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

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
Rad: 02-086657- 00011-0000
Fec: 2006-06-18 18:01:49 Dep. 2020 NUECREACIONES
Tra. 2 PATENTES
Evo: 1 REGDEPOSITO
Act 444 RESPUESTAREQUE Folios: 11

Trámite : 002
Evento : 001
Actuación : 444

Referencia : Expediente No. 02066657

Asunto : TRASPASO EN SOLICITUD PENDIENTE DE PATENTE
**PROCEDIMIENTOS DE FABRICACION DE PREFORMAS Y
DE ENVASES EN PET TALES COMO BOTELLAS DE USO
ALIMENTICIO, ENVASES Y PREFORMAS INTERMEDIAS
OBTENIDOS**

Solicitante : NESTLE WATERS MANAGEMENT & TECHNOLOGY

Fecha de solicitud : 31 de Julio de 2002

1. Yo, Emilio FERRERO, obrando como apoderado del solicitante en el asunto antes identificado, me refiero al oficio número 1420 notificado por fijación en lista del 9 de Febrero de 2006.

2. Mediante el memorial radicado el 26 de Abril de 2005 solicité un plazo de 30 días para atender el oficio No. 1420.

3. Mediante el oficio número 1420 se puso en conocimiento del solicitante el informe que contiene las observaciones hechas por su Despacho sobre la presente solicitud de patente. Atiendo a las observaciones de la manera siguiente:

3.1 EXCEPCIONES DE PATENTABILIDAD

3.1.1 Reivindicaciones de uso

Ese Despacho considera que las reivindicaciones 1 a 4 y 10 explícitamente hablan del uso de una resina de PET y del uso de un envase.

Con el objeto de subsanar esta objeción, presento un nuevo capítulo reivindicatorio en donde se han eliminado las expresiones que hacen referencia al uso de la resina y del envase respectivamente. Adicionalmente, aclaro que en la presente solicitud no se está reclamando el uso de dichos productos sino el proceso de producción de las preformas y contenedores de resina de PET y las preformas y contenedores obtenidos por medio de dichos procesos. Así entonces, en el nuevo capítulo reivindicatorio se establecen claramente las reivindicaciones de proceso y de producto los cuales están definidos en los parámetros permitidos, esto es, por las etapas del proceso y por las características del producto, respectivamente.

En consecuencia, el nuevo capítulo reivindicatorio cumple con los requisitos del Art.14 de la Decisión 486.

3.2 EVALUACION DE LA NOVEDAD

Ese Despacho considera que la presente solicitud carece de novedad y argumenta que el emplear polímeros como el PET (o muy similares al mismo) con viscosidades intrínsecas del orden de 0.45 dl/g y 0.65 dl/g era muy común en el arte previo a la presente solicitud.

Respetuosamente ponemos de presente que de acuerdo con autorizada Doctrina nacional e internacional y profusa jurisprudencia del Tribunal de Justicia de la Comunidad Andina, el examen de novedad, a diferencia del de nivel inventivo, es objetivo, es decir, que se debe contraer exclusivamente a comparar lo revelado por la invención frente a lo revelado en el

estado del arte, de tal manera que no le es dable al examinador efectuar interpretación alguna y por ello expresamente en dicho Manual se ha señalado:

"Un antecedente del estado de la técnica no puede ser interpretado. Solamente lo que está descrito claramente o lo que es directamente derivable de la divulgación de dicho antecedente puede ser usado en contra de la novedad de un objeto reivindicado.

Modificaciones obvias o equivalentes del objeto descrito en el estado de la técnica no pueden ser citadas en contra de la novedad del objeto reivindicado sino cuando están descritas ellas mismas en el antecedente".

Es precisamente con fundamento en lo anterior que concluimos que la presente invención sí es novedosa frente a los documentos D1 a D4, puesto que estos documentos no contienen ni sugieren todas y cada una de las características técnicas reivindicadas por la presente invención, en los términos en que el Manual Andino de Patentes señala que debe efectuarse este examen.

Lo anterior se evidencia de la comparación de las características técnicas de la materia reivindicada en la presente solicitud frente a las enseñanzas de los documentos D1 a D4.

En cuanto a D1, éste enseña un copolíéster con una viscosidad Intrínseca comprendida entre 0.3 dl/g y 1.5 dl/g, preferiblemente entre 0.6 dl/g y 1.0 dl/g y más preferiblemente mayor que 0.8 dl/g (ver página 5, línea 58 y página 10 línea 16). Adicionalmente, en los ejemplos de D1 (tabla 1, página 13) se enseñan valores de viscosidad intrínseca superiores a los reivindicados por la presente solicitud, estando la IV en el rango de 0.75 dl/g a 0.83 dl/g.

Por otro lado, los poliésteres del documento D1 contienen ácido naftalenodicarboxílico, compuesto que está excluido del alcance de la presente invención puesto que, como se establece en el nuevo pliego reivindicatorio, la resina de PET se obtiene de dihidroxí monómeros y monómeros aromáticos diácidos excluyendo el ácido naftalenodicarboxílico.

De lo anterior se deduce que D1 no podría afectar la novedad de la solicitud toda vez que enseña poliésteres con valores de IV superiores a los aquí reivindicados y considerando que la resina se prepara a partir de ácido naftalenodicarboxílico, el cual no es empleado en las resinas en la presente invención.

En cuanto a D2, este enseña un copoliéster, en el cual la parte diácida contiene 80-99.5% mol, preferiblemente 90-99.0% mol de ácido tereftálico o un derivado del mismo y 0.5-4.5%mol, preferiblemente 1.0%-4.0% mol de un derivado del ácido fenilendioxiacético. En los ejemplos 1 a 7 y en los ejemplos comparativos 2, 4, 6 y 7 la cantidad de éste último compuesto está siempre entre 3 y 6%mol y la viscosidad intrínseca está siempre sobre 0.65 dl/g. En los ejemplos comparativos 1, 3, 5, en los cuales se usa PET puro, no mencionan valores de viscosidad intrínseca que puedan ser comparados con los rangos de IV aquí reivindicados.

Adicionalmente, las partículas de poliéster obtenidas en D2 se someten, después de la polimerización, a post-polimerización en estado sólido con el fin de incrementar significativamente la viscosidad intrínseca de los copoliésteres, los cuales son usados posteriormente para fabricar preformas (ver ejemplo 1 donde la viscosidad intrínseca final es 0.88 dl/g). Lo anterior difiere completamente de la presente invención ya que aquí no se usa la policondensación y el PET, materia prima para manufacturar las preformas, y además tiene una viscosidad intrínseca menor que 0.65 dl/g.

En consecuencia, el documento D2 tampoco puede considerarse como una anterioridad que afecte la novedad de la presente invención, puesto que este no comprende todas las características técnicas aquí reivindicadas.

El documento D3, enseña artículos producidos por moldeo por soplado a partir de poliésteres que tienen una viscosidad intrínseca entre 0.5 y 1.5 dl/g, preferiblemente entre 0.6 y 1.2 dl/g, algunos de los cuales tienen una viscosidad intrínseca entre 0.8 y 0.85 dl/g (ver columna 65, líneas 24-26). En ninguno de los ejemplos, los poliésteres tienen una IV menor que 0.65 dl/g y

los valores indicados están alrededor de 0.8 dl/g (ver ejemplo 5: 0.79 dl/g; ejemplo 6: 0.80 dl/g; ejemplo 13: 0.78 dl/g; ejemplo 18: 0.81 dl/g; ejemplo 41: 0.85 dl/g...).

Adicionalmente, las composiciones de los ejemplos 1 y 2 de D3 contienen 1 a 10% de 2,6-ácido naftalenodicarboxílico, excluido en la presente invención. Los demás políesteres enseñados en D3 y que no incluyen este monómero específico tienen una viscosidad intrínseca mucho mayor y cercana a 0.8dl/g (ver por ejemplo los ejemplos 5, 6, 9, 10, 13, 14, 17, 18, 21, 22...)

Así entonces, no puede considerarse que D3 afecte la novedad de la solicitud puesto que éste documento no comprende todas y cada una de las características técnicas de la presente invención.

El documento D4 describe el uso de un políester con una viscosidad intrínseca de por lo menos 0.5 dl/g y preferiblemente mayor que 0.7 dl/g, (ver columna 7, líneas 35-45; reivindicación 3) para manufacturar cuerpos huecos. Adicionalmente, los ejemplos 1 y 2 de D4 enseñan valores de viscosidad intrínseca de 0.72 dl/g. Por lo anterior D4 tampoco afectaría la novedad de la presente solicitud puesto que no comprende todas las características técnicas del proceso reivindicado por la presente solicitud.

3.3 EVALUACION DEL NIVEL INVENTIVO

Ese Despacho considera que los documentos D1 a D4 afectan el nivel inventivo de la presente solicitud, sin embargo no argumenta las razones que llevarían a un técnico medio en la materia a deducir evidentemente las características técnicas reivindicadas por la presente solicitud.

Teniendo en cuenta lo descrito anteriormente en cuanto a las enseñanzas de los documentos D1 a D4, es claro que una persona versada en la materia técnica no deduciría evidentemente

la materia reivindicada por la presente invención, esto es, un proceso para producir preformas de resina de baja viscosidad Intrínseca y las preformas y contenedores obtenidas.

Lo anterior por cuanto el objeto de la presente invención es solucionar el problema existente en el estado del arte que consiste en la dificultad que se presenta en la etapa de Inyección cuando se utilizan ,en la producción de preformas, las resinas conocidas en el estado del arte, cuya viscosidad Intrínseca está entre 0.72 dl/g y 0.83 dl/g sin que éstas pierdan sus propiedades mecánicas y de barrera a los gases.

Como se indica en la página 1 de la descripción de la presente solicitud, los polímeros de PET utilizados en la producción de botellas presentan propiedades de barrera a los gases que aumentan con la viscosidad intrínseca del material empleado, es decir, con la longitud de las cadenas de los polímero aplicado. Así entonces, una persona versada en la materia no produciría preformas a partir de PET de baja viscosidad intrínseca puesto que esto llevaría a una pérdida de las propiedades de barrera a los gases. Por ejemplo, partiendo de D1, cuyo objeto es proporcionar un poliéster de alta temperatura de transición vítrea y excelentes propiedades de barrera a los gases y de superficie y, considerando los valores de viscosidad intrínseca preferidos allí considerados (preferiblemente mayores que 0.8 dl/g, ver numeral 3.2 de este escrito), una persona versada en la materia técnica no intentaría la producción de las preformas partiendo de una resina de baja viscosidad intrínseca, tal y como se reivindica en la presente solicitud ,puesto que las preformas y envases obtenidos no tendrían las excelentes propiedades de barrera a los gases y de superficie objeto de dicha invención.

Al igual que D1, el documento D2 busca proporcionar un poliéster con alta transparencia, propiedades mecánicas y propiedades de barrera a los gases. Entonces, una persona versada en la materia técnica no partiría de Pet con baja viscosidad intrínseca para la producción de preformas y botellas.

Por otro lado, el documento D2 enseña que el poliéster es sometido a post-condensación en fase sólida con el objeto de incrementar la viscosidad Intrínseca, lo que es contrario al objeto

aquí reivindicado y por lo tanto un técnico medio en la materia no excluiría la etapa de post-condensación en fase sólida pues no lograría los valores de IV deseados para el poliéster.

Partiendo de D3, donde se emplea ácido naftalenodicarboxílico en la composición de la resina, no se entiende cómo una persona versada en la materia llegaría a la presente invención toda vez que las propiedades mecánicas de un poliéster que contiene dicho monómero naftalénico son muy diferentes de las propiedades de poliésteres preparados de monómeros aromáticos los cuales no contienen ciclos condensados. En consecuencia, los poliésteres obtenidos a partir de dicho monómero naftalénico no pueden ser usados para obtener la baja viscosidad intrínseca reivindicada por la presente solicitud.

En cuanto al documento D4, este no llevaría a una persona versada en la materia a producir preformas de baja viscosidad intrínseca puesto que allí se enseña que los valores preferidos para la viscosidad intrínseca del poliéster están por encima de 0.7 dl/g con el objeto de fabricar preformas no redondeadas.

En conclusión, toda vez que en ni individualmente ni en conjunto los documentos D1, D2, D3 y D4 enseñan y/o sugieren la invención acá reivindicada y que la solución planteada para el problema técnico existente en la producción de preformas que acá se reivindica no es considerada por ninguno de los documentos citados, resulta preciso concluir que la presente invención sí tiene nivel inventivo porque no se deriva de manera obvia ni evidente del estado de la técnica. En efecto, ninguno de los documentos citados, ni solos ni en combinación, guiarían a una persona versada en la materia a producir preformas y envases partiendo de un poliéster con viscosidad intrínseca inferior a 0.65 dl/g garantizando al mismo tiempo las propiedades químicas y físicas acordes con las exigencias al momento de la invención y futuras.

Considero que con los argumentos expuestos anteriormente, así como con las modificaciones realizadas al pílego reivindicatorio se deben tener por superadas las objeciones que sobre excepciones de patentabilidad, novedad y nivel inventivo planteó ese Despacho en el oficio No.

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1420. Sin embargo, en el evento que el Despacho considere que dichas objeciones no han sido todavía superadas y más aún dada la generalidad de las objeciones planteadas al pliego reivindicatorio en la acción oficial, respetuosamente le solicito hacer uso de la facultad que le otorga el artículo 45 inciso 2 de la Decisión 486 de la Comisión de la Comunidad Andina a efecto de requerir nuevamente de nuestra parte cualquier complementación o aclaración que considere necesaria para efectos de proceder al examen de patentabilidad definitivo correspondiente.

3. Puesto que se han atendido a cabalidad las observaciones hechas por su Despacho sobre la presente solicitud de patente, atentamente solicito que se continúe su tramitación.

Anexos:

1. Nuevo pliego reivindicatorio
2. Formulario para modificaciones
3. Recibo por valor de \$95.000 por concepto de modificaciones en solicitud pendiente

Bogotá, 9 de JUN 2006
Señora Jefe,


EMILIO FERRERO
T.P.A. No. 31.929

003 COLO 15133-803-002-7
COLO 13366-801-002-7
ZCA/ZCA/ID-000006/WPC15133

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Espacio reservado para el adhesivo de radicación

**FORMULARIO UNICO DE CORRECCIONES Y MODIFICACIONES
2000-F03**

1	SOLICITUD DE: ☐ Corrección de Error Material ☒ Modificación a una solicitud	
2 SOLICITANTE	Nombre: NESTLE WATERS MANAGEMENT AND TECHNOLOGY Dirección: 20 Rue Rouget de Lisle, 92130 Issy-Les- Moulineaux Francia Nacionalidad o Domicilio: Issy-Les- Moulineaux, Francia Lugar de Constitución: Francia Teléfono: 548 09 70 Fax: 547 31 70 E-mail: clientes@camyp.com	IDENTIFICACION C.C. ☐ NIT ☐ C.E. ☐ Otro ☐ Número: _____
3 REPRESENTANTE O APODERADO	Nombre: Emilio FERRERO Dirección: Carrera 4ª No. 72-35 Teléfono: 347 36 11 Fax: 211 86 50 E-mail: cavelier@caveller.com	IDENTIFICACION C.C. ☒ NIT ☐ C.E. ☐ Otro ☐ Número: <u>438.019 TP 31.929</u>
4	Número de expediente: <u>02066657</u>	
5	Descripción de la corrección o modificación solicitada: Se presenta nuevo capítulo reivindicatorio con 9 reivindicaciones con el objeto de subsanar las objeciones que ese despacho hizo en cuanto a excepciones de patentabilidad, novedad y nivel inventivo de la solicitud y sobre el cual solicito se efectue el examen de patentabilidad	
6	Comprobante de pago No. _____ Fecha: _____	
7	Anexos ☒ Comprobante de pago de la tasa por \$ 95.000 ☐ Poderes, si fuere el caso ☐ Documento que acredita la existencia y representación legal de las partes, cuando sean personas jurídicas.	
8	NOMBRE: EMILIO FERRERO FIRMA: C.C. 438.019 de Usaquén T.P.A. 31.929	

ZCA

REIVINDICACIONES

1. Un proceso para producir preformas de resina de PET, el proceso caracterizado por las etapas:

- Obtener una resina de PET de baja viscosidad intrínseca a partir de dihidroximonómeros y monómeros aromáticos excluyendo el ácido naftalenodicarboxílico, donde la resina de PET tiene una viscosidad intrínseca menor que 0.65 dl/g.
- Secar la resina de PET de baja viscosidad intrínseca
- Fundir la resina por calentamiento en una funda de plastificación particularmente provista de un eje helicoidal,
- Transferir la resina de la funda hacia un distribuidor o bloque caliente provisto al menos de una boquilla y de al menos un obturador calentado,
- Inyectar la resina fundida en al menos un molde de la preforma que se desea obtener,
- Compensar el retiro de material inyectado por inyección adicional de resina fundida a medida que la preforma se forma en el o los moldes en el momento del enfriamiento de la resina inyectada, y
- Eyectar la preforma fabricada del o de los moldes y dejarla enfriar en el exterior.

Ver folio 10

2. El proceso de acuerdo con la reivindicación 1, caracterizado porque la viscosidad intrínseca de la resina de PET está entre 0.45 dl/g y 0.65 dl/g.
3. La preforma de resina de Pet obtenida de acuerdo con el proceso de la reivindicación 1, caracterizada porque está compuesta por un material que tiene una cristalinidad menor que 10%, preferiblemente menor que 5%.
4. La preforma de resina de PET obtenida de acuerdo con el proceso de la reivindicación 1, caracterizada porque la viscosidad intrínseca de la paredes que forman la preforma está entre 0.45 dl/g y 0.65 dl/g.
5. Envase de resina de PET caracterizado porque está compuesto por una resina de PET que tiene viscosidad intrínseca menor que 0.65 dl/g.
6. Envase de acuerdo con la reivindicación 5, caracterizado porque la viscosidad del PET que forma las paredes de dicho contenedor esta entre 04.5 dl/g y 0.65 dl/g.
7. Envase según las reivindicaciones 5 o 6, caracterizado porque la densidad el poliéster que forma las paredes del citado envase está comprendida entre 1.36 y 1.37.
8. Envase según cualquiera de las reivindicaciones 5 a 7, caracterizado porque la cristalinidad promedio del poliéster que forma las paredes del citado envase está comprendida entre 25% y 35%.
9. Envase según cualquiera de las reivindicaciones 5 a 8 caracterizado por que la permeabilidad al dióxido de carbono esta mejorada en al menos 5% con relación al a del envase obtenido con una resina de PET de viscosidad intrínseca superior o igual a 0.65 dl/g.

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 06 - 42,142
FECHA : JUNIO 5 DE 2006

CONSIGNACION

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	55274899	05/06/2006	46,343,000.00

CONCEPTO

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-03	CAMBIO DE MODALIDAD Y MODIFICA	
		12 MARCAS Y LENAS COMERCIALES	95,000.00
		TOTAL :	95,000.00

SON: NOVENTA Y CINCO MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.

010 15133-803-002-7

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

2020

Bogotá, D. C., 25 de Julio de 2008

Doctor

EMILIO FERRERO

Representante NESTLE WATERS MANAGEMENT AND TECHNOLOGY

ASUNTO	Radicación No.	02-86657
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	8377
	Folios	018

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

1) Documentos estudiados:

- a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 4 a 22 de la solicitud en estudio.
- b) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 9 reivindicaciones en el folio 246 de la solicitud en estudio. Se aceptan las modificaciones realizadas por el solicitante a este capítulo ya que no implican ampliación de la solicitud inicial, conforme lo establece el artículo 34 de la Decisión 486.
- c) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 31 de Julio de 2002, y en el momento de la radicación SI se reclamo prioridad de la primera solicitud presentada en Francia FR0110280

2) Objeto de la invención

- a) Las reivindicaciones 1 a 9 de la solicitud en estudio se refieren a un proceso para producir preformas de resina de PET, el proceso caracterizado por las etapas de -obtener una resina de PET de baja viscosidad Intrínseca a partir de dihidroximonómeros y monómeros aromáticos excluyendo el ácido naftalenodicarboxílico, donde la resina de PET tiene una viscosidad Intrínseca menor que 0,65 dl/g. - Secar la resina PET de baja viscosidad Intrínseca. - Fundir la resina por calentamiento en una funda de plastificación particularmente provista de un eje helicoidal. - Transferir la resina de la funda hacia un distribuidor o bloque caliente provisto al menos de una boquilla y de al menos de un obturador calentado. -Inyectar la resina fundida en al menos un molde de la preforma que se desea obtener. - Compensar el retiro de material inyectado por inyección adicional de resina fundida a medida que la preforma se forma en el o los moldes en el momento de enfriamiento de la resina inyectada, y - eyectar la preforma fabricada del o de los moldes y dejarla enfriar en el exterior.

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

3) Claridad de la Solicitud

- a) El artículo 30 de la Decisión 486 de la Comisión de la Comunidad Andina establece que

"Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior.- Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará reivindicación dependiente múltiple."

El capítulo reivindicatorio no es claro toda vez que la reivindicación 9 se caracteriza por el resultado a alcanzar, mas no por la forma en que se llegó a ese resultado. Esto es inadmisibles. Las reivindicaciones deben caracterizar un producto por la forma o constitución del mismo, las partes que lo componen y todo lo que permita establecer de cómo se llegó a ese resultado. No se aceptan reivindicaciones que caractericen resultados.

De acuerdo a lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad de acuerdo a lo establecido en el Art. 30 de la Decisión 486.

4) Determinación del Estado de la Técnica

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

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

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido 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 B 65 D 01/02 y las más cercanas a ellas, se encontró que antes del 31 de julio de 2001 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con envases fabricados con compuestos tipo PET.

De acuerdo con 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 0 368 278	Copolyester, polyester composition containing the Copolyester, and polyester laminated structure...	1989.11.08
D2	US 0 492 999	Copolyester and hollow container and oriented film comprising the copolyester	1992.07.01
D3	US 5 641 548	Blow molded articles	1997.01.24
D4	US 4 254 080	Forming substantially rectangular articles from performs of polyalkylene terephthalate	1981.03.03
D5	US 4 340 721	Novel polyester for the packing of comestibles	1982.07.20
D6	US 5 239 045	Copolyester and hollow container and oriented film comprising the copolyester	1993.08.24
D7	US 5 939 516	Modified polyester polymers	1999.08.17

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 proceso revelado por el solicitante es el que maneja cualquiera que conozca del arte. Su diferencia radica en que se configura con polietilenterftalato con una viscosidad intrínseca menor de 0,65 dl/g. de la misma forma pretende que se le proteja un envase con resina inferior a este valor.

D1 (EP 0 368 278) muestra viscosidades intrínsecas de entre 0,3 a 1,5 dl/g. Como se observa el rango perfectamente coincide con lo que el solicitante desea proteger. Ahora bien, el solicitante excluye el ácido naftalenodicarboxílico para que no le afecte la novedad del nuevo proceso presentado en su nuevo pliego reivindicatorio. Sin embargo, resulta obvio a todas luces para un experto que si se logra unas propiedades de un polímero PET basado en el ácido naftalenodicarboxílico, estas propiedades se pueden lograr con otros polímeros PET basados en ácidos diferentes y con la misma viscosidad intrínseca lograda, que es el espíritu de la solicitud. En otras palabras, para un experto es evidente que lo que se logra con un polímero PET basado en el ácido naftalenodicarboxílico con una viscosidad intrínseca específica, se logra con otro polímero PET que no se basa en el ácido naftalenodicarboxílico pero con la misma viscosidad específica. Es más, el mismo solicitante es el que corrobora esto en el folio 6 porque afirma "el procedimiento de fabricación de preformas en resina PET según la invención se caracteriza porque consiste en utilizar una resina PET de viscosidad intrínseca inferior a 0,65 dl/g." Además de esto, el solicitante no tiene ningún sustento en su descripción para afirmar que el excluir el ácido naftalenodicarboxílico permite diferenciar claramente su solicitud de las anterioridades. Aún más, el solicitante explícitamente coloca en la descripción dicho ácido (folio 10), lo que implica que no existe ninguna diferencia entre dicho ácido o cualquier otro que se emplee para obtener un PET. En conclusión el objetivo de la presente solicitud es obtener un PET con una viscosidad intrínseca específica, donde, de acuerdo a la solicitud, pueden emplearse muchos diácidos incluyendo el ácido naftalenodicarboxílico, y, que el hecho que el solicitante lo excluya del capítulo reivindicatorio no conlleva a que la solicitud sea más inventiva.

Ahora bien, este documento D1, claramente refiere envases constituidos por resinas de PET con viscosidades intrínsecas menores que 0,65 dl/g. Por tanto, D1 afecta la novedad de la presente solicitud en algunas reivindicaciones y los argumentos de los folios 238 y 239 se toman sin sentido, y no pasan de ser manifestaciones inválidas. Ahora bien, en su sustento el solicitante acude a que los intervalos no son iguales. Aquel con experiencia en el arte de las patentes conoce que esto no tiene que ser así. Y este es uno de esos casos. En efecto cualquier PET que contenga menos de 0,65 dl/g de viscosidad intrínseca afecta la novedad de la presente solicitud. Y D1 contiene PET con viscosidades intrínsecas entre 0,3 y 1,5 dl/g es decir, que todos los PET con viscosidades entre 0,3 y 0,65 que se relacionan en D1 afectan totalmente la novedad. Por tanto, los argumentos del solicitante carecen de cualquier validez.

De la misma forma que se estudió D1, puede hacerse con D2 (US0492999). Lo relevante, como quedó establecido, es la viscosidad intrínseca del PET. D2 es explícito en afirmar que en su documento lo relevante es una viscosidad intrínseca entre 0,4 y 2,0 (folio 139). Es decir, que el rango que va de 0,4 a 0,65 afecta directamente a la presente solicitud. Es importante anotar, que el solicitante en sus argumentos no puede tomar elementos separados y sesgados que le sirvan para demostrar la patentabilidad de la solicitud, sino que tiene que contemplar TODA la solicitud. D2 también afecta la patentabilidad de la presente solicitud.

D3 (US 5 641 548) relaciona copoliésteres (que involucran PET) con viscosidades intrínsecas entre 0,5 y 1,5 dl/g. Por lo que los copoliésteres que comprendan una viscosidad intrínseca entre 0,5 y 0,65 afectan directamente a la presente solicitud.

D4 (US 4 254 080) habla que la viscosidad debe ser por lo menos de 0,55 (folio 194), es decir, que también afecta la presente solicitud.

Aun más. Existen otros documentos tales como D5 (US 4 340 721) que relacionan PET con viscosidades intrínsecas alrededor de 0,65. En la columna 3 se menciona un intervalo entre 0,55 y 0,70 para el prepolímero, para obtener máximo un intervalo igual o apenas superior a 0,65. En esencia lo mismo que aquí se quiere proteger.

D6 (US 5 239 045) habla que las viscosidades intrínsecas deben ser entre 0.4 y 2, con ejemplos que muestran que la viscosidad intrínseca puede ser 0,65 en varios ejemplos.

D7 (US 5 939 516) habla de rangos de 0,8 a 0,9 en la viscosidad intrínseca del PET.

b) Resumen

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

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	EP 0 368 278	1 -8	Novedad
			Nivel inventivo
D2	US 0 492 999	1 -8	Novedad
			Nivel inventivo
D3	US 5 641 548	1 -8	Novedad
			Nivel inventivo
D4	US 4 254 080	1 -8	Novedad
			Nivel inventivo
D5	US 4 340 721	1 -8	Novedad
			Nivel inventivo
D6	US 5 239 045	1 -8	Novedad
			Nivel inventivo
D7	US 5 939 516	1 -8	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

03 AGO. 2006

Concepto Técnico N°	EXAMINADOR TÉCNICO	EXAMINADOR JURÍDICO
1166	Código No. 202003	Código No.

030106.

[54] NOVEL POLYMER FOR THE PACKAGING OF COMESTIBLES
[57] Inventors: Charles Barnard, Patrick Connelly, Gilbert Heston, Channing Van Velsor, Carole, all of France
[73] Assignee: Rhone-Poulenc Industries, Paris, France
[21] Appl. No. 282,282
[22] Filed: May 19, 1981
[30] Foreign Application Priority Data
[31] Int. Cl. 282,282
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[33] U.S. CO. 282,282, 282,282, 282,282
[34] U.S. CO. 282,282, 282,282, 282,282
[35] U.S. CO. 282,282, 282,282, 282,282
[36] U.S. CO. 282,282, 282,282, 282,282
[37] U.S. CO. 282,282, 282,282, 282,282
[38] U.S. CO. 282,282, 282,282, 282,282
[39] U.S. CO. 282,282, 282,282, 282,282
[40] U.S. CO. 282,282, 282,282, 282,282

ABSTRACT
Novel polymer for the packaging of comestible materials, e.g., as barrier for still or enhanced natural flavors, is polypropylene glycol terephthalate (PTT) having an inherent viscosity ranging from 0.65 to 1.05 dl/g and density of more than 1.35, comprising 55.5 to 75.5% of ethylene terephthalate repeating units and 24.5 to 75.5% of terephthalate units of at least one polybutene terephthalate diacid comonomers crystallization temperature, the 45-militer terephthalate glycol content thereof being less than 1.5 and 96 per cent of diacid units present in the polymer chain, and PTT also having residual comonomer concentration of less than 1.5% with comonomer being reduced depending on rate of less than 5 ppm/decade, at 220° C., and said PTT being devoid of volatile crystallization in an of less than 4 mm thick test plate shaped in said cavity than said sheet.

25 Claims, No Drawing

BACKGROUND OF THE INVENTION

1 Field of the Invention
The present invention relates to improved natural polymers comprising ethylene glycol terephthalate repeating units, and to comonomer shaped structures useful for the packaging of comestibles and beverages. The invention also relates to process for the preparation of such improved polymers.

2 Description of the Prior Art

It is well known to this art that diethylene glycol terephthalate (PET) repeating units comprising ethylene glycol terephthalate repeating units with comonomer units having suitable melting points for the packaging of food products, in the form of films, sheets and containers, and especially in the form of bottles intended for storing liquid or still liquid or carbonated beverages.

One of the principal properties which such packaging, and more particularly bottles, must possess, is transparency and lightness. By drawing from the art, the present invention discloses a novel comonomer, polypropylene glycol terephthalate (PTT) repeating units, which at the same time displays the advantages of an improved crystalline phase which considerably reduces its mechanical properties and permeability to gases. However, the transparency and the lightness can be adversely affected by the formation of crystalline structures, especially in the case of comonomer with relatively thick walls. The production of bottles by injection molding and/or extrusion-blowing, or blow molding, necessarily involves the prior production of preforms having thick walls, which is obtained by quenching from the molten state, and the formation of crystalline structures in the preform stage adversely affects the transparency of the finished article. It has thus proved advantageous to recommend grades of polymer having lower rates of crystallization.

Another property which packaging material fabricated from a polyamide terephthalate must possess is the absence of any compound or additive which is capable of migrating into the food product or the drink and of imparting its taste or its smell. It has been known, though, that polymer makes release comonomers by degradation, and this process, along with and deterioration to some extent, occurs at relatively low temperatures.

The above-mentioned problem is particularly significant and acute in the packaging (bottling) of mineral water. Thus, polymer bottles intended for mineral water must have an amorphous composition of less than 3 ppm (parts per million) of polymer by weight, weighed in the well known manner for volume of between 1 liter and 3 liters. It is desired to ensure that, under storage conditions, at temperatures which are much above 40° C., the amount of comonomer which is capable of migrating into the liquid remains less than the acceptable quantity thereof, that is to say 40-50 ppm (parts per million by weight) of liquid. The amount of comonomer present in the finished shaped article depends both on the residual amount present in the polymer granules, before they are converted, and on the amount released during the conversion in the molten state, as a result of degradation under the conditions of time and temperature which are adopted for molding.

Various processes have to date been proposed for reducing the concentration and/or the release of comonomer in polypropylene glycol terephthalate resins. Typically, such processes feature operating conditions, during the stages of drying, crystallization or post-crystallization of the polymer, low molecular weight polypropylene which are of the kind commonly used in the manufacture of high-velocity resins.

Thus, according to published French Patent Application No. 70/10,000, for example, the drying of the polymer chips is carried out at 180°-220° C. for 4 to 12 hours, in an inert atmosphere, in order to reduce the comonomer concentration in the chips to less than 2.5 ppm. According to published French Patent Application No. 70/10,000, reduction in the rate of formation of comonomer is achieved by treating the amorphous polypropylene polymer in sulfuric acid, under an inert atmosphere.

And according to published French Patent Application No. 70/11,000 the polymer is crystallized by heating to 180°-220° C., and the post-crystallization is carried out at temperatures above the crystallization temperature.

U.S. Pat. No. 4,154,525 discloses a two-step process starting from polypropylene having an inherent viscosity of 0.1 to 0.3 dl/g, in accordance with which the polymer is first crystallized in the molten state to form this layer and then post-crystallized in the solid state.

Finally, according to published French patent application No. 70/12,000, the polymer contains post-crystallized and stabilized by heating at 180°-220° C. for 2 to 20 hours, in air, thus increasing the inherent viscosity to values of between 0.60 and 0.97 dl/g.

SUMMARY OF THE INVENTION

It has now been determined, and which is one of the advantages of the present invention, that the amount of comonomer which is present in the wall thickness of molded shaped article and which is capable of migrating, namely, the residual amount present in the granules together with the amount which is released during the conversion in the molten state to form the molded article, not only depends on the conditions of treatment of the polymer (polypropylene glycol terephthalate and post-crystallization), but is related, on the one hand, to the inherent properties of the polymer polypropylene obtained in the initial stage of the polymerization in molten state, and, on the other hand, to the crystallization characteristics of the polymer during the quenching operation in the molten state.

In fact, the present polypropylene must possess the lowest possible number of sites which induce subsequent degradation, namely, vinyl and carboxyl groups. The inherent properties of the units can be very different for one and the same method system, depending on the conditions of polymerization. The best stability of the polymer can be obtained indirectly by measuring the inherent viscosity of comonomer in the polymer when the latter is heated at high temperatures. Furthermore, the content of comonomer which is released is directly proportional to the preceding temperature of the material, and this temperature will be the higher the faster the rate of crystallization during quenching.

The present invention discloses an improved polypropylene glycol terephthalate having characteristics which are useful for the injection or blow molding.

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more extensive 40 days.
The extruded sheet was subjected to dimensional stability according to ASTM D 1208 in both the machine and transverse directions by Long Dimensional Machine (manufactured by T. M. Long Co. USA) having an lower temperature of 20° C., and then heat set at 250° C. under tension for 120 seconds in an oven.
The extruded film showed thermal good appearance and superior oxygen gas barrier property (oxygen gas permeability of 0.7 cc./cm.²/day/cm).

The extruded film was further subjected to water treatment for one hour in an atmosphere of 100° C. and 100% relative humidity in pressure vessel (manufactured by Rheometric Solutions E.T.A.) and oxygen gas permeability was again measured. The oxygen gas permeability was 1.00 cc./cm.²/day/cm, which was substantially the same as that before the water treatment. Also, no change in its appearance was observed.

EXAMPLE 6

Into an extruder, were charged 6500 parts of terephthalic acid (94 and 6 of the acid component), 670 parts of 1,3-phenylenedimethyl dicarboxylic acid (5 and 5 of the acid component), and 3025 parts of ethylene glycol, and esterification reaction was carried out at 230° to 240° C. for 3 hours with stirring under nitrogen gas atmosphere (2.5 kg/cm²) while distilling off the water produced during the reaction. The reaction product was added with 1.5 parts of octadecylphosphoric acid and 1.5 parts of germanium dimethyl. Then, in accordance with the method in Example 5, extrusion and transparent copolyester chips having 0.60 of lactide viscosity were obtained.

A stretched film having good appearance was obtained from the chips in the same procedure as in Example 5, except that the stretching ratio in both the machine and transverse directions were changed to 3.5 times respectively. The oxygen gas permeability of the stretched film was 0.95 cc./cm.²/day/cm. Also, there was no change in oxygen gas permeability and its appearance before and after the water treatment similar to Example 5.

EXAMPLE 7

Colobene and transparent copolyester chips having 0.67 of lactide viscosity was obtained in the same procedure as in Example 5 except the use of 9775 parts of dimethyl terephthalate (97 and 3 of the acid component), 6500 parts of ethylene glycol and 330 parts of 1,3-phenylenedimethyl dicarboxylic acid (5 and 5 of the acid component).

A stretched film having good appearance was obtained from the chips in the same procedure as in Example 5, except that the stretching ratio in both the machine and transverse directions was changed to 3.5 times respectively. The oxygen gas permeability of the stretched film was 0.66 cc./cm.²/day/cm. Also, there was no change in oxygen gas permeability and its appearance before and after the water treatment similar to Example 5.

COMPARATIVE EXAMPLE 5

A stretched film having good appearance was obtained from TWT for polybutene (Dibutyl-1) manufactured by Dical Company (Japan) in the same procedure as in Example 5. The oxygen permeability of the stretched film was 1.50 cc./cm.²/day/cm. Although almost no change was observed in the oxygen gas permeability before and after the water treatment,

same as in Example 5, the oxygen barrier property was inferior to those of Examples 5 to 7.

COMPARATIVE EXAMPLE 6

Transparent copolyester chips having 0.66 of lactide viscosity was obtained in the same procedure as in Example 5 except the use of 9900 parts of dimethyl terephthalate (94 and 6 of the acid component), 6500 parts of ethylene glycol and 400 parts of 1,3-phenylenedimethyl dicarboxylic acid (5 and 5 of the acid component).
The oxygen gas permeability of stretched film obtained from the chips in the same procedure as in Example 5 was 1.10 cc./cm.²/day/cm, being inferior to gas barrier property compared with that of the film in Example 5. The film of Comparative Example 6 had bad stretching property. tendency of non-uniform stretching, uneven film thickness and inferior appearance.

COMPARATIVE EXAMPLE 7

A stretched film was obtained in the same procedure as in Comparative Example 6 except that the stretching ratio in both the machine and transverse directions were changed to 3.5 times respectively. The stretching property of the film was poor and the film had tendency of non-uniform stretching, uneven film thickness and inferior appearance.

When it claimed in
1. A copolyester comprising dicarboxylic acid component which consists of two acid components of acid derived from terephthalic acid and acid derived from phenylenedimethyl dicarboxylic acid, and diol component, said dicarboxylic acid component containing 1.5 to 4.0 and 0.5 of the mole derived from phenylenedimethyl dicarboxylic acid.

2. A copolyester according to claim 1, wherein said copolyester has an lactide viscosity of 0.4 to 2.0, the lactide viscosity having been determined at 20° C. in 11 by weight solvent system of phenol and tetrahydrofuran.

3. A copolyester according to claim 1, wherein the phenylenedimethyl dicarboxylic acid is 1,3-phenylenedimethyl dicarboxylic acid.

4. A copolyester according to claim 1, wherein the diol component comprises ethylene glycol.

5. A copolyester having structure produced by the steps of:
a) forming product by injection molding or extrusion molding the copolyester according to claim 1, and subjecting the product to thermal-stretching blow molding;

6. A copolyester having structure produced by the steps of:
a) forming product by injection molding or extrusion molding the copolyester according to claim 1, subjecting the product to thermal-stretching blow molding, and heat setting the blow-molded product.

7. A stretched copolyester film produced by the steps of:
a) injection molding or extrusion molding the copolyester according to claim 1 to obtain sheet, and stretching the sheet in the machine direction or transverse direction;

8. A stretched copolyester film produced by the steps of:
a) injection molding or extrusion molding the copolyester according to claim 1 to obtain sheet, and stretching the sheet in the machine direction or transverse direction, and heat setting the stretched film.

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of the use of chain branching agents—the potential to speed up solid phase polymerization to be realized. It will not be realized unless the chain branching agent is incorporated into the polymer before solid phase polymerization. The chain branching agent can be added to the polymer reaction system as part of the initial starting materials or to the site of intermediate polymerization stages, particularly at the start of each phase polymerization.

The chain branching agent can be added at the start, middle, but the relatively very small amounts involved could give rise to uneven distribution in the polymer, particularly if the addition is made in the solid phase polymerization step. In, where there is some oligomeric or polymeric material present. To avoid this the addition can be made as solution in suitable solvent such as water, ethylene glycol, dimethylene glycol, acetone.

Alternatively, as is mentioned above in reference to the use of polyol solvents as the solvent, it can be added as derivative such as an ester, which will have higher molecular weight and thus added mass (for the same molar amount) providing less of problem. The chain branching agent can be added as one of the materials used at the start of polymerization, at the start or, less preferably, during each phase polymerization. Addition during each phase polymerization is not particularly preferred as the typical reaction conditions make such addition particularly inconvenient. The general idea is to add the chain branching agent at a stage as early as possible so that the desired reaction can be incorporated into the polymer by the start of solid phase polymerization.

When the final polymer is obtained the CRO application, the intermediate polymer at the end of each phase polymerization typically has a viscosity of from 80 to 200 Pa.s (800 to 2000 Poise), more usually at least 100 and typically about 120 to 220 Pa.s (1200 to 2200 Poise). When the final polymer is obtained for solvent water bottle applications, the intermediate polymer at the end of each phase polymerization typically has a viscosity of from 18 to 140 Pa.s (180 to 1400 Poise), more usually from 32 to 90 Pa.s (320 to 900 Poise).

The effect of including the molasses derived from polyhydroxy chain branching agent is to speed up the solid phase polymerization of the polymer. We have observed that reactions in solid phase polymerization to achieve typical target viscosities of more than 250 Pa.s. The speed gains available in any particular case seems to depend on the particular polymer used and on the solid phase polymerization conditions. The gain appears to be real in that molecular weight measurements using gel permeation chromatography indicate that the products of this invention have smaller and possibly higher molecular weights than similar polymers made using no chain branching agent, but having the same end viscosity. This indicates that the viscosities achieved in this invention are not merely an artifact of additional branching of polymer chains brought about by the chain branching.

In practice, the solid phase polymerization is typically used to increase the viscosity of the polymer by at least 100 Pa.s (1000 Poise) and more usually at least 250 Pa.s (2500 Poise) or by a factor of at least 1.5 more usually at least 2 and commonly by 4 or more times.

As well as the monomeric units referred to above (including and the standard commercial units of acrylates and methacrylates of PBT), the polymers of the invention can include units of repeated caprolactone units generally of the formula:



(n=3) may also be present. Such units are almost inevitably present in PBT polymers even if the corresponding diols have not been specifically added as reactants in fact other linkages between arylene glycol units and/or terephthalic units compete with the esterification reaction. Typically, the level of such repeated caprolactone units in PBT polymers, including polymers of this invention, is up to about 7 more commonly 3 to 5 e.g. about 4.5, mole %. In some circumstances e.g. in polymers for reliable bottles as described in our EP 040420(A), it can be advantageous to have a definite level of such units in the polymer and, to this end, starting materials including such units e.g. the corresponding diols, can be advantageously used, can be advantageously added to achieve the desired level.

Chain branching agents/additives are monomers included in PBT polymers to control the molecular weight; as described above, this is particularly known of U.S. Pat. No. 4,234,708 A. Generally, the inclusion of chain branching monomers will, and indeed is intended to, slow down the polymerization and, as a significant advantage of this invention is to speed up at least the solid phase polymerization step, is intended to be harmful to the reaction. We have not noted any offsetting advantage from their inclusion (as distinct from the teaching (U.S. Pat. No. 4,234,708 A) and, accordingly, chain branching monomers or their precursors will not normally be added in the polymer or used in the method of the invention. Doubtless, such monomers are substantially slower than the present polymer and method.

Apart from the components that are referred to above, other materials and additives can and usually will be used in the method of or incorporated into the polymers of this invention. Such materials include polymerization catalysts, of which the most common is antimony (III) trioxide, Sb₂O₃, at levels of from 100 to 400, most usually about 200, ppm by weight on the final polymer; phosphoric acid as additive, at levels of from 75 to 400, usually about 200, ppm by weight on the final polymer; and esters (II) additively. Typical amounts in other and early literature. For CRO bottle applications the level of esters typically from 100 to 200, usually about 140, ppm and for solvent water bottle applications, from 32 to 90 ppm by weight on the final polymer. The level of esters in may be somewhat lower and can be from 50 to 200, usually from about 70 to about 140 for example 80 to 100, ppm by weight on the final polymer (calculated as the anhydrous salt). Other additives which do not adversely affect the polymer such as processing aids, fillers, stabilizers, plasticizers and lubricants, pigments and/or dyes can also be included.

Particularly where the polymer is intended for the manufacture of bottles, particularly CRO bottles, viscosity by injection (normally flow molding using injection moulded systems which are substituted for extrusion blow molding, it can be advantageous to include fine metal particles in the polymer. The inclusion of such fine metal particles speeds up the reaction step, particularly at typically lower temperatures, such as those in the range 200 to 250°C, which are used in the reaction. This possibility is described in more detail for otherwise conventional PBT polymers in our European Published Patent Application EP 0403011 A, to which reference should be made for more detail and to which is incorporated herein by reference.

This invention includes modified polyethylene terephthalate copolymers, particularly suitable for making containers and such other bottles, including:

- from 0.0027 to 0.046 mole %, particularly 0.014 to 0.043, mole % of molasses derived from polyhydroxy chain branching agent;

optionally, but desirably, from 0.5 to 5 mole % of molasses derived from chain branching monomers; and fine metal particles, which have a particle size distribution in the wavelength range 200 nm to 2000 nm, in quantity such that the solvent time of the polymer is less than the solvent time of the polymer in the absence of that quantity of particles, which polymer has a viscosity of from 300 to 1000 Pa.s. The invention also includes bottles produced from this polymer by injection moulding, bottles made therefrom and method of making such bottles by forming preforms from the polymer by injection moulding and subsequently, reheating the preforms using infra red radiation and blow moulding, particularly stretch blow moulding the preforms into bottles.

The metal particles are typically of antimony, tin, copper or silver or some mixture. Antimony is particularly useful as it is effective and convenient as polymerization catalyst as it is formed in situ in the polymer by oxidation of antimony (III) compounds such as the oxide, Sb₂O₃, used as polymerization catalyst. The particles are desirably sufficiently fine for them not to be visible to the eye and have a range of sizes such that absorption of radiation occurs over relatively wide part of the wavelength range and not just in one particular wavelength or over a narrow band. The amount used is a balance between the desired reduction in the solvent time of the polymer and the amount of time that is acceptable for glass applications. Typically, the amount will be from 5 to 300, more particularly 5 to 150, especially 10 to 100, ppm by weight on the polymer.

The metal particles may be added to the polymer as finely divided metal particles or, alternatively, the metal may be present as the polymer in the form of a suitable compound of the metal and a suitable reducing agent can be added to the polymer. When a suitable metal compound is used, the quantity of reducing agent used will usually be the appropriate stoichiometric amount, if necessary, with an excess to allow for losses arising from competing effects such as absorption of the reducing agent with oxygen dissolved in the polymer. Suitable reducing agents include phosphorus (III) compounds such as phosphorous, mild or triphenyl phosphine. Commercial oxidation of the phosphorus compounds is likely to generate phosphine and this can contribute to the any phosphine included in the polymer as additive.

Flow metal particles included as described above may act as nucleation sites in the polymer during injection moulding of preforms. Particularly in CRO bottle polymers, which have relatively high viscosities (viscosity measured at 200°C or 250°C) this can be noticeable and the presence of nucleation of chain branching agent incorporated into the polymer is thus particularly relatively lower than in polymers which either have lower viscosities or do not include the fine metal particles as is used in solvent water bottle polymers.

The polymer of the invention, which particles are in the injection blow and especially injection stretch blow moulding of bottles and similar hollow articles. The invention accordingly includes the use of the polymer of the invention in the manufacture of these articles by injection blow and injection stretch blow moulding and the products made thereby.

The following Examples illustrate the invention. All parts and percentages are by weight unless otherwise indicated. Test and Experimental Methods

Melt Viscosity—was measured using Davenport Melt Viscositymeter operating at 250°C, which measures the Poise (conversion into Pa.s) and Intrinsic Viscosity

(IV) figures quoted herein are those calculated in the Davenport instrument from the measured melt viscosity data.

Flow Stress and Viscosity—were measured using an extrusion die with diameter 2.5 mm and length 10 mm. The flow stress was calculated from the pressure drop across the die and the rate of flow of the polymer melt (calculated from the extrusion rate and the die diameter).

Stress Relaxation—was measured using a Hagen-Rohrbaugh single stage pressure vessel at a constant temperature of 250°C.

Flow on polymers, chip size and solid phase polymerization

The rate of solid phase polymerization achieved in practice is determined by a variety of factors. These include the rate of antimony to triphenyl and groups in and the size of the polymer pellets (shape) of the intermediate polymer used and possible changes in concentration of polymerization catalyst.

In the Examples, the intermediate polymers after each phase polymerization had 27 to 45 moles of antimony and groups and 70 to 100 moles of triphenyl and groups per 10⁶ g (moles) of polymer. The values in particular Examples and corresponding Comparative Examples were similar and not his comparison of solid state polymerization rates could be made.

Catalyst levels were measured using X-ray fluorescence on the polymers at various stages of the process. This confirmed that the levels of catalyst in the polymer during each phase polymerization and in solid state polymerization within Examples and in respective Comparative Examples were similar. This indicates that changes in solid state polymerization rate are not artifacts of changes in catalyst concentrations.

Chip size is important because the rate of solid phase polymerization is strongly influenced by diffusion of low molecular weight species (mainly ethylene glycol and water) from the polymer chip into the vapor phase outside the chip. Small chips offer lower diffusion barrier and higher surface area per unit mass both leading to give higher solid phase polymerization rates. The effect of chip size should be taken into account when comparing results from different experiments.

Typically, commercial scale solid phase polymerization plants are fed with polymer having a chip size of 10 to 20 mm. The experimental solid phase polymerization equipment used in most of the Examples has a large extruder and cutter that gives chips having a mean size of about 50 mm. To enable closer comparison with practical operation, in some Examples we replicated the 50 mm chip polymer to give commercial polymer with a chip size of 15 to 20 mm, in doing this we first crystallized and dried the 50 mm chip polymer before re-extruding and cutting it. Crystallization was done to avoid agglomeration of the polymer chip in the feed before to the (n-butane).

EXAMPLE 1

Terephthalic acid (4.15 kg, 25 mol), ethylene glycol (1.8 kg, 31 mol) and NaOH (52 g) were placed in a stirred pressure reactor equipped with heater and condenser. The reactants were heated with stirring to a temperature of 230°C under a pressure of 40 psi (ca. 275 kPa, gauge). Water was distilled off until about 1.7 molar equivalents based on terephthalic acid (750 ml) had been removed.

At this stage the reactor contained about 5.35 kg of low molecular weight oligomer having a mean degree of polymerization of about 4. The pressure was reduced to ambient pressure and p-toluenesulfonyl chloride (0.6 ml of 20% w/w aqueous solution) 0.6 g, 5.5 mmol, ca. 0.1% weight % and ca. 0.014 mole % on the final polymer), phosphoric acid (10 g of 10%

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wt% solution in ethylene glycol ca. 200 ppm by weight on the final polymer) as stabilizer; antimony (III) oxide (15 g of 10% wt% slurry in ethylene glycol ca. 200 ppm by weight on the final polymer) as polymeric stabilizer; and cobalt (II) acetate (0.7 g) as color and clarity improver, were added to the oligomer. The vessel was then closed, the pressure reduced to 1 value and the temperature raised to 200° C. over about 0.5 hour and the mixture was melt phase polymerized until the melt viscosity of the polymer was 500 Poise (500 Pa.s) (1 to 3 hours). The intermediate molecular weight polymer (ca. 4.8 kg) was extruded as two lots: water quenching bath and cut into chips of mass mass from 40 to 50 mg.

The chips of intermediate molecular weight polymer were loaded in an oven for about 1 hour at 160° C. to crystallize the polymer. The crystallized chips were then solid phase polymerized in glass columns in a stream of dry nitrogen (40 l/min) at 205 to 225° C. until the polymer reached melt viscosity of 5000 Poise (500 Pa.s). The solid phase polymerization took about 5 hours.

This polymer was used to make bottle preforms by injection molding and yielded preforms of excellent clarity and glass, showing no signs of inclusions or stress crystallization. Samples of the preforms were subsequently processed into bottles suitable for packaging automotive low-creep by stretch blow molding to give high quality products.

Comparative Example 1

Example 1 was repeated except that the postcrystallized was omitted. Solid phase polymerization of this polymer took 7 hours to reach the melt viscosity of 5000 Poise (500 Pa.s). This indicates that according to the invention, solid phase polymerization rate is more than 25% faster than for otherwise similar but conventional polymers.

EXAMPLE 2

A mixed two-*trans*-phthalate oligomer (77 kg, made using 364 mol of phthalic anhydride) was prepared using the general method described in Example 1 above, but on a correspondingly larger scale and using mixtures of terephthalic acid and *trans*-phthalic acid in weight (not mole) ratio of about 95.5 to 4.5 instead of the isophthalic acid alone used in Example 1.

Prior to the melt phase polymerization postcrystallized (640 ml of 4% wt% solution in 2000 by volume ethylene glycol/water mixture: 17.5 g, 120 mmol, ca. 0.025 weight % and ca. 0.025 mole % on the final polymer); phosphoric acid (21 ml of 10% wt% solution in ethylene glycol ca. 200 ppm by weight on the final polymer) as stabilizer; antimony (III) oxide (175 ml of 10% wt% slurry in ethylene glycol ca. 200 ppm by weight on the final polymer) as color and clarity improver were added to the initial oligomer. The mixture was melt polymerized as described in Example 1 until the melt viscosity of the intermediate polymer was 2000 Poise (200 Pa.s) and the polymer was then extruded as two lots: water quenching bath and cut into chips of mass weight of about 50 mg. The chips of the intermediate molecular weight polymer were loaded into ballbeds and crystallized postcrystallized, dried and re-extruded as chips of mass weight of 15 to 20 mg (of amorphous polymer). These chips were subsequently crystallized and solid phase polymerized

200 to 215° C. in a stream of 1.5 bar in a stream of dry nitrogen (10 m³/hour) until the melt viscosity of the polymer was 5000 Poise (500 Pa.s) which took about 4 hours.

As with the polymer of Example 1 this polymer was used to make bottle preforms by injection molding and yielded preforms of excellent clarity and glass, showing no signs of inclusions or stress crystallization. Samples of the preforms were subsequently processed into bottles suitable for packaging automotive low-creep by stretch blow molding to give high quality products.

Comparative Example 2

Example 2 was repeated except that postcrystallized (28 g, 420 mmol, ca. 0.1 weight % and ca. 0.15 mole % on the final polymer) was added as stabilizer to the 'initial' oligomer prior to melt phase polymerization. The time to reach the target viscosity 5000 Poise (500 Pa.s) was about 20% less than that in Example 2. The intermediate polymer was extruded as two lots: water quenching bath and cut into chips of mass weight of about 50 mg, postcrystallized, dried and re-extruded as chips of mass weight of 15 to 20 mg. Subsequent solid phase polymerization to target melt viscosity of 5000 Poise (500 Pa.s) took about 1 hour.

Bottle preforms were injection molded from this polymer, but the preforms had substantial crystalline regions and were thus not suitable for subsequent processing into bottles with properties adequate for packaging automotive low-creep by stretch blow molding to give high quality products.

EXAMPLE 3

A 'mixed' oligomer including terephthalic acid and *trans*-phthalic acid in mole ratio of 95:5 was prepared from terephthalic acid (20.3 kg, 577 mol), *trans*-phthalic acid (1.2 kg, 7.2 mol) and ethylene glycol (26.7 kg, 430 mol) as generally described in Example 2, with the removal of water (about 11%).

Postcrystallized (250 ml of 4% wt% solution in 2000 by volume ethylene glycol/water mixture: 14 g, 163 mmol, ca. 0.03 weight % and ca. 0.020 mole % on the final polymer) also including phosphoric acid (21 g, ca. 200 ppm by weight on the final polymer) as stabilizer; antimony (III) oxide (175 ml of 10% wt% slurry in ethylene glycol ca. 200 ppm by weight on the final polymer) as polymeric stabilizer; and cobalt (II) acetate (10 g, ca. 140 ppm by weight on the final polymer) as color and clarity improver were added to this mixture. The mixture was melt polymerized as described in Example 1 until the melt viscosity of the intermediate molecular weight polymer was 2000 Poise (200 Pa.s). The polymer was then extruded as two lots: water quenching bath and cut into chips of mass weight of about 50 mg. These chips were crystallized, and re-extruded and cut to give chips having mass mass of from 15 to 20 mg.

The chips of this intermediate molecular weight polymer were loaded into ballbeds and re-crystallized under nitrogen stream of dry nitrogen and were heated to 200 to 215° C. using heating profile to allow polymer crystallization without melting the chips to stick together. The polymer was solid phase polymerized 200 to 215° C. until the melt viscosity of the product was 5000 Poise (500 Pa.s), which took about 4 hours.

20 Samples of this polymer were used to injection mold standard 50 g bottle preforms which were of excellent clarity and glass and while in use were stretch blow molded into good quality bottles.

EXAMPLE 4

Example 3 was repeated except that the amount of postcrystallized was 7 g (0.15 mmol, 0.01 weight % and ca.

0.014 mole % on the final polymer) and the *trans*-phthalic acid was omitted. The preforms and bottles were made as described in Example 3 and the preforms and bottles had excellent clarity and glass.

EXAMPLE 5

An intermediate polymer was prepared as described in Example 3 except that the postcrystallized was added as solid (21 g, ca. 154 mmol, 0.025 % by weight, ca. 0.043 mole % on the final polymer) and the melt phase polymerization was carried out in a polymer melt viscosity of 5000 Poise (500 Pa.s). The chips were pre-crystallized and dried in ballbeds but in a stream of dry nitrogen and then re-crystallized using low shear convection and cut to give chips of 15 to 20 mg mass mass. These polymer chips were then heated at ambient temperature into ballbeds and heated under nitrogen using a stream of dry nitrogen and were heated to 200 to 215° C. using heating profile to allow polymer crystallization without melting the chips to stick together. The polymer was solid phase polymerized at 200 to 215° C. until the melt viscosity of the product was 5000 Poise (500 Pa.s), which took about 1 to 3 hours.

The product polymer was extruded into good quality clear preforms which were subsequently stretch blow molded into good quality clear bottles.

Comparative Example 5

Example 4 was repeated except that the postcrystallized was omitted. The solid phase polymerization was carried out on the re-crystallized chips at a variety of temperatures in the range 200 to 215° C. The time to give product melt viscosity of 5000 Poise (500 Pa.s) was from 5 to 7 hours depending on the temperature used with higher temperatures yielding the desired viscosity at reduced times as compared with lower temperatures. The solid phase polymerization was significantly slower than in Example 4.

EXAMPLE 6

An intermediate polymer was prepared as described in Example 5 except that melt phase polymerization was stopped at polymer melt viscosity of 1000 Poise (100 Pa.s). The polymer was extruded and cut to chips 15 to 20 mg mass mass. These chips were solid phase polymerized as described in Example 4 to a product melt viscosity of 5000 Poise (500 Pa.s) taking 3 to 6 hours.

Comparative Example 6

Example 6 was repeated except that the postcrystallized was omitted. Solid phase polymerization to a product melt viscosity of 5000 Poise (500 Pa.s) took about 8 hours.

EXAMPLE 7

The melt viscosity characteristics of the polymers produced in Examples 3, 4 and Comparative Example 5 were studied to assess the respective melt flow properties. The results for each of these polymers lie in the range 10⁴ to 10⁵ Poise (10⁴ to 10⁵ Pa.s) at 200° C. This indicates that the limitation of chain branching reduces in the polymers of the invention does not necessarily enhance the melt strength of the polymers.

EXAMPLE 8

An intermediate polymer was prepared as described in Example 5 with the postcrystallized added as solid at a level

of 0.025% by weight (ca. 0.049 mole %) on the final polymer except that the melt phase polymerization was carried out at 200° C. to a polymer melt viscosity of 945 Poise (94.5 Pa.s—IV 0.53). The polymer was extruded and directly cut into chips of mass mass about 15 mg. The polymer chips were solid phase polymerized generally as described in Example 4 but at a temperature of 210° C. until the melt viscosity of the polymer was 5000 Poise (500 Pa.s—IV 0.73 IV), which took approximately 5 hours.

Comparative Example 8

Example 8 was repeated except that the postcrystallized was omitted. Solid phase polymerization at 210° C. to the same product melt viscosity took about 7 hours.

1. A modified polyethylene terephthalate polymer for making bottles by injection blow molding which has been made by process which includes melt phase polymerization step and subsequent solid phase polymerization step, solid polymer comprising from 0.007 to 0.05 mole % of molten derived from poly(pentenyl) chain branching agent which enhanced the polymerization rate in the solid phase polymerization step used in the manufacture of the polymer from 0.5 to 5 mole % of molten derived from chain extension disrupting comonomer, having melt viscosity at 200° C. of from 300 to 1000 Poise (300 to 1000 Pa.s) and an Intrinsic Viscosity (IV) of from 0.7 to 0.9.

2. A modified terephthalate polymer for making bottles by injection blow molding which has been made by process which includes melt phase polymerization step and subsequent solid phase polymerization step, solid polymer comprising from 0.007 to 0.05 mole % of molten derived from poly(pentenyl) chain branching agent which enhanced the polymerization rate in the solid phase polymerization step used in the manufacture of the polymer from 0.5 to 5 mole % of molten derived from chain extension disrupting comonomer, having melt viscosity at 200° C. of from 300 to 1000 Poise (300 to 1000 Pa.s) and an Intrinsic Viscosity (IV) of from 0.7 to 0.9.

3. A modified terephthalate polymer for making bottles by injection blow molding which has been made by process which includes melt phase polymerization step and subsequent solid phase polymerization step, solid polymer comprising from 0.007 to 0.05 mole % of molten derived from poly(pentenyl) chain branching agent which enhanced the polymerization rate in the solid phase polymerization step used in the manufacture of the polymer, from 0.5 to 5 mole % of molten derived from chain extension disrupting comonomer, having melt viscosity at 200° C. of from 300 to 1000 Poise (300 to 1000 Pa.s) and an Intrinsic Viscosity (IV) of from 0.7 to 0.9.

4. A polymer as claimed in claim 3 wherein the chain extension disrupting comonomer is an aromatic dimethylene acid and copolymer from 0.5 to 5 mole % of the terephthalic acid and used in the modified polyethylene terephthalate polymer.

5. A polymer as claimed in claim 4 wherein the chain extension disrupting comonomer is *trans*-phthalic acid.

6. A polymer as claimed in claim 5 wherein the molten of the poly(pentenyl) chain branching agent are molten of one or more of isobutyl groups, isopropylated, debited (quaternized), isobutyl (quaternized) or postcrystallized.

7. An injection molded low-molecular bottle preform made from modified polymer as claimed in claim 6.

8. An injection blow-molded bottle made from modified polymer as claimed in claim 6.

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9. A modified polyethylene terephthalate polymer as claimed in claim 8, wherein the additive derived from the polyethylene terephthalate branching agent is present in an amount of from 0.024 to 0.045 mole %.

10. A modified polyethylene terephthalate polymer as claimed in claim 9 which has an inherent viscosity at 285° C. of from 0.10 to 0.15 Poise (0.100 to 0.150 Poise).

11. A modified polyethylene terephthalate polymer for making molded water bottles by injection blow molding which has been made by a process which includes an melt phase polymerization step and subsequent solid phase polymerization step, said polymer comprising from 0.01 to 0.075 mole % of additive derived from a polyethylene terephthalate branching agent which enhanced the polymerization rate in the solid phase polymerization step used in the manufacture of the polymer from 0.5 to 5 mole % of additive derived from a chain extender having an inherent viscosity at 285° C. of from 200 to 1000 Poise (200 to 1000 Poise) and an inherent viscosity (IV) of from 0.7 to 0.9.

12. A modified polyethylene terephthalate polymer as claimed in claim 11, wherein the additive derived from the polyethylene terephthalate branching agent is present in an amount of from 0.02 to 0.05 mole %.

13. A modified polyethylene terephthalate polymer as claimed in claim 12 which has an inherent viscosity at 285° C. of from 0.10 to 0.15 Poise (0.100 to 0.150 Poise).

14. A modified polyethylene terephthalate polymer as claimed in claim 11 which additionally comprises fine metal particles, which tend to be randomly distributed in the melt phase of the polymer in the absence of the additive.

15. A modified polyethylene terephthalate polymer as claimed in claim 14, wherein the fine metal particles are present in an amount of from 10 to 100 ppm by weight based on the weight of the polymer.

