate was pulverized by a freezer mill then acetaldehyde contained in the sample is extracted with hot water and the acetaldehyde is quantitatively determined by means of gas chromatography in accordance with an internal standard method

Measurement of heat-up crystallization temperature

The heat-up crystallization temperature (T_{ci}) of the polyester is measured as follows. The polyester chips are dried at about 140 °C under a pressure of about 5 mmHg for about 5 hours or more and about 10 mmg of a thin piece as a sample is taken out from the central part of the polyester chips and potted into an aluminum pan for liquid under a nitrogen atmosphere. The measurement is conducted using DSC-2 type differential scanning calorimeter available from Perkin Elmer Co. under the conditions such that the sample is first heated rapidly from room temperature to 290 °C at which temperature the sample is kept at molten state for 10 minutes and then cooled rapidly to room temperature, and thereafter the top temperature of an exothermal peak detected at the time of elevating the temperature at a heat-up rate of 10 °C/min is obtained

Measurement of intrinsic viscosity

The intrinsic viscosity (dl/g) of the polyester is determined as follows. A sample is heated and dissolved in o-chlorophenol (OCP) and a solution viscosity is measured by a capillary viscometer. From the value of solution viscosity and an empirical formula preliminary prepared the intrinsic viscosity is determined

Example 1

To 100 parts by weight of terephthalic acid were added 50.5 parts by weight of ethylene glycol and 0.028 part by weight of germanium dioxide to perform esterification reaction in a conventional manner. When the reaction was completed, the solution temperature was 240 °C. Then to the reaction mixture was added 0.030 part by weight of trimethyl phosphate to perform polycondensation reaction in three stages. In the last stage the polycondensation reaction was carried out at a temperature of 270 °C under a pressure of 1 Torr to obtain a polyester having an intrinsic viscosity of 0.84 dl/g. The polyester chips had an acetaldehyde concentration of 90 ppm and a heat-up crystallization temperature of 184.8 °C

Subsequently the polyester chips were precrystallized at 170 °C for 2 hours in a stream of nitrogen. After completion of the precrystallization the polyester chips had an intrinsic viscosity of 0.83 dl/g and an acetaldehyde concentration of 22 ppm. Thereafter, the polyester chips were immersed in hot water at 95 °C for 4 hours and then subjected to low-temperature drying at 130 °C for 2 hours in a stream of nitrogen, followed by heating at 180 °C for 2 hours. The intrinsic viscosity, acetaldehyde concentration and water content of the polyester chips obtained in each of the steps are shown in Table 1

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Table 1

	Polyester chips after				
	[A] (a)	[B] (b)	[C] (c-1)	[D-1]	[D-2] (d-1)
Intrinsic viscosity (dl/g)	0.84	0.83	0.80	0.80	0.79
CH ₃ CHO (ppm)	90	22	21	17	4.5
Water (ppm)		-	8,500	300	50
[A] Polycondensation [B] Precrystallization [C] Hot-water treatment [D-1] Low-temperature drying [D-2] Heat treatment					

The polyester chips (d-1) were further dried at 180 °C for 3 hours in a stream of nitrogen to reduce the water content in the chips to 20 ppm. The thus-dried chips had an intrinsic viscosity of 0.79 dl/g and an acetaldehyde concentration of 3.8 ppm. Then the chips were melted under heating at 290 °C and molded into a stepped square plate molded article as shown in Fig. 3. The molded article had an acetaldehyde concentration of 15 ppm.

Separately, the chips were molded into a preform by means of a molding machine of M-100A produced by Meiki Seisakusho K.K. under the conditions of a molding temperature of 270 °C, a nozzle temperature of 310 °C and a mold temperature of 10 °C. The preform had an acetaldehyde concentration of 10 ppm.

Comparative Example 1

The polyester chips (a) as obtained in Example 1 were precrystallized at 170 °C for 2 hours in a stream of nitrogen and then subjected to low-temperature drying at 130 °C for 2 hours followed by heating at 180 °C for 2 hours. The polyester chips obtained after these treatments had an intrinsic viscosity of 0.80 dl/g and an acetaldehyde concentration of 4.4 ppm. After drying at 180 °C for 3 hours, the chips were molded into a stepped square plate molded article as in Example 1. The molded article had an acetaldehyde concentration of 30 ppm.

Further, a preform prepared from the chips in the same manner as in Example 1 had an acetaldehyde concentration of 25 ppm.

Example 2

The polyester chips (a) as obtained in Example 1 were treated in the same manner as in Example 1 except that the precrystallization was omitted and the heat treatment was carried out at 170 °C for 4 hours. The intrinsic viscosity, acetaldehyde concentration and water content of the polyester chips obtained in each of the steps are shown in Table 2.

Table 2

	Polyester chips after			
	[A] (a)	[C] (c-1)	[D-1]	[D-2] (d-1)
Intrinsic viscosity (dl/g)	0.84	0.81	0.81	0.80
CH ₃ CHO (ppm)	90	75	64	6.8
Water (ppm)		12,000	340	70
[A] Polycondensation [C] Hot-water treatment [D-1] Low-temperature drying [D-2] Heat treatment				

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Further after drying at 160 °C for 3 hours the chips (d 1) were molded into a stepped square plate molded article as in Example 1. The molded article had an acetaldehyde concentration of 17 ppm. Furthermore, a preform prepared from the chips in the same manner as in Example 1 had an acetaldehyde concentration of 11 ppm.

Example 3

To 100 parts by weight of terephthalic acid were added 48.8 parts by weight of ethylene glycol and 0.031 part by weight of germanium dioxide to perform esterification reaction in a conventional manner. When the reaction was completed the solution temperature was 240 °C. Then to the reaction mixture was added 0.030 part by weight of trimethyl phosphate to perform polycondensation reaction in three stages. In the last stage the polycondensation reaction was carried out at a temperature of 270 °C under a pressure of 1 Torr to obtain a polyester having an intrinsic viscosity of 0.83 dl/g. The polyester chips had an acetaldehyde concentration of 53 ppm and a heat-up crystallization temperature of 159.0 °C.

Subsequently the polyester chips were precrystallized at 170 °C for 2 hours in a stream of nitrogen then heated at 180 °C for 3 hours and immersed in hot water at 85 °C for 3 hours. Thereafter the chips were subjected to low-temperature drying at 130 °C for 2 hours. The intrinsic viscosity, acetaldehyde concentration and water content of the polyester chips obtained in each of the steps are set forth in Table 3.

Table 3

	Polyester chips after				
	[A] (a)	[B] (b)	[D-2] (c-2)	[C] (d-2)	Low-temp drying
Intrinsic viscosity (dl/g)	0.83	0.82	0.82	0.82	0.81
CH ₃ CHO (ppm)	53	11	2.5	2.2	2.2
Water (ppm)	-	-	40	8000	300
[A] Polycondensation [B] Precrystallization [D-2] Heat treatment [C] Hot-water treatment					

The polyester chips (d-2) having been subjected to the low-temperature drying were further dried at 160 °C for 3 hours in a stream of nitrogen to reduce the water content in the chips to 40 ppm. The thus-dried chips had an intrinsic viscosity of 0.81 dl/g and an acetaldehyde concentration of 1.7 ppm. Thereafter the chips were molded into a stepped square plate molded article as in Example 1. The molded article had an acetaldehyde concentration of 12 ppm.

Further a preform prepared from the chips in the same manner as in Example 1 had an acetaldehyde concentration of 8 ppm.

Comparative Example 2

The polyester chips (a) as obtained in Example 3 were precrystallized at 170 °C for 2 hours in a stream of nitrogen and then heated at 180 °C for 3 hours, followed by low-temperature drying at 130 °C for 2 hours. The polyester chips obtained after these treatments had an intrinsic viscosity of 0.82 dl/g and an acetaldehyde concentration of 1.5 ppm. After drying at 160 °C for 3 hours, the chips were molded into a stepped square plate molded article as in Example 1. The molded article had an acetaldehyde concentration of 27 ppm.

Further a preform prepared in the same manner as in Example 1 had an acetaldehyde concentration of 26 ppm.

Example 4

The polyester chips (a) as obtained in Example 3 were treated in the same manner as in Example 3 except that the heat treatment was carried out at 170 °C for 4 hours. The intrinsic viscosity, acetaldehyde concentration and water content of the polyester chips obtained in each of the steps are shown in Table 4.

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Table 4

	Polyester chips after				
	[A] (a)	[B] (b)	[D-2] (c-2)	[C] (d-2)	Low-temp drying
Intrinsic viscosity (dl/g)	0.83	0.82	0.81	0.81	0.80
CH ₃ CHO (ppm)	53	11	3.0	3.0	2.5
Water (ppm)	-	-	180	7500	800
[A] Polycondensation [B] Precrystallization [D-2] Heat treatment [C] Hot-water treatment					

The polyester chips (d-2) having been subjected to the low-temperature drying were further dried at 180 °C for 3 hours and were molded into a stepped square plate molded article as in Example 1. The molded article had an acetaldehyde concentration of 13 ppm. Further, a preform prepared in the same manner as in Example 1 had an acetaldehyde concentration of 9 ppm.

Claims

1. A process for preparing a polyester comprising

[A] a liquid phase polycondensation step in which a dicarboxylic acid including terephthalic acid or its ester derivative and a diol including ethylene glycol or its ester derivative are subjected to polycondensation reaction in liquid phase and molten state under heating in the presence of a polycondensation catalyst to produce a polyester (a) having an intrinsic viscosity as measured in o-chlorophenol of 0.7 to 1.5 dl/g

[C] a hot water treatment step in which the polyester (a) is contacted with hot water of 80 to 130 °C for 5 minutes to 10 hours,

[D-1] a drying step in which the polyester (c-1) having passed the hot water treatment step is dried at a temperature of 110 to 150 °C for 30 minutes to 6 hours, and

[D-2] a heat treatment step in which the polyester (c-1) having passed the drying step is heated at a temperature of 180 to 200 °C for 1 to 10 hours, wherein

the finally obtained polyester (d-1) has an acetaldehyde content of not more than 10 ppm.

2. A process for preparing a polyester comprising

[A] a liquid phase polycondensation step in which a dicarboxylic acid including terephthalic acid or its ester derivative and a diol including ethylene glycol or its ester derivative are subjected to polycondensation reaction in liquid phase and molten state under heating in the presence of a polycondensation catalyst to produce a polyester (a) having an intrinsic viscosity as measured in o-chlorophenol, of 0.7 to 1.5 dl/g

[B] a precrystallization step in which the polyester (a) is kept in an atmosphere having a temperature of a heat-up crystallization temperature (T_{CH}) to 200 °C for 1 minute to 4 hours

[C] a hot water treatment step in which the polyester (b) having passed the precrystallization step is contacted with hot water of 80 to 130 °C for 5 minutes to 10 hours,

[D-1] a drying step in which the polyester (c-1) having passed the hot water treatment step is dried at a temperature of 110 to 150 °C for 30 minutes to 6 hours, and

[D-2] a heat treatment step in which a polyester (c-1) having passed the drying step is heated at a temperature of 180 to 200 °C for 1 to 10 hours, wherein

the finally obtained polyester (d-1) has an acetaldehyde content of not more than 10 ppm.

3. The process for preparing a polyester as claimed in claim 1 or 2, wherein the polyester (a) obtained in the liquid phase polycondensation step [A] has an intrinsic viscosity as measured in o-chlorophenol of 0.8 to 1.2 dl/g.

4. The process for preparing a polyester as claimed in any one of claims 1, 2 or 3 wherein the liquid phase polycondensation step [A] consists of an esterification reaction step [A-1] and a polyconden-

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ation reaction step [A-2] and the polycondensation reaction step [A-2] comprises polycondensation reactions of three or more stages

5. The process for preparing a polyester as claimed in claim 4, wherein the polyester obtained after the polycondensation reaction of the second stage in the polycondensation reaction step [A-2] has an intrinsic viscosity of 0.4 to 0.7 dl/g
6. The process for preparing a polyester as claimed in claim 2, wherein the precrystallized polyester (b) obtained in the precrystallization step [B] has a crystallinity of 20 to 50 %
7. The process for preparing a polyester as claimed in any one of the preceding claims wherein the polyester (d-1) has a crystallinity of 30 to 50 %
8. The process for preparing a polyester as claimed in any one of the preceding claims wherein the polyester (d-1) has an acetaldehyde content of not more than 5 ppm
9. A process for preparing a polyester comprising
 - [A] a liquid phase polycondensation step in which a dicarboxylic acid including terephthalic acid or its ester derivative and a diol including ethylene glycol or its ester derivative are subjected to polycondensation reaction in liquid phase and molten state under heating in the presence of a polycondensation catalyst to produce a polyester (a) having an intrinsic viscosity, as measured in o-chlorophenol of 0.7 to 1.5 dl/g
 - [B] a precrystallization step in which the polyester (a) is kept in an atmosphere having a temperature of a heat-up crystallization temperature (T_{CI}) to 200 °C for 1 minute to 4 hours
 - [D-2] a heat treatment step in which the polyester (b) having passed the precrystallization step is heated at a temperature of 180 to 200 °C for 1 to 10 hours, and
 - [C] a hot water treatment step in which the polyester (c-2) having passed the heat treatment step is contacted with hot water of 80 to 130 °C for 5 minutes to 10 hours, wherein
 - (i) the intrinsic viscosity of the polyester does not substantially increase in the steps [B] and [D-2], and
 - (ii) the finally obtained polyester (d-2) has an acetaldehyde content of not more than 10 ppm
10. The process for preparing a polyester as claimed in claim 9 wherein the polyester (a) obtained in the liquid phase polycondensation step [A] has an intrinsic viscosity as measured in o-chlorophenol of 0.8 to 1.2 dl/g
11. The process for preparing a polyester as claimed in claims 9 or 10 wherein the liquid phase polycondensation step [A] consists of an esterification reaction step [A-1] and a polycondensation reaction step [A-2], and this polycondensation reaction step [A-2] comprises polycondensation reactions of three or more stages
12. The process for preparing a polyester as claimed in claim 11 wherein the polyester subjected to the polycondensation reaction of the last stage in the polycondensation reaction step [A-2] has an intrinsic viscosity of 0.4 to 0.7 dl/g
13. The process for preparing a polyester as claimed in any one of claims 9 to 12 wherein the precrystallized polyester (b) obtained in the precrystallization step [B] has a crystallinity of 20 to 50 %
14. The process for preparing a polyester as claimed in any one of claims 9 to 13 wherein the polyester (d-2) has a crystallinity of 30 to 50 %
15. The process for preparing a polyester as claimed in any one of claims 9 to 14 wherein the polyester (d-2) has an acetaldehyde content of not more than 5 ppm
16. A preform formed from the polyester preparable by the process as claimed in any one of the preceding claims and a beverage bottle formed from the preform

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17 The preform and the beverage bottle as claimed in claim 16 wherein the preform has an acetaldehyde content of not more than 20 ppm

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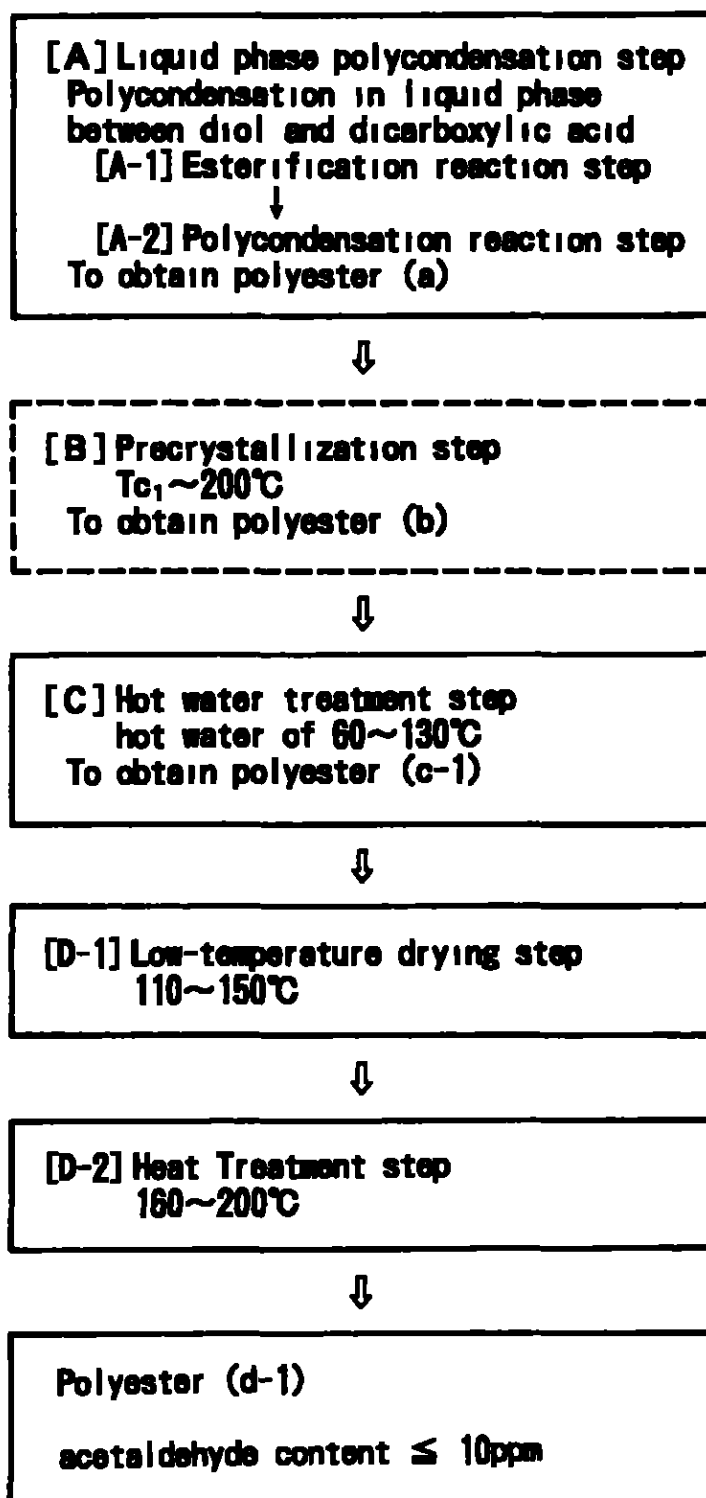
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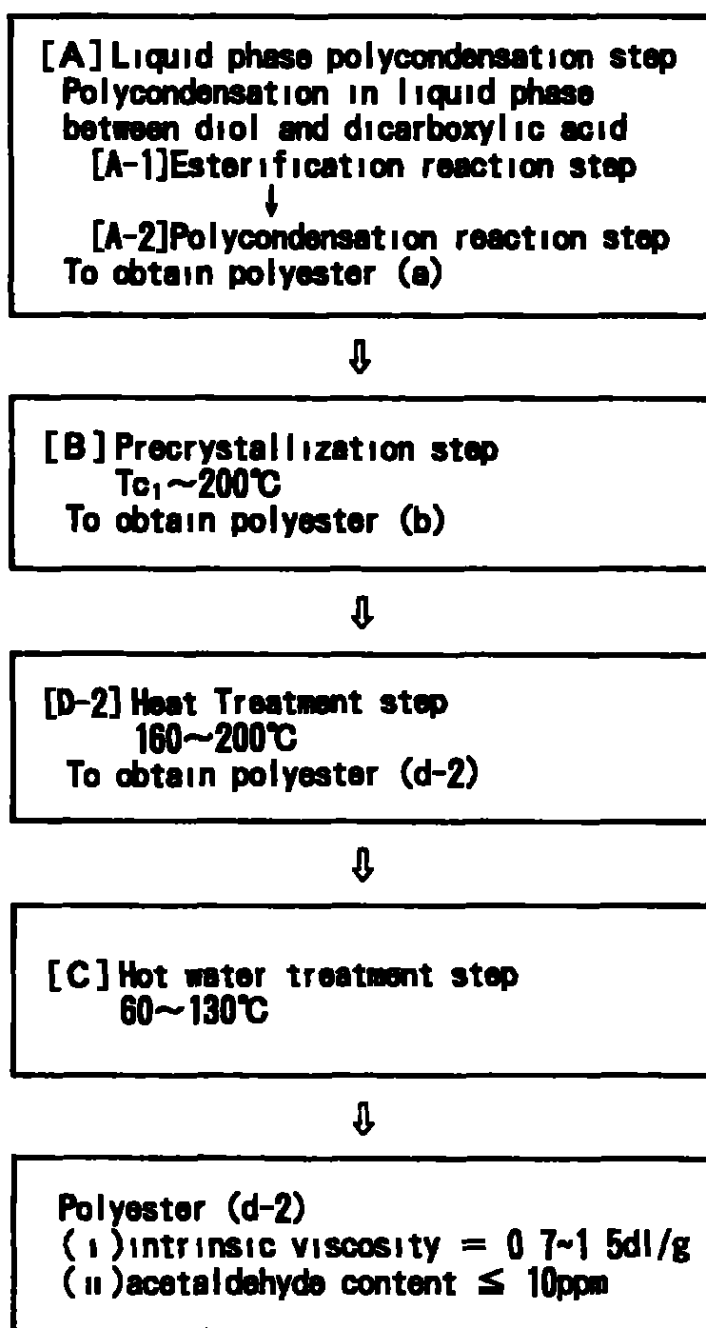
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Fig. 1

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Fig. 2

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Fig. 3