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FORMULARIO ÚNICO DE SOLICITUD DE PATENTE

PCT

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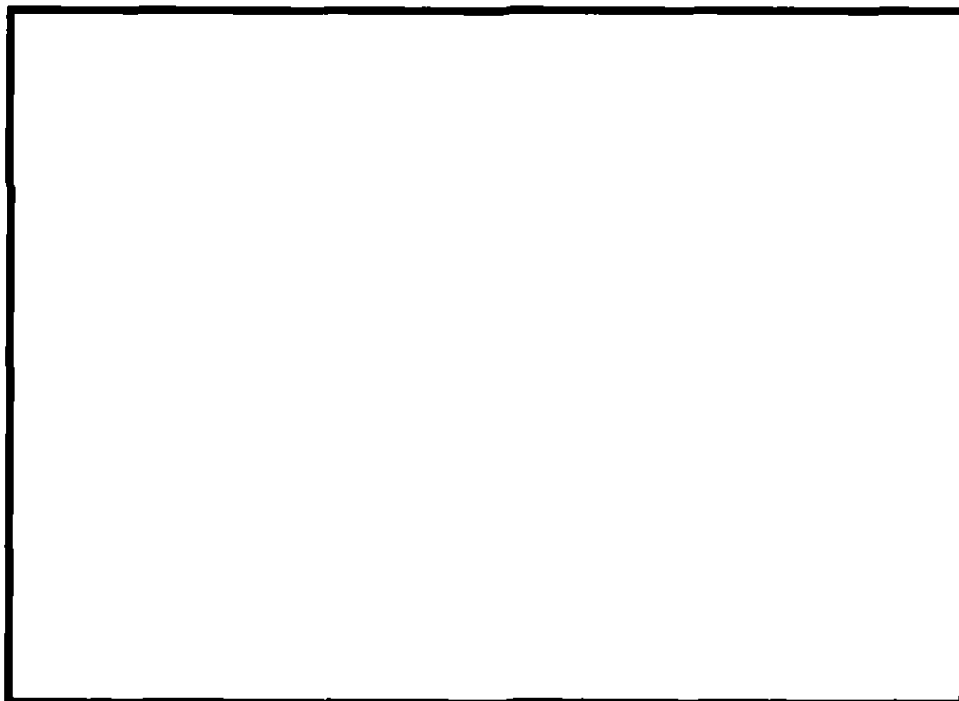
1 SOLICITUD DE:			
☒ Patente de Invención		☐ Patente de Modelo de Utilidad	
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2 SOLICITANTE (71)	Nombre RHODIA STER S.A. Dirección WTC - World Trade Center, Avenida Das Nações Unidas, 12.551 8o andar 04578-903 - Sao Paulo - SP Brasil Nacionalidad o Domicilio BRASIL Lugar de Constitución. BRASIL Teléfono: Fax E-mail:		IDENTIFICACION CC ☐ NIT ☐ CE ☐ Otro ☐ Cual _____ Número _____
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Instrucciones para el diligenciamiento del presente formulario, ver reverso de esta página			

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ANEXOS

- ☒ Comprobante de pago de la tasa de presentación de la solicitud \$378.000
- ☒ Comprobante de pago por reivindicación de prioridad \$108.000
- ☐ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☐ Poderes, si fuere el caso. Protocolo No.18679
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☐ Declaraciones
- ☒ Copia de la solicitud internacional (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Copia del examen preliminar efectuado por la IPEA.
- ☐ Traducción del examen preliminar efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico.
- ☐ Arte final 12x12
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud
- ☐ Otros

11 FIGURA CARACTERÍSTICA.



12. Solicito la concesión de la patente:

NOMBRE: RAMIRO CASTRO DÚQUE

FIRMA:

C.C. 170.322 de Bogotá T.P. 1003 del C.S.J.

Instrucciones para la presentación de los anexos, ver reverso de esta página

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CONSIGNACION

C O N C E P T

80M: CIENTO SEIS MIL PESOS

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____



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CONSIGNACION

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
BRIGARD & CASTRO LTDA	CONSIGNACION	BANCO POPULAR	050-00110-6	2736280	16/03/2002	6.635.560.00
BRIGARD & CASTRO LTDA	CONSIGNACION	BANCO POPULAR	050-00110-6	2740131	16/03/2002	530.000.00

CONCEPTO

CANT. HISTORICO	CONCEPTO	TOTAL CONCEPTO
1 50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE IN	378.000.00
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SOM: TRESCIENTOS SETENTA Y OCHO MIL PESOS

RESPONSABLE :

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**“COMPOSICIONES A BASE DE POLIÉSTER QUE TIENEN
MEJORADAS PROPIEDADES TERMOMECAÑICAS Y PROCESO
PARA PRODUCIR DICHAS COMPOSICIONES”**

La presente invención se refiere a composiciones a base de poliéster que presentan mejoradas propiedades termomecánicas, que comprenden partículas minerales de tamaño fino. Estas composiciones son especialmente útiles para la fabricación de botellas. La presente invención se refiere adicionalmente a un proceso para producir dichas composiciones.

Los poliésteres, especialmente el tereftalato de polietileno, son polímeros termoplásticos ampliamente usados para la producción de artículos moldeados o extruidos. Se emplean generalmente como hilos o fibras, artículos moldeados por inyección, películas (artículos extruidos y dirigidos) o recipientes, por ejemplo obtenidos a través de un proceso de extrusión-soplado. Las propiedades de los artículos producidos dependen en gran medida de las propiedades termomecánicas del polímero, tal como el módulo, la flexibilidad, la temperatura de transición del vidrio, la distorsión de calor bajo carga.

La distorsión de calor bajo carga es una característica importante para el uso de poliésteres como botellas, más particularmente para botellas para contener bebidas. Para propósito de preservación e higiene de alimentos, ciertas bebidas deben llenarse en caliente en las botellas, y eventualmente sin oxígeno. Este es particularmente el caso para jugos de frutas, productos pasteurizados o esterilizados, especialmente productos de dieta, bebidas de té o café, cerveza. Si la temperatura de llenado es demasiado alta, y/o si el líquido permanece mucho tiempo en la botella durante una cierta temperatura, esta última se deforma. Este inconveniente puede limitar el campo de uso del poliéster, y

particularmente del tereftalato de polietileno, para la contención de bebidas. Consecuentemente, algunas bebidas no pueden colocarse en botellas de tereftalato de polietileno, o no pueden excepto bajo limitadas condiciones de temperatura.

Continuos intentos se ha hecho para elaborar poliésteres, composiciones a base de poliéster o procesos para formar artículos de poliéster, en forma tal que se mejoran las propiedades termomecánicas, particularmente tal que la distorsión de calor bajo carga se mejora. Consecuentemente, una primera solución puede consistir en la utilización de un naftalato de polietileno en ves de un tereftalato de polietileno, o copolímeros que comprenden unidades naftálicas y tereftálicas. Esta solución es sin embargo costosa, y no se usa industrialmente excepto para aplicaciones muy específicas.

Otra solución consiste en modificar el proceso de formación de botellas con el fin de sobre-cristalizar el polímero. El proceso de acuerdo con esta solución se denomina generalmente 'termo-fijación". En breve, se trata de cristalizar una botella de tereftalato de polietileno modificando las operaciones de soplado. La puesta en práctica de este proceso requiere sin embargo, de una importante modificación de las líneas de producción de botellas y consecuentemente requiere de importantes inversiones. Los cuellos de las botellas obtenidas de acuerdo con este proceso se cristalizan y consecuentemente pierden su transparencia. Lo anterior puede constituir un defecto visual.

El objetivo de la presente invención es proponer rellenos que pueden utilizarse para mejorar las propiedades termomecánicas de los poliésteres, especialmente rellenos fácilmente incorporables, bien dispersados en la matriz. Es un adicional objetivo proponer un proceso

para producir composiciones a base de poliéster que presentan mejoradas propiedades termomecánicas.

Con este fin, la presente invención propone una composición a base de poliéster caracterizada porque comprende una matriz basada en poliéster partículas de mineral de tamaño nanométrico, el factor de forma que varía dentro del rango entre 1 y 10, a una concentración en peso que varía dentro del rango de entre 0,01% y 25%.

La matriz de la composición puede ser completamente a base de poliéster. Puede estar constituida de un único polímero, el poliéster, o de una mezcla de polímeros donde por lo menos uno de los componentes es un poliéster. También puede consistir de un agente amorfo, un copolímero donde la mayoría de las unidades de repetición comprenden funciones éster.

Los poliésteres adecuados para llevar a cabo la invención se obtienen generalmente a través de la poli-condensación de dioles y ácidos dicarboxílicos o ésteres de ácidos dicarboxílicos.

Entre los dioles adecuados para llevar a cabo la invención, etilenglicol, dietilenglicol, propilenglicol, 1,3-propanodiol, 1,4-butanodiol, 1,3-butanodiol, 2,2-dimetilpropanodiol, neopentilglicol, 1,5-pentanodiol, 1,2-hexanodiol, 1,8-octanodiol, 1,10-decanodiol, 1,4-ciclohexanodimetanol, 1,5-ciclohexanodimetanol, 1,2-ciclohexanodimetanol, o sus mezclas pueden mencionarse.

Entre los ácidos dicarboxílicos adecuados para llevar a cabo la invención, ácido tereftálico, ácido isoftálico, ácido ortoftálico, 2,5-naftaleno ácido dicarboxílico, 2,6-naftaleno ácido dicarboxílico, 1,3-naftaleno ácido

dicarboxílico, 2,7-naftaleno ácido dicarboxílico, metil ácido tereftálico, 4,41-difenil ácido dicarboxílico, 2,2'-difenil ácido dicarboxílico, 4,4'-difenil éter ácido dicarboxílico, 4,4'-difenil metano ácido dicarboxílico, 4,4'-difenil sulfono ácido dicarboxílico, 4,4'-difenil-isopropilideno-ácido dicarboxílico, sulfo-5-ácido isoftálico, ácido oxálico, ácido succínico, ácido adípico, ácido sebácico, ácido asélaico, dodecano ácido dicarboxílico, ácido dímero, ácido maleico, ácido fumárico, y todos los diácidos alifáticos, ciclohexano ácido dicarboxílico pueden mencionarse.

Los ácidos di-carboxílicos pueden introducirse en el medio de poli-condensación en una forma esterificada, por ejemplo vía metoxi o vía etoxi.

Los poliésteres preferidos para llevar a cabo la invención son, el tereftalato de polietileno, tereftalato de poli-trimetileno, tereftalato de poli-butileno, tereftalato de poli-naftaleno, copolímeros y sus mezclas.

Las partículas de mineral nanométricas de acuerdo con la invención confirieren mejoradas propiedades mecánicas a la composición en relación con una composición idéntica que no comprende dichas partículas. La distorsión al calor bajo carga se mejora notablemente.

El factor de forma de una partícula se define como la relación entre la dimensión más larga y la dimensión más corta de una partícula. Por ejemplo, si las partículas tienen forma de plaquetas, el factor de forma se define por la relación entre la longitud de las plaquetas y su ancho. Si las plaquetas son en forma de aguja, su factor de forma se define por la relación entre la longitud de la aguja y el diámetro en sección transversal de la aguja. Si las partículas tienen una forma sustancialmente esférica, el factor de forma es igual a 1.

Las partículas de acuerdo con la invención presentan un bajo factor de forma, que varía dentro del rango de entre 1 y 10. El factor de forma es preferiblemente de entre 1 y 2.

Por partículas de tamaño nanométrico, se entiende que la dimensión corta es inferior a 200 nm, y el parámetro largo es menor de 2 000 nm, preferiblemente menor de 400 nm. De acuerdo con una modalidad preferida, la dimensión corta es menor de 100 nm y la dimensión larga es menor de 200 nm.

De acuerdo con una modalidad ventajosa de la invención, las partículas son sustancialmente de forma esférica con un diámetro promedio inferior de o igual a 200 nm. El diámetro promedio preferiblemente varía dentro del rango de entre 5 y 100 nm.

Las partículas minerales se escogen preferiblemente a partir de partículas a base de óxido de metal, por ejemplo, sílice, dióxido de titanio, alúmina, zirconio. Pueden comprender un tratamiento superficial o revestimiento. Dichos tratamientos se consideran, por ejemplo, para mejorar la dispersión de partículas en el polímero, para proteger las partículas contra el deterioro, o para proteger el polímero de degradaciones a través del contacto con las partículas. Todos los tratamiento superficiales y revestimientos conocidos en el campo de rellenos de polímero, particularmente aquellos conocidos y usados como rellenos que tienen dimensiones por encima de aquellas que se refieren a la invención, pueden usarse. Se puede usar, por ejemplo, partículas de dióxido de titanio parcial o completamente revestidas con un compuesto a base de sílice.

Las partículas a base de sílice son particularmente adecuadas para llevar a cabo la invención. Cualquier tipo de sílice conocida puede emplearse en las composiciones a base de poliéster.

Por ejemplo, sílices fumantes, sílices de combustión, sílices precipitadas, soluciones de sílice. El uso de soluciones es particularmente adecuado para la obtención de una composición que tiene buena dispersión de partículas.

La concentración pesada de partículas en la composición varía dentro del rango de entre 0,1 y 20%. Preferiblemente varía dentro del rango de entre 5 y 15%.

Cualquier método para introducir un compuesto dentro de una composición puede emplearse. Un primer método consiste en introducir las partículas dentro del medio de reacción de poliéster, usualmente antes de que haya comenzado la polimerización. La polimerización se lleva entonces a cabo en presencia de las partículas. Las partículas pueden introducirse como un polvo o como una dispersión dentro del medio líquido.

Un segundo método consiste en introducir las partículas como un polvo dentro del poliéster fundido y luego desprender la mezcla con el fin de obtener una dispersión homogénea. La operación puede por ejemplo llevarse a cabo mediante un tornillo extrusor, único o gemelo.

Un tercer método consiste en introducir las partículas como lote maestro en el poliéster fundido. La mezcla puede efectuarse mediante cualquiera de los métodos arriba mencionados. La introducción del lote maestro en el polímero puede efectuarse mediante un extrusor.

De acuerdo con una modalidad particularmente ventajosa de la invención, las partículas se introducen como una solución dentro del medio de reacción del polímero. La solución puede ser por ejemplo una solución acuosa o glicólica. Las soluciones de sílice son particularmente adecuadas para esta modalidad.

Un proceso para preparar las composiciones de acuerdo con esta modalidad comprende por ejemplo los siguientes pasos:

- a) Introducir en una mezcla con agua por lo menos un diol con por lo menos un ácido dicarboxílico o un éster de ácido dicarboxílico de una solución de sílice donde las partículas tienen un diámetro promedio menor de o igual a 200 nm
- b) Esterificar o transesterificar el ácido o el éster ácido con el diol,
- c) Poli-condensar bajo vacío el producto de la esterificación,
- d) Formar el producto final.

Excepto por la introducción de la solución de sílice dentro de la mezcla de monómeros, el proceso para producir las composiciones es clásico. Los procesos se describen por ejemplo en Las Técnicas del Ingeniero J 6 020, 2151-2160. El proceso no es en ninguna forma objetivo de cualquier limitación del alcance de la invención.

El paso de esterificación o transesterificación b) es un paso comúnmente llevado a cabo dentro de los procedimientos de fabricación industrial del poliéster. Por ejemplo, dos rutas se emplean principalmente para producir el tereftalato de polietileno).

La primera ruta de obtención es la denominada ruta de "tereftalato de metil" (DMT). Comprende una reacción de transesterificación. El DMT fundido es solubilizado en etilenglicol (EG) presente en exceso, la

relación molar de EG/DMT que es de alrededor de 1,9 a 2, 2, y la reacción se conduce a presión atmosférica y temperaturas de alrededor de 130°C a 250°C. La presencia de un catalizador, por ejemplo acetato de manganeso, es necesaria. El metanol liberado durante la reacción se elimina a través de destilación. El etilenglicol presente en exceso se elimina a través de evaporación después de la reacción de transesterificación. El catalizador, el cual es también un catalizador de degradación del poliéster, se bloquea mediante compuestos fosforosos después de la reacción. El producto resultante de la transesterificación es una mezcla de bis-hidroxi-etil-tereftalato (BHET) y oligómeros.

La segunda ruta es la denominada "esterificación directa". Comprende una reacción de esterificación entre ácido tereftálico y etilenglicol. Se lleva a cabo a temperaturas de 130°C a 280°C. El ácido tereftálico, fundido a dichas temperaturas no es soluble en etilenglicol pero lo es en el producto éster de la reacción. La solubilización del reactivo en el medio es sin embargo progresiva. El etilenglicol está presente a una relación molar de EG/ácido tereftálico de alrededor de 1 a 1,5. De esta reacción resulta en una mezcla de oligómeros que tienen ácido tereftálico o hidroxietil tereftalato.

La utilización de estos procesos ha sido el objetivo de numerosos estudios descritos en la literatura. Las condiciones indicadas aquí arriba no deben considerarse como limitaciones del alcance de la presente invención.

Los subsecuentes pasos de poli-condensación se catalizan usualmente a través de compuestos metálicos, por ejemplo compuestos de antimonio, titanio o germanio. Ellos pueden catalizarse mediante cualquier catalizador de poliéster poli-condensación de poliéster. Son usualmente

llevados a cabo a bajas presiones, con el fin de favorecer la eliminación de etilenglicol formado durante la reacción de condensación.

El polímero se forma entonces en el producto final, por ejemplo extruyendo una cadena a través de un orificio, enfriando, y granulando. La formación está usualmente precedida por una filtración de la fase fundida. Los pasos de poli-condensación de la fase fundida y formación del producto final pueden seguirse de un paso de post-condensación de fase sólida.

Las composiciones, por ejemplo en una forma granulada, pueden formarse en artículos moldeados. Ellos pueden más particularmente usarse en forma de botellas. Todos los procesos para la fabricación de botellas a partir de polímeros termoplásticos son adecuados para la invención. El proceso de modelo por extrusión-soplado se prefiere en general.

Las botellas así producidas pueden llenarse con líquidos a altas temperaturas y/o con líquidos que permanecen calientes en la botella durante largos periodos de tiempo.

Otros detalles o ventajas de la presente invención serán más evidentes a partir de los siguientes ejemplos, establecidos únicamente con propósitos indicativos.

Diferentes composiciones a base de poliéster se sintetizaron, cuyas siguientes características se midieron:

- Índice de viscosidad (VI, en ml/g); medido de acuerdo con ISO 1628/5 estándar; medido en una solución de 0,5% de la composición en una mezcla en peso de 50/50 de fenol/ortodichlorobenzeno, a 25°C. La

concentración del polímero usado para los cálculos del índice de viscosidad en la concentración actual del polímero, considerando la presencia de partículas en la composición.

- Masa molecular en peso absoluto (g/mol); determinada mediante Cromatografía de Permeabilidad de Gel (GPC).
- Color de acuerdo con el sistema de laboratorio CIE: mediciones de L^* , a^* , b^* .
- Propiedades termomecánicas: módulo a 23°C, módulo a 160°C, Temperatura de transición de vidrio (T_g) Mediciones dinámicas (Análisis mecánico dinámico) en un aparato RSA, usando muestras de 40x4x2 mm, después de secado y cristalización a 130°C bajo vacío durante 16 horas.
- Distorsión de calor bajo carga (HDT), evaluada de acuerdo con ISO 75-2 estándar.
- Cristalización: el polímero seco se plastifica a 290°C en forma tal de destruir cualquier germen de cristalización. El producto fundido es inyectado en una serie de moldes donde el espesor varía progresivamente para obtener así placas a espesores entre 2 y 6 mm. La temperatura de la pared del molde se ajustó a 37°C. Se registró el espesor al cual ocurre un ligero disturbio correspondiente al comienzo de la cristalización.

Ejemplo 1

Dentro de un reactor de polimerización de 7,5 litros, permitiendo la obtención de 3 kg de polímero a través de poli-condensación, equipado con un agitador provisto con un torsiómetro para vigilar la viscosidad del medio de la reacción, varias mallas de introducción, una columna de destilación para eliminar agua formada durante la esterificación, así como el exceso de etilenglicol, y un circuito de vacío para el paso de poli-condensación, se carga lo siguiente:

- 2 656 g de ácido tereftálico (16,0 moles)

- 1 190 g de etilenglicol (19,2 moles)
- 384 g de una solución acuosa de nanopartículas de sílice de 50 nm de diámetro, comercializadas por Hoechst bajo el nombre comercial Klebosol® 40R50, correspondiente a 143,6 g de sílice.

Después de una purga de nitrógeno, el medio de la reacción se calienta a 275°C bajo agitación y bajo una presión absoluta de 6,6 bar.

El periodo de esterificación se define como el tiempo necesario para la destilación del agua.

El tiempo de esterificación es de 66 minutos.

La presión se lleva entonces a presión atmosférica a lo largo de un periodo de 20 minutos.

Una solución de óxido de antimonio se introduce dentro del medio de la reacción (250 ppm de antimonio, basado en el polímero).

La presión se mantuvo durante 20 minutos a presión atmosférica, antes de una progresiva aplicación de vacío de desde 1 bar hasta menos de 1 mm de mercurio a lo largo de un periodo de 90 minutos. La columna de destilación se pasa colateralmente entonces para aplicación de vacío directo tan pronto como la presión alcanza 20 mm de mercurio.

La masa de la reacción se lleva a 285°C tan pronto como la presión cae por debajo de 1 mm de mercurio.

El tiempo de poli-condensación se define como el tiempo requerido para alcanzar el deseado nivel de viscosidad partiendo del momento en el cual la presión es por debajo de 1 mm de mercurio. El tiempo de poli-condensación es de 32 minutos.

Una vez que se ha obtenido el deseado nivel de viscosidad, la agitación se interrumpe y el reactor se presuriza a 3 bar para descargar y granular el polímero obtenido.

Los gránulos de polímero se secan durante 15 horas a 50°C. Fotografías tomadas con un Microscopio Electrónico de Transmisión se muestran en

la figura 1. La fotografía 1 se toma a una magnificación de alrededor de 2×10^4 y la fotografía 2 se magnifica a alrededor de 10^5 .

Ejemplo 2 (ejemplo comparativo)

Se preparó un polímero de acuerdo con el ejemplo 1, excepto porque no se agregan las nanopartículas de sílice.

El tiempo de esterificación es de 54 minutos.

El tiempo de poli-condensación es de 67 minutos.

Ejemplo 3

Se preparó un polímero de acuerdo con el ejemplo 1, excepto porque la solución acuosa de partículas de sílice se agregan conjuntamente con la solución de óxido de antimonio.

El tiempo de esterificación time es de 87 minutes.

El tiempo de poli-condensación es de 59 minutos.

Ejemplo 4

Se preparó un polímero de acuerdo con el ejemplo 1, excepto porque en vez de los 2 656 g de ácido tereftálico, se agregó lo siguiente:

- 2 592 g de ácido tereftálico
- 63, 7 g de ácido isoftálico (correspondiente a 2,4 moles de la cantidad de ácido)

El tiempo de esterificación es de 65 minutos.

El tiempo de poli-condensación es de 59 minutos.

Ejemplo 5

Se preparó un polímero de acuerdo con el ejemplo 1, excepto porque la solución acuosa de partículas de sílice es una solución acuosa de nanopartículas de sílice de 25 nm de diámetro, comercializada por Hoechst bajo el nombre comercial Klebosol 40R50.

El tiempo de esterificación es de 68 minutos.

El tiempo de poli-condensación es de 32 minutos.

Ejemplo 6

Se preparó un polímero de acuerdo con el ejemplo 1, excepto porque se agregaron los siguientes compuestos:

- 2 592 g de ácido tereftálico**
- 63,7 g de ácido isoftálico (correspondiente a 2,4 moles de la cantidad de ácido)**
- 37 g de etilenglicol**
- 1 306 g de una solución de sílice glicólica a 11,8 % en peso de sílice, la solución que se sintetiza a través de un proceso del tipo Stober, las partículas de sílice que tienen un diámetro de 50 nm.**

El tiempo de esterificación es de 54 minutos.

El tiempo de poli-condensación es de 73 minutos.

Ejemplo 7

Se preparó un polímero de acuerdo con el ejemplo 1, excepto porque en vez de los 2 656 g de ácido tereftálico, se agregó lo siguiente:

- 2 497 g de ácido tereftálico**
- 159 g de ácido isoftálico (correspondiente a 6 moles de la cantidad de ácido)**

El tiempo de esterificación es de 61 minutos.

El tiempo de poli-condensación es de 68 minutos.

Estas características de las composiciones de acuerdo con los ejemplos 1 a 7 se muestran en la tabla I.

Tabla I

Ejemplo	IV (ml/g)	Mw (g/mol)	l*	a*	b*	HDT	Módulo 23°C (Mpa)	Módulo 160°C (Mpa)	Tg (Mpa)	Crista- lización (mm)
1	67,0	37 900	54	-0,4	2,1	67°C	1 165	82	107	
2	79,5		72	-0,9	6,5	59	988	61	99	4
3	72,1	41 000	75	-1,0	15,0					
4	71,1		66	-2,3	6,4					3
5	62,4	33 700	59	-1,5	9,1	67	1 195	88	107	
6	68,5		78	-2,7	11,0		1 015	65	103	4,5
7	74,8		71,0	-0,7	6,4					6

Ejemplo 8

100 kg de una composición se preparó de acuerdo con el ejemplo 4 en un reactor de doble recipiente a 200°C, con 1,9 moles de ácido isoftálico.

Ejemplo 9

Se preparó una composición de acuerdo con el ejemplo 8, excepto porque no se agregan nanopartículas de sílice. Las composiciones de los ejemplos 8 y 9 son moldeadas en botellas, a través de inyección/soplado en una máquina integrada ABS F100. Las preformas pesaron 32 g, las botellas tienen una capacidad de 600 ml.

Se llevó a cabo una prueba en estas botellas; las botellas se llenaron a diferentes temperaturas y se midió su variación de volumen. A mayor variación, peor la composición.

La Tabla II muestra la temperatura de llenado (°C) y la deformación (ml) para una botella obtenida a partir de las composiciones de acuerdo con los ejemplos 8 y 9.

Tabla II

Temperatura	Ejemplo 8	Ejemplo 9
70	76,6	50,6
75	109,6	70,3
80	149,1	129,1
85	205,8	176,6

REIVINDICACIONES

1. Una composición a base de poliéster que tiene mejoradas propiedades termomecánicas, caracterizada porque comprende una matriz a base de poliéster y partículas de mineral de tamaño nanométrico, que tienen un factor de forma que comprende entre 1 y 10, a una concentración pesada dentro de 0,01 y 25%.
- 2 La composición, de acuerdo con la reivindicación 1, caracterizada porque las partículas son en forma sustancialmente esférica que tienen un diámetro bajo o igual a 200 nm.
3. La composición, de acuerdo con la reivindicación 2, caracterizada porque el diámetro promedio de las partículas está comprendido entre 5 y 100 nm.
4. La composición, de acuerdo con una cualquiera de las reivindicaciones precedentes, caracterizada porque las partículas están basadas en óxidos de metal.
5. La composición, de acuerdo con la reivindicación 4, caracterizada porque las partículas están basadas en un compuesto seleccionado a partir de sílice, dióxido de titanio, zirconio, alúmina.
6. La composición, de acuerdo con la reivindicación 5, caracterizada porque las partículas están basadas en sílice y porque la composición se obtiene introduciendo una solución de sílice dentro del medio de síntesis del poliéster.

7. La composición, de acuerdo con la reivindicación 6, caracterizada porque la solución de sílice es una solución acuosa o glicólica.

8. La composición, de acuerdo con una cualquiera de las reivindicaciones precedentes, caracterizada porque el poliéster es tereftalato de poli-trimetileno, tereftalato de poli-butileno, tereftalato de poli-naftaleno, mezclas y copolímeros basados en estos poliésteres.

9. La composición, de acuerdo con una cualquiera de las reivindicaciones precedentes, caracterizada porque el poliéster contiene un agente amorfo.

10. La composición, de acuerdo con la reivindicación 9, caracterizada porque el agente amorfo es un comonomero del poliéster.

11. La composición, o proceso de acuerdo con la reivindicación 10, caracterizada porque el comonomero se selecciona a partir de ácido isoftálico, 1,4-ciclohexanodimetanol, dietilenglicol, sus mezclas, y donde representa entre 1 y 20 moles de las unidades de repetición en el poliéster.

12. Un proceso para producir una composición a base de poliéster, como se definió en una cualquiera de las reivindicaciones precedentes, caracterizado porque comprende los siguientes pasos:

- a) Introducir en una mezcla con agua por lo menos un diol con por lo menos un ácido dicarboxílico o un éster de ácido dicarboxílico de una solución de sílice donde las partículas tienen un diámetro promedio menor de o igual a 200 nm,
- b) Esterificar o transesterificar el ácido o el éster ácido con el diol,
- c) Poli-condensar bajo vacío el producto de la esterificación,

d) Formar el producto final.

13. El proceso, de acuerdo con la reivindicación 12, caracterizado porque ese paso c) se lleva a cabo en presencia de un catalizador a base de antimonio o titanio.

14. Un artículo, caracterizado porque se obtiene formado a partir de las composiciones como se definen en una cualquiera de las reivindicaciones precedentes.

15. Una botella, caracterizada porque se obtiene mediante la formación a partir de las composiciones como se definen en una cualquiera de las reivindicaciones precedentes.

16. Un proceso para llenar en caliente botellas de tereftalato de polietileno con un líquido, caracterizado porque las botellas se producen a partir de las composiciones como se definen en una cualquiera de las reivindicaciones 1 a 13.

EXTRACTO

“COMPOSICIONES A BASE DE POLIÉSTER QUE TIENEN MEJORADAS PROPIEDADES TERMOMECÁNICAS Y PROCESO PARA PRODUCIR DICHAS COMPOSICIONES”

La presente invención se refiere a composiciones a base de poliéster que tienen mejoradas propiedades termomecánicas, que comprenden partículas de mineral finamente divididas. Estas composiciones son particularmente útiles para la fabricación de botellas. La presente invención se refiere adicionalmente a un proceso para producir dichas composiciones. Las composiciones comprenden una matriz a base de poliéster y partículas de tamaño nanométrico.

PATENT COOPERATION TREATY

17 OCT 2001

From the INTERNATIONAL BUREAU

PCT

NOTICE INFORMING THE APPLICANT OF THE
COMMUNICATION OF THE INTERNATIONAL
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

To:

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Date of mailing (day/month/year)

04 October 2001 (04.10.01)

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29 March 2000 (29.03.00)

Applicant

RHODIA STER S.A. et al

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:

US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

BR,CA,CO,MX

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 04 October 2001 (04.10.01) under No. WO 01/72881

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

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(54) Title: POLYESTER-BASED COMPOSITIONS HAVING IMPROVED THERMOMECHANICAL PROPERTIES AND
PROCESS TO PRODUCE SAID COMPOSITIONS

(57) Abstract: The present invention refers to polyester-based compositions having improved thermomechanical properties, comprising finely divided mineral particles. These compositions are particularly useful for manufacturing bottles. The present invention further refers to a process for producing said compositions. The compositions comprise a polyester-based matrix and nanometric-sized particles.

WO 01/72881 A1

"POLYESTER-BASED COMPOSITIONS HAVING IMPROVED THERMOMECHANICAL PROPERTIES AND PROCESS TO PRODUCE SAID COMPOSITIONS".

The present invention refers to polyester-based compositions presenting improved thermomechanical properties, comprising fine sized mineral particles. These compositions are especially useful for manufacturing bottles. The present invention further refers to a process to produce such compositions.

5 Polyesters, especially polyethylene terephthalate, are thermoplastic polymers widely used for the production of molded or extruded articles. They are generally employed as yarns or fibers, injection molded articles, films (extruded and drawn articles) or
10 vessels for example obtained through an extrusion-blow process. The properties of the articles produced are greatly dependent on the thermomechanical properties of the polymer, such as the modulus, the flexibility, the glass transition temperature, the heat distortion
15 under load.

The heat distortion under load is an important feature for the use of polyesters as bottles, more particularly for bottles meant to contain beverages. For preservation and food hygiene purposes, certain
25 beverages must be hot-filled into the bottles, and eventually in the absence of oxygen. This is particularly the case for fruit juices, pasteurized or sterilized products, especially dairy products, tea or coffee beverages, beer. If the filling temperature is
30 too high, and/or if the liquid remains too long in the bottle over a certain temperature, the latter deforms. This shortcoming can limit the field of use of the polyester, and particularly of polyethylene terephthalate, for containing beverages. Hence,
35 certain beverages cannot be disposed in polyethylene

terephthalate bottles, or cannot except under limited temperature conditions.

Continuous attempts are being made to elaborate polyesters, polyester-based compositions or processes
5 for forming polyester articles, such that thermomechanical properties are improved, particularly such that the heat distortion under load is improved. Therefor, a first solution may consist in utilizing a polyethylene naphthalate instead of a polyethylene
10 terephthalate, or copolymers comprising naphthalic and terephthalic units. This solution is however costly, and is not industrially used except for very specific applications.

Another solution consists in modifying the process of
15 forming the bottles in order to over-crystallize the polymer. The process according to this solution is generally called "thermofixing". In short, it consists in crystallizing a polyethylene terephthalate bottle by modifying the blowing operations. The carrying out
20 of this process requires however an important modification of the bottle production lines and hence requires important investments. The necks of the bottles obtained according to this process are crystallized and thus lose their transparency. This
25 may constitute a visual defect.

The object of the present invention is to propose fillers which may be utilized to improve thermomechanical properties of polyesters, especially easily incorporable fillers, well dispersed in the
30 matrix. It is a further object to propose a process to produce polyester-based compositions presenting improved thermomechanical properties.

To this avail, the present invention proposes a polyester-based composition characterized in that it
35 comprises a polyester-based matrix and nanometrical-

sized mineral particles, the shape factor ranging between 1 and 10, at a weighted concentration ranging between 0,01% and 25%.

The matrix of the composition may be full polyester-based. It may be constituted of a single polymer, the polyester, or of a polymer blend where at least one mais component is a polyester. It may also consist of, as an amorphing agent, a copolymer where most of the repeating units comprise ester functions.

10 Polyesters adequate for carrying out the invention are generally obtained through polycondensation of diols and dicarboxylic acids or esters of dicarboxylic acids.

15 Among the diols adequate to carry out the invention, ethylene glycol, diethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,3-butanediol, 2,2-dimethylpropanediol, neopentyl glycol, 1,5-pentanediol, 1,2-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,4-cyclohexanedimethanol, 1,5-cyclohexanedimethanol, 1,2-cyclohexanedimethanol, or mixtures thereof can be mentioned.

Among the dicarboxylic acids adequate for carrying out the invention, terephthalic acid, isophthalic acid, orthophthalic acid, 2,5-naphthalene dicarboxylic acid, 25 2,6-naphthalene dicarboxylic acid, 1,3-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, methyl terephthalic acid, 4,4'-diphenyldicarboxylic acid, 2,2'-diphenyldicarboxylic acid, 4,4'-diphenylether dicarboxylic acid, 4,4'-diphenylmethanedicarboxylic acid, 4,4'-diphenylsulfonedicarboxylic acid, 4,4'-diphenylisopropylidene-dicarboxylic acid, sulfo-5-isophthalic acid, oxalic acid, succinic acid, adipic acid, sebacic acid, azelaic acid, dodecanedicarboxylic acid, dimer 35 acid, maleic acid, fumaric acid, and all aliphatic

diacids, cyclohexane dicarboxylic acid can be mentioned.

The dicarboxylic acids can be introduced in the polycondensation medium in an esterified form, for
5 example via methoxy or via ethoxy.

The preferred polyesters for carrying out the invention are, polyethylene terephthalate, polytrimethylene terephthalate, polybutylene terephthalate, polynaphtha-lene terephthalate,
10 copolymers and mixtures thereof.

The nanometrical mineral particles according to the invention confer improved mechanical properties to the composition relative to an identical composition not comprising said particles. The heat distortion under
15 load is noticeably improved.

The shape factor of a particle is defined as the ratio between the largest dimension and the smallest dimension of a particle. For example, if the particles are platelet-shaped, the shape factor is defined by
20 the ratio between the length of the platelets and their width. If the platelets are needle-shaped, their shape factor is defined by the ratio between the length of the needle and the cross-sectional diameter of the needle. If the particles have a substantially
25 spherical shape, the shape factor equals 1.

The particles according to the invention present a low shape factor, ranging between 1 and 10. The shape factor is preferably between 1 and 2.

By nanometric-sized particles, it is meant that the
30 small dimension is lower than 200 nm, and the large parameter is lower than 2000 nm, preferably lower than 400 nm. According to a preferred embodiment, the small dimension is lower than 100 nm and the large dimension is lower than 200 nm.

35 According to an advantageous embodiment of the

invention, the particles are substantially spherical-shaped with an average diameter lower than or equal to 200 nm. The average diameter preferably ranges between 5 and 100 nm.

- 5 The mineral particles are preferably chosen from metal oxide-based particles, for example, silica, titanium dioxide, alumina, zirconia. It may comprise a surface treatment or coating. Such treatments are meant, for example, to improve the particle dispersion in the
- 10 polymer, to protect the particles against deterioration, or to protect the polymer from degradations through contact with the particles. All the known surface treatments and coatings known in the field of polymer fillers, particularly those known and
- 15 used as fillers having dimensions above those referring to the invention, can be used. One can use, for example, titanium dioxide particles partially or fully coated with a silica-based compound.
- Silica-based particles are particularly adequate for
- 20 carrying out the invention. Any type of known silica can be employed in the polyester-based compositions. For example, fumed silicas, combustion silicas, precipitated silicas, silica sols. The use of sols is particularly adequate for the obtention of a
- 25 composition having a good particle dispersion.
- The weighted concentration of particles in the composition ranges between 0,1 and 20%. It preferably ranges between 5 and 15%.
- Any method for introducing a compound into a
- 30 composition may be employed. A first method consists in introducing the particles into the polyester reaction medium, usually before the polymerization has begun. The polymerization is then carried out in the presence of the particles. The particles can be
- 35 introduced as a powder or as a dispersion into a

liquid medium.

A second method consists in introducing the particles as a powder into the molten polyester and then shearing the mixture in order to obtain a homogeneous dispersion. This operation can for example be carried out by means of an extruder, single or twin screw.

A third method consists in introducing the particles as a master batch in the molten polyester. The blending can be effected by any of the above-mentioned methods. The introduction of the master batch in the polymer can be effected by means of an extruder.

According to a particularly advantageous embodiment of the invention, the particles are introduced as a sol into the polymer reaction medium. The sol can be for example an aqueous or glycolic sol. Silica sols are particularly adequate for this embodiment.

A process to prepare the compositions according to this embodiment comprises for example the following steps:

- a) Introducing in a mixture with water at least one diol with at least one dicarboxylic acid or a dicarboxylic acid ester of a silica sol where the particles have an average diameter smaller than or equal to 200 nm
- b) Esterifying or transesterifying the acid or the acid ester with the diol,
- c) Polycondensing under vacuum the esterification product,
- d) Forming the final product.

Except for the introduction of the silica sol into the monomer mixture, the process for producing the compositions is classical. Processes are described for example in Les techniques de l'ingénieur J 6 020, 2151-2160. The process is in no way the object of any limitation of the scope of the invention.

Esterification or transesterification step b) is a step commonly carried out within the industrial polyester manufacturing procedures. For example, two routes are mainly employed for producing poly(ethylene terephthalate).

The first obtention route is the so called "methyl terephthalate" (DMT) route. It comprises a transesterification reaction. Molten DMT is solubilized in ethylene glycol (EG) present in excess, the molar ratio of EG/DMT being of about 1,9 to 2,2, and the reaction is conducted at atmospheric pressure and temperatures of about 130°C to 250°C. The presence of a catalyst, for example manganese acetate, is necessary. Methanol released during the reaction is eliminated through distillation. The ethylene glycol present in excess is eliminated through evaporation after the transesterification reaction. The catalyst, which is also a polyester degradation catalyst, is blocked by means of phosphorous compounds after the reaction. The product resulting from the transesterification is a blend of bis-hydroxyethyl-terephthalate (BHET) and oligomers.

The second route is the so called "direct esterification". It comprises an esterification reaction between terephthalic acid and ethylene glycol. It is carried out at temperatures of 130°C to 280°C. Terephthalic acid, molten at such temperatures is not soluble in ethylene glycol but is in the ester product of the reaction. The solubilization of the reactant in the medium is however progressive. Ethylene glycol is present at a molar ratio of EG/terephthalic acid of about 1 to 1,5. From this reaction results a mixture of oligomers having terephthalic acid or hydroxyethyl terephthalate.

The utilization of these processes has been the object

of numerous studies described in literature. The conditions indicated hereabove should not be regarded as limiting the scope of the present invention.

The subsequent polycondensation steps are usually catalyzed through metallic compounds, for example antimonium, titanium or germanium compounds. They can be catalyzed by any polyester polycondensation catalyst. They are usually carried out at low pressures, in order to favor the elimination of ethylene glycol formed during the condensation reaction.

The polymer is then formed into the final product, for example by extruding a strand through an orifice, cooling, and granulating. The formation is usually preceded by a molten phase filtration. The molten phase polycondensation and final product formation steps can be followed by a solid phase post-condensation step.

The compositions, for example in a granulated form, can be formed into molded articles. They can more particularly be used in the form of bottles. All the processes for manufacturing bottles from thermoplastic polymers are adequate for the invention. The extrusion-blow molding process is in general preferred.

The bottles thus produced can be filled with liquids at high temperatures and/or with liquids remaining hot in the bottle during long periods of time.

Other details or advantages of the presente invenção will become more apparent from the following examples, set forth for indicative purposes only.

Different polyester-based compositions were synthesized, the following characteristics of which are measured:

- Viscosity index (VI, in ml/g); measured according to

ISO 1628/5 standard; measured in a solution of 0,5% of the composition in a 50/50 by weight mixture of phenol/orthodichlorobenzene, at 25°C. The polymer concentration used for the calculations of the

5 viscosity index is the actual polymer concentration, considering the presence of particles in the composition.

- Molecular mass in absolute weight (g/mole); determined by Gel Permeation Chromatography (GPC).

10 - Color according to the CIE lab system: measurements of L^* , a^* , b^* .

- Thermomechanical properties: modulus at 23°C, Modulus at 160°C, Glass transition temperature (T_g). Dynamical measurements (Dynamical mechanic analysis)

15 on an RSA apparatus, using 40*4*2 mm samples, after drying and crystallization at 130°C under vacuum during 16 hours.

- Heat distortion under load (HDT), evaluated according to ISO 75-2 standard.

20 - Crystallization: the dry polymer is plastified at 290°C such as to destroy any crystallization germ. The molten product is injected in a series of molds where the thickness varies progressively whereby to obtain plates at thicknesses between 2 and 6 mm. The mold

25 wall temperature is adjusted at 37°C. The thickness at which a slight disturbance corresponding to the beginning of crystallization occurs is registered.

Example 1

Into a 7,5 liter polymerization reactor, permitting

30 the obtention of 3 kg of polymer through polycondensation, equipped with an agitator provided with a torsionmeter to monitor the viscosity of the reaction medium, several introduction sieves, a distillation column to eliminate water formed during

35 the esterification, as well as the excess of ethylene

glycol, and a vacuum circuit for the polycondensation step, the following are loaded:

- 2656 g of terephthalic acid (16,0 moles)
- 1190 g of ethylene glycol (19,2 moles)
- 5 - 384 g of an aqueous sol of 50 nm diameter nanoparticles of silica, commercialized by Hoechst under the tradename Klebosol[®] 40R50, corresponding to 143,6 g of silica.

After a nitrogen purge, the reaction medium is heated
10 to 275°C under agitation and under 6,6 bar absolute pressure.

The esterification period is defined as the necessary time for the distillation of the water.

The esterification time is 66 minutes.

15 The pressure is then brought to atmospheric pressure along a period of 20 minutes.

A solution of antimony oxide is introduced into the reaction medium (250 ppm antimony, based on the polymer).

20 The pressure is maintained during 20 minutes at atmospheric pressure, before a progressive application of vacuum from 1 bar to less than 1 mm mercury along a period of 90 minutes. The distillation column is then bypassed for direct vacuum to be applied as soon as

25 the pressure reaches 20 mm mercury.

The reaction mass is brought to 285°C as soon as the pressure goes under 1 mm mercury.

The polycondensation time is defined as the time required to reach the desired viscosity level parting
30 from the moment where pressure is under 1 mm mercury.

The polycondensation time is 32 minutes.

Once the desired viscosity level is attained, agitation is interrupted and the reactor is pressurized to 3 bar to discharge and granulate the
35 obtained polymer.

The polymer granules are dried during 15 hours at 50°C.

Photographs taken with an Electronic Transmission Microscope are shown in figure 1. Photo 1 is taken at
5 an about $2 \cdot 10^4$ magnification and photo 2 is magnified at about 10^5 .

Example 2 (comparative example)

A polymer is prepared according to example 1, except that the nanoparticles of silica are not added.

10 The esterification time is 54 minutes.

The polycondensation time is 67 minutes.

Example 3

A polymer is prepared according to example 1, except that the aqueous silica particle sol is added together
15 with the antimonium oxide solution.

The esterification time is 87 minutes.

The polycondensation time is 59 minutes.

Example 4

A polymer is prepared according to example 1, except
20 that instead of the 2656 g of terephthalic acid, the following is added:

- 2592 g of terephthalic acid

- 63,7 g of isophthalic acid (corresponding to 2,4 mole% of the amount of acid)

25 The esterification time is 65 minutes.

The polycondensation time is 59 minutes.

Example 5

A polymer is prepared according to example 1, except that the aqueous silica particle sol is an aqueous sol
30 of 25 nm diameter silica nanoparticles, commercialized by Hoechst under the tradename Klebosol® 40R50.

The esterification time is 68 minutes.

The polycondensation time is 32 minutes.

Example 4

35 A polymer is prepared according to example 1, except

that the following compounds are added:

- 2592 g of terephthalic acid
- 63,7 g of isophthalic acid (corresponding to 2,4 mole% of the amount of acid)
- 5 - 37 g of ethylene glycol
- 1306 g of a glycolic silica sol at 11,8 % by weight silica, the sol being synthesized through a Stöber type process, the silica particles having a 50 nm diameter.
- 10 The esterification time is 54 minutes.
- The polycondensation time is 73 minutes.

Example 7

- A polymer is prepared according to example 1, except that instead of the 2656 g of terephthalic acid, the
- 15 following is added:
 - 2497 g of terephthalic acid
 - 159 g of isophthalic acid (corresponding to 6 mole% of the amount of acid)
- The esterification time is 61 minutes.
- 20 The polycondensation time is 68 minutes.
- The features of the compositions according to examples 1 through 7 are shown in table I.

Table I

Ex.	VI (ml/g)	Mw g/mole	l*	a*	b*	HDT	Modulus 23°C (Mpa)	Modulus 160°C (Mpa)	Tg (Mpa)	Crystal- lization (mm)
1	67,0	37900	54	-0,4	67°C	1165	82	107		
2	79,5		72	-0,9	59	988	61	99	4	
3	72,1	41000	75	-1,0						
4	71,1		66	-2,3					3	
5	62,4	33700	59	-1,5	67	1195	88	107		
6	68,5		78	-2,7		1015	65	103	4,5	
7	74,8		71,0	-0,7					6	

Example 8

100 kg of a composition are prepared according to example 4 in a double vessel reactor at 200°C, with 1,9 mole% isophthalic acid.

5 Example 9

A composition is prepared according to example 8, except that the nanoparticles of silica are not added. The compositions of examples 8 and 9 are molded into bottles, through injection/blowing in an integrated
10 ABS F100 machine. The preforms weigh 32 g, the bottles have a 600 ml capacity.

A hot-filling test is carried out on these bottles; the bottles are filled at different temperatures and the their volume variation is measured. The higher the
15 variation, worse is the composition.

Table II shows the filling temperature (°C) and the deformation (ml) for a bottle obtained from the compositions according to examples 8 and 9.

Table II

Temperature	Example 8	Example 9
70	76,6	50,6
75	109,6	70,3
80	149,1	129,1
85	205,8	176,6

CLAIMS

1. Polyester-based composition having improved thermomechanical properties, characterized by comprising a polyester-based matrix and nanometrical-sized mineral particles, having a shape factor comprised between 1 and 10, at a weighted concentration within 0,01 and 25%.
2. Composition, according to claim 1, characterized in that the particles are substantially spherical-shaped having a diameter under or equal to 200 nm.
3. Composition, according to claim 2, characterized in that the average diameter of the particles is comprised between 5 and 100 nm.
4. Composition, according to any one of the preceding claims, characterized in that the particles are based on metal oxides.
5. Composition, according to claim 4, characterized in that the particles are based on a compound selected from silica, titanium dioxide, zirconia, alumina.
6. Composition, according to claim 5, characterized in that the particles are based on silica and that the composition is obtained by introducing a silica sol within the polyester synthesis medium.
7. Composition, according to claim 6, characterized in that the silica sol is an aqueous or glycolic sol.
8. Composition, according to any one of the preceding claims, characterized in that the polyester is selected from polyethylene terephthalate, polytrimethylene terephthalate, polybutylene terephthalate, polynaphthalene terephthalate, mixtures and copolymers based on these polyesters.
9. Composition, according to any one of the preceding claims, characterized in that the polyester contains an amorphing agent.
10. Composition, according to claim 9, characterized

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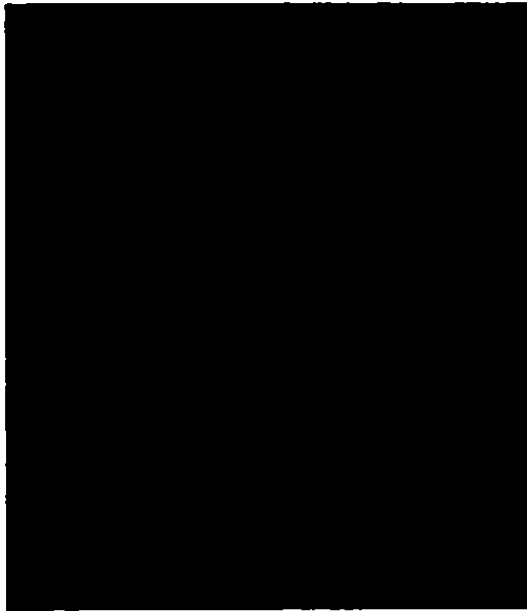


PHOTO 1

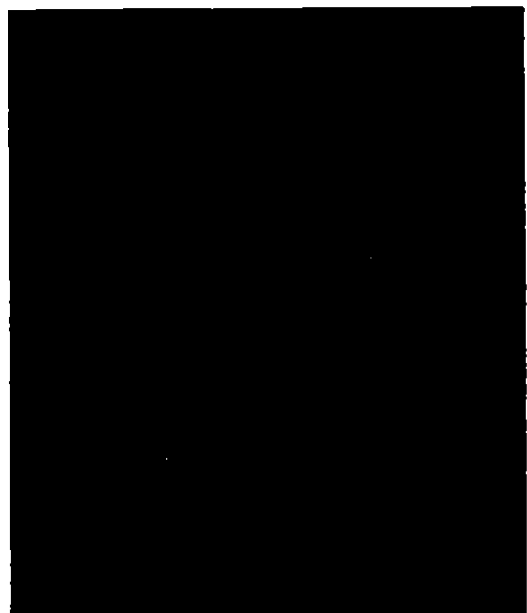


PHOTO 2

INTERNATIONAL SEARCH REPORT

International Application No

PCT/BR 01/00030

35

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 0401689	A	12-12-1990	JP	2856283 B	10-02-1999
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			KR	9604479 B	06-04-1996
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			EP	0932497 A	04-08-1999
			US	5972448 A	26-10-1999

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/BR 01/00030

36

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K3/22 C08K3/36 C08K7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 401 689 A (DIAFOIL CO LTD) 12 December 1990 (1990-12-12) claims 1-6	1-16
A	DATABASE WPI Section Ch, Week 200008 Derwent Publications Ltd., London, GB; Class A23, AN 2000-092715 XP002152079 & JP 11 335542 A (TEIJIN LTD), 7 December 1999 (1999-12-07) abstract	1-16
A	WO 98 01346 A (LAURENT JACQUES ;TETRA LAVAL HOLDINGS & FINANCE (CH); FRISK PETER) 15 January 1998 (1998-01-15) claims 1-9	1-16

☐ Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claims or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document relating to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "S" document member of the same patent family

Date of the actual completion of the international search

4 July 2001

Date of mailing of the international search report

12/07/2001

Name and mailing address of the ISA

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Siemens, T

PAT. NO 01 / 0 0 0 30

"POLYESTER-BASED COMPOSITIONS HAVING IMPROVED THERMOMECHANICAL PROPERTIES AND PROCESS TO PRODUCE SAID COMPOSITIONS".

The present invention refers to polyester-based
5 compositions presenting improved thermomechanical properties, comprising fine sized mineral particles. These compositions are especially useful for manufacturing bottles. The present invention further refers to a process to produce such compositions.

10 Polyesters, especially polyethylene terephthalate, are thermoplastic polymers widely used for the production of molded or extruded articles. They are generally employed as yarns or fibers, injection molded articles, films (extruded and drawn articles) or
15 vessels for example obtained through an extrusion-blow process. The properties of the articles produced are greatly dependent on the thermomechanical properties of the polymer, such as the modulus, the flexibility, the glass transition temperature, the heat distortion
20 under load.

The heat distortion under load is an important feature for the use of polyesters as bottles, more particularly for bottles meant to contain beverages. For preservation and food hygiene purposes, certain
25 beverages must be hot-filled into the bottles, and eventually in the absence of oxygen. This is particularly the case for fruit juices, pasteurized or sterilized products, especially dairy products, tea or coffee beverages, beer. If the filling temperature is
30 too high, and/or if the liquid remains too long in the bottle over a certain temperature, the latter deforms. This shortcoming can limit the field of use of the polyester, and particularly of polyethylene terephthalate, for containing beverages. Hence,
35 certain beverages cannot be disposed in polyethylene

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terephthalate bottles, or cannot except under limited temperature conditions.

Continuous attempts are being made to elaborate polyesters, polyester-based compositions or processes for forming polyester articles, such that thermomechanical properties are improved, particularly such that the heat distortion under load is improved. Therefor, a first solution may consist in utilizing a polyethylene naphthalate instead of a polyethylene terephthalate, or copolymers comprising naphthalic and terephthalic units. This solution is however costly, and is not industrially used except for very specific applications.

Another solution consists in modifying the process of forming the bottles in order to over-crystallize the polymer. The process according to this solution is generally called "thermofixing". In short, it consists in crystallizing a polyethylene terephthalate bottle by modifying the blowing operations. The carrying out of this process requires however an important modification of the bottle production lines and hence requires important investments. The necks of the bottles obtained according to this process are crystallized and thus lose their transparency. This may constitute a visual defect.

The object of the present invention is to propose fillers which may be utilized to improve thermomechanical properties of polyesters, especially easily incorporable fillers, well dispersed in the matrix. It is a further object to propose a process to produce polyester-based compositions presenting improved thermomechanical properties.

To this avail, the present invention proposes a polyester-based composition characterized in that it comprises a polyester-based matrix and nanometrical-

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sized mineral particles, the shape factor ranging between 1 and 10, at a weighted concentration ranging between 0,01% and 25%.

The matrix of the composition may be full polyester-based. It may be constituted of a single polymer, the polyester, or of a polymer blend where at least one main component is a polyester. It may also consist of, as an amorphous agent, a copolymer where most of the repeating units comprise ester functions.

10 Polyesters adequate for carrying out the invention are generally obtained through polycondensation of diols and dicarboxylic acids or esters of dicarboxylic acids.

Among the diols adequate to carry out the invention,
15 ethylene glycol, diethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,3-butanediol, 2,2-dimethylpropanediol, neopentyl glycol, 1,5-pentanediol, 1,2-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,4-cyclohexanedimethanol, 1,5-cyclohexanedimethanol, 1,2-cyclohexanedimethanol, or
20 mixtures thereof can be mentioned.

Among the dicarboxylic acids adequate for carrying out the invention, terephthalic acid, isophthalic acid, orthophthalic acid, 2,5-naphthalene dicarboxylic acid,
25 2,6-naphthalene dicarboxylic acid, 1,3-naphthalene dicarboxylic acid, 2,7-naphthalene dicarboxylic acid, methyl terephthalic acid, 4,4'-diphenyldicarboxylic acid, 2,2'-diphenyldicarboxylic acid, 4,4'-diphenylether dicarboxylic acid, 4,4'-
30 diphenylmethanedicarboxylic acid, 4,4'-diphenylsulfonedicarboxylic acid, 4,4'-diphenylisopropylidene-dicarboxylic acid, sulfo-5-isophthalic acid, oxalic acid, succinic acid, adipic acid, sebacic acid, azelaic acid, dodecanedicarboxylic acid, dimer
35 acid, maleic acid, fumaric acid, and all aliphatic

diacids, cyclohexane dicarboxylic acid can be mentioned.

The dicarboxylic acids can be introduced in the polycondensation medium in an esterified form, for example via methoxy or via ethoxy.

The preferred polyesters for carrying out the invention are, polyethylene terephthalate, polytrimethylene terephthalate, polybutylene terephthalate, polynaphthalene terephthalate, copolymers and mixtures thereof.

The nanometrical mineral particles according to the invention confer improved mechanical properties to the composition relative to an identical composition not comprising said particles. The heat distortion under load is noticeably improved.

The shape factor of a particle is defined as the ratio between the largest dimension and the smallest dimension of a particle. For example, if the particles are platelet-shaped, the shape factor is defined by the ratio between the length of the platelets and their width. If the platelets are needle-shaped, their shape factor is defined by the ratio between the length of the needle and the cross-sectional diameter of the needle. If the particles have a substantially spherical shape, the shape factor equals 1.

The particles according to the invention present a low shape factor, ranging between 1 and 10. The shape factor is preferably between 1 and 2.

By nanometric-sized particles, it is meant that the small dimension is lower than 200 nm, and the large parameter is lower than 2000 nm, preferably lower than 400 nm. According to a preferred embodiment, the small dimension is lower than 100 nm and the large dimension is lower than 200 nm.

According to an advantageous embodiment of the

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invention, the particles are substantially spherical-shaped with an average diameter lower than or equal to 200 nm. The average diameter preferably ranges between 5 and 100 nm.

- 5 The mineral particles are preferably chosen from metal oxide-based particles, for example, silica, titanium dioxide, alumina, zirconia. It may comprise a surface treatment or coating. Such treatments are meant, for example, to improve the particle dispersion in the
- 10 polymer, to protect the particles against deterioration, or to protect the polymer from degradations through contact with the particles. All the known surface treatments and coatings known in the field of polymer fillers, particularly those known and
- 15 used as fillers having dimensions above those referring to the invention, can be used. One can use, for example, titanium dioxide particles partially or fully coated with a silica-based compound.
- 20 Silica-based particles are particularly adequate for carrying out the invention. Any type of known silica can be employed in the polyester-based compositions. For example, fumed silicas, combustion silicas, precipitated silicas, silica sols. The use of sols is particularly adequate for the obtention of a
- 25 composition having a good particle dispersion. The weighted concentration of particles in the composition ranges between 0,1 and 20%. It preferably ranges between 5 and 15%.
- 30 Any method for introducing a compound into a composition may be employed. A first method consists in introducing the particles into the polyester reaction medium, usually before the polymerization has begun. The polymerization is then carried out in the presence of the particles. The particles can be
- 35 introduced as a powder or as a dispersion into a

liquid medium.

A second method consists in introducing the particles as a powder into the molten polyester and then shearing the mixture in order to obtain a homogeneous dispersion. This operation can for example be carried out by means of an extruder, single or twin screw.

A third method consists in introducing the particles as a master batch in the molten polyester. The blending can be effected by any of the above-mentioned methods. The introduction of the master batch in the polymer can be effected by means of an extruder.

According to a particularly advantageous embodiment of the invention, the particles are introduced as a sol into the polymer reaction medium. The sol can be for example an aqueous or glycolic sol. Silica sols are particularly adequate for this embodiment.

A process to prepare the compositions according to this embodiment comprises for example the following steps:

- 20 a) Introducing in a mixture with water at least one diol with at least one dicarboxylic acid or a dicarboxylic acid ester of a silica sol where the particles have an average diameter smaller than or equal to 200 nm
- 25 b) Esterifying or transesterifying the acid or the acid ester with the diol,
- c) Polycondensing under vacuum the esterification product,
- d) Forming the final product.

30 Except for the introduction of the silica sol into the monomer mixture, the process for producing the compositions is classical. Processes are described for example in Les techniques de l'ingénieur J 6 020, 2151-2160. The process is in no way the object of any
35 limitation of the scope of the invention.

Esterification or transesterification step b) is a step commonly carried out within the industrial polyester manufacturing procedures. For example, two routes are mainly employed for producing poly(ethylene terephthalate).

The first obtention route is the so called "methyl terephthalate" (DMT) route. It comprises a transesterification reaction. Molten DMT is solubilized in ethylene glycol (EG) present in excess, the molar ratio of EG/DMT being of about 1,9 to 2,2, and the reaction is conducted at atmospheric pressure and temperatures of about 130°C to 250°C. The presence of a catalyst, for example manganese acetate, is necessary. Methanol released during the reaction is eliminated through distillation. The ethylene glycol present in excess is eliminated through evaporation after the transesterification reaction. The catalyst, which is also a polyester degradation catalyst, is blocked by means of phosphorous compounds after the reaction. The product resulting from the transesterification is a blend of bis-hydroxyethyl-terephthalate (BHET) and oligomers.

The second route is the so called "direct esterification". It comprises an esterification reaction between terephthalic acid and ethylene glycol. It is carried out at temperatures of 130°C to 280°C. Terephthalic acid, molten at such temperatures is not soluble in ethylene glycol but is in in the ester product of the reaction. The solubilization of the reactant in the medium is however progressive. Ethylene glycol is present at a molar ratio of EG/terephthalic acid of about 1 to 1,5. From this reaction results a mixture of oligomers having terephthalic acid or hydroxyethyl terephthalate.

The utilization of these processes has been the object

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of numerous studies described in literature. The conditions indicated hereabove should not be regarded as limiting the scope of the present invention.

5 The subsequent polycondensation steps are usually catalyzed through metallic compounds, for example antimony, titanium or germanium compounds. They can be catalyzed by any polyester polycondensation catalyst. They are usually carried out at low pressures, in order to favor the elimination of
10 ethylene glycol formed during the condensation reaction.

The polymer is then formed into the final product, for example by extruding a strand through an orifice, cooling, and granulating. The formation is usually
15 preceded by a molten phase filtration. The molten phase polycondensation and final product formation steps can be followed by a solid phase post-condensation step.

The compositions, for example in a granulated form,
20 can be formed into molded articles. They can more particularly be used in the form of bottles. All the processes for manufacturing bottles from thermoplastic polymers are adequate for the invention. The extrusion-blow molding process is in general
25 preferred.

The bottles thus produced can be filled with liquids at high temperatures and/or with liquids remaining hot in the bottle during long periods of time.

Other details or advantages of the presente invenção
30 will become more apparent from the following examples, set forth for indicative purposes only.

Different polyester-based compositions were synthesized, the following characteristics of which are measured:

35 - Viscosity index (VI, in ml/g); measured according to

ISO 1628/5 standard; measured in a solution of 0,5% of the composition in a 50/50 by weight mixture of phenol/orthodichlorobenzene, at 25°C. The polymer concentration used for the calculations of the viscosity index is the actual polymer concentration, considering the presence of particles in the composition.

- Molecular mass in absolute weight (g/mole); determined by Gel Permeation Chromatography (GPC).
- 10 - Color according to the CIE lab system: measurements of L^* , a^* , b^* .
- Thermomechanical properties: modulus at 23°C, Modulus at 160°C, Glass transition temperature (T_g). Dynamical measurements (Dynamical mechanic analysis) on an RSA apparatus, using 40*4*2 mm samples, after drying and crystallization at 130°C under vacuum during 16 hours.
- Heat distortion under load (HDT), evaluated according to ISO 75-2 standard.
- 20 - Crystallization: the dry polymer is plastified at 290°C such as to destroy any crystallization germ. The molten product is injected in a series of molds where the thickness varies progressively whereby to obtain plates at thicknesses between 2 and 6 mm. The mold wall temperature is adjusted at 37°C. The thickness at which a slight disturbance corresponding to the beginning of crystallization occurs is registered.

Example 1

Into a 7,5 liter polymerization reactor, permitting the obtention of 3 kg of polymer through polycondensation, equipped with an agitator provided with a torsionmeter to monitor the viscosity of the reaction medium, several introduction sieves, a distillation column to eliminate water formed during the esterification, as well as the excess of ethylene

glycol, and a vacuum circuit for the polycondensation step, the following are loaded:

- 2656 g of terephthalic acid (16,0 moles)

- 1190 g of ethylene glycol (19,2 moles)

- 5 - 384 g of an aqueous sol of 50 nm diameter nanoparticles of silica, commercialized by Hoechst under the tradename Klebosol® 40R50, corresponding to 143,6 g of silica.

10 After a nitrogen purge, the reaction medium is heated to 275°C under agitation and under 6,6 bar absolute pressure.

The esterification period is defined as the necessary time for the distillation of the water.

The esterification time is 66 minutes.

- 15 The pressure is then brought to atmospheric pressure along a period of 20 minutes.

A solution of antimony oxide is introduced into the reaction medium (250 ppm antimony, based on the polymer).

- 20 The pressure is maintained during 20 minutes at atmospheric pressure, before a progressive application of vacuum from 1 bar to less than 1 mm mercury along a period of 90 minutes. The distillation column is then bypassed for direct vacuum to be applied as soon as
25 the pressure reaches 20 mm mercury.

The reaction mass is brought to 285°C as soon as the pressure goes under 1 mm mercury.

- The polycondensation time is defined as the time required to reach the desired viscosity level parting
30 from the moment where pressure is under 1 mm mercury.

The polycondensation time is 32 minutes.

- Once the desired viscosity level is attained, agitation is interrupted and the reactor is pressurized to 3 bar to discharge and granulate the
35 obtained polymer.

The polymer granules are dried during 15 hours at 50°C.

Photographs taken with an Electronic Transmission Microscope are shown in figure 1. Photo 1 is taken at an about 2.10^4 magnification and photo 2 is magnified at about 10^5 .

Example 2 (comparative example)

A polymer is prepared according to example 1, except that the nanoparticles of silica are not added.

10 The esterification time is 54 minutes.

The polycondensation time is 67 minutes.

Example 3

A polymer is prepared according to example 1, except that the aqueous silica particle sol is added together with the antimonium oxide solution.

15 The esterification time is 87 minutes.

The polycondensation time is 59 minutes.

Example 4

A polymer is prepared according to example 1, except that instead of the 2656 g of terephthalic acid, the following is added:

- 2592 g of terephthalic acid
- 63,7 g of isophthalic acid (corresponding to 2,4 mole% of the amount of acid)

25 The esterification time is 65 minutes.

The polycondensation time is 59 minutes.

Example 5

A polymer is prepared according to example 1, except that the aqueous silica particle sol is an aqueous sol of 25 nm diameter silica nanoparticles, commercialized by Hoechst under the tradename Klebosol® 40R50.

30 The esterification time is 68 minutes.

The polycondensation time is 32 minutes.

Example 4

35 A polymer is prepared according to example 1, except

that the following compounds are added:

- 2592 g of terephthalic acid
- 63,7 g of isophthalic acid (corresponding to 2,4 mole% of the amount of acid)

- 5 - 37 g of ethylene glycol
- 1306 g of a glycolic silica sol at 11,8 % by weight silica, the sol being synthesized through a Stöber type process, the silica particles having a 50 nm diameter.

- 10 The esterification time is 54 minutes.
 The polycondensation time is 73 minutes.

Example 7

- (A polymer is prepared according to example 1, except that instead of the 2656 g of terephthalic acid, the
- 15 following is added:

- 2497 g of terephthalic acid
- 159 g of isophthalic acid (corresponding to 6 mole% of the amount of acid)

 The esterification time is 61 minutes.

- 20 The polycondensation time is 68 minutes.
 The features of the compositions according to examples 1 through 7 are shown in table I.

Table I

Ex.	VI (ml/g)	Mw g/mole	l*	a*	b*	HDT	Modulus 23°C (Mpa)	Modulus 160°C (Mpa)	Tg (Mpa)	Crystal- lization (mm)
1	67,0	37900	54	-0,4	67°C	1165	82	107		
2	79,5		72	-0,9	59	988	61	99	4	
3	72,1	41000	75	-1,0						
4	71,1		66	-2,3					3	
5	62,4	33700	59	-1,5	67	1195	88	107		
6	68,5		78	-2,7		1015	65	103	4,5	
7	74,8		71,0	-0,7					6	

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Example 8

100 kg of a composition are prepared according to example 4 in a double vessel reactor at 200°C, with 1,9 mole% isophthalic acid.

5 Example 9

A composition is prepared according to example 8, except that the nanoparticles of silica are not added. The compositions of examples 8 and 9 are molded into bottles, through injection/blowing in an integrated
10 ABS F100 machine. The preforms weigh 32 g, the bottles have a 600 ml capacity.

A hot-filling test is carried out on these bottles; the bottles are filled at different temperatures and the their volume variation is measured. The higher the
15 variation, worse is the composition.

Table II shows the filling temperature (°C) and the deformation (ml) for a bottle obtained from the compositions according to examples 8 and 9.

Table II

Temperature	Example 8	Example 9
70	76,6	50,6
75	109,6	70,3
80	149,1	129,1
85	205,8	176,6

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CLAIMS

1. Polyester-based composition having improved thermomechanical properties, characterized by comprising a polyester-based matrix and nanometrical-sized mineral particles, having a shape factor comprised between 1 and 10, at a weighted concentration within 0,01 and 25%.
5
2. Composition, according to claim 1, characterized in that the particles are substantially spherical-shaped having a diameter under or equal to 200 nm.
10
3. Composition, according to claim 2, characterized in that the average diameter of the particles is comprised between 5 and 100 nm.
4. Composition, according to any one of the preceding claims, characterized in that the particles are based on metal oxides.
15
5. Composition, according to claim 4, characterized in that the particles are based on a compound selected from silica, titanium dioxide, zirconia, alumina.
6. Composition, according to claim 5, characterized in that the particles are based on silica and that the composition is obtained by introducing a silica sol within the polyester synthesis medium.
20
7. Composition, according to claim 6, characterized in that the silica sol is an aqueous or glycolic sol.
25
8. Composition, according to any one of the preceding claims, characterized in that the polyester is selected from polyethylene terephthalate, polytrimethylene terephthalate, polybutylene terephthalate, polynaphthalene terephthalate, mixtures and copolymers based on these polyesters.
30
9. Composition, according to any one of the preceding claims, characterized in that the polyester contains an amorphing agent.
- 35 10. Composition, according to claim 9, characterized

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in that the amorphing agent is a comonomer of the polyester.

11. Composition, or process according to claim 10, characterized in that the comonomer is selected from

5 isophthalic acid, 1,4-cyclohexanedimethanol, diethylene glycol, mixtures thereof, and wherein it represents between 1 and 20 moles% of the repeating units in the polyester.

12. Process to produce a polyester-based composition, as defined in any one of the preceding claims, characterized by comprising the following steps:

a) Introducing in a mixture with water at least one diol with at least one dicarboxylic acid or a dicarboxylic acid ester of a silica sol where the
15 particles have an average diameter smaller than or equal to 200 nm

b) Esterifying or transesterifying the acid or the acid ester with the diol,

c) Polycondensing under vacuum the esterification
20 product,

d) Forming the final product.

13. Process, according to claim 12, characterized in that step c) is carried out in the presence of an antimonium- or titanium-based catalyst.

25 14. Article, characterized by being obtained by forming from compositions as defined in any one of the preceding claims.

15. Bottles, characterized by being obtained by forming from compositions as defined in any one of the
30 preceding claims.

16. Process for hot-filling polyethylene terephthalate bottles with a liquid, characterized in that the bottles are produced from compositions as defined in any one of claims 1 through 13.

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ABSTRACT

"POLYESTER-BASED COMPOSITIONS HAVING IMPROVED THERMOMECHANICAL PROPERTIES AND PROCESS TO PRODUCE SAID COMPOSITIONS".

5 The present invention refers to polyester-based compositions having improved thermomechanical properties, comprising finely divided mineral particles. These compositions are particularly useful for manufacturing bottles. The present invention
10 further refers to a process for producing said compositions. The compositions comprise a polyester-based matrix and nanometric-sized particles.

54

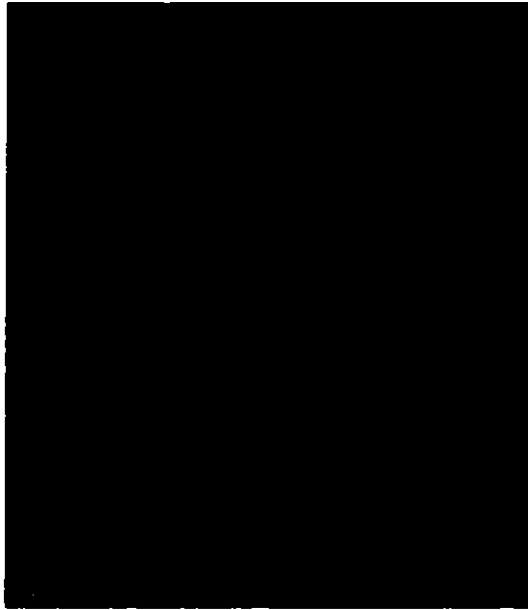


PHOTO 1

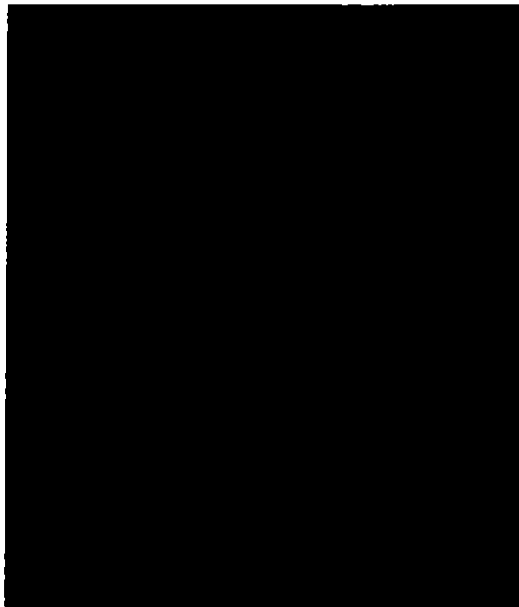


PHOTO 2

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BREVET D'INVENTION

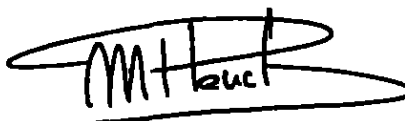
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Fait à Paris, le 12 AVRIL 2001

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TITRE DE L'INVENTION (200 caractères ou espaces maximum) COMPOSITIONS A BASE DE POLYESTERS PRESENTANT DES PROPRIETES THERMOMECHANQUES AMELIOREES ET PROCEDE DE FABRICATION DE CES COMPOSITIONS.			
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**COMPOSITIONS A BASE DE POLYESTERS PRESENTANT DES PROPRIETES
THERMOMECHANIQUES AMELIOREES ET PROCEDE DE FABRICATION DE CES
COMPOSITIONS.**

5 La présente invention concerne des compositions à base de polyester présentant des propriétés thermomécaniques améliorées, comportant des particules minérales de faible taille. Ces compositions sont notamment utiles pour la fabrication de bouteilles. La présente invention concerne également un procédé de fabrication de ces compositions.

10 Les polyesters, notamment le polyéthylène téréphtalate, sont des polymères thermoplastiques largement utilisés pour la réalisation d'articles moulés ou extrudés. Ils sont généralement utilisés sous forme de fils ou fibres, d'articles moulés à l'aide d'une presse à injecter, de films (articles extrudés et étirés) ou de récipients par exemple obtenus par un procédé d'extrusion-soufflage. Les propriétés des articles réalisés sont en grande partie liées aux propriétés thermomécaniques du polymère, telles que le module,
15 la ductilité, la température de transition vitreuse, la température de déformation sous charge.

20 La température de déformation sous charge est une caractéristique importante pour l'utilisation des polyesters sous forme de bouteilles, plus particulièrement pour des bouteilles destinées à contenir des boissons. Pour des raisons de conservation et d'hygiène alimentaire, certaines boissons doivent être remplies à chaud dans les bouteilles, et éventuellement en absence d'oxygène. C'est notamment le cas pour les jus de fruits, les produits pasteurisés ou stérilisés, notamment les produits laitiers, les boissons au thé ou au café, la bière. Si la température de remplissage est trop élevée, et/ou si le liquide reste trop longtemps dans la bouteille au delà d'une certaine
25 température, celle-ci est déformée. Cet inconvénient peut limiter le champ d'utilisation du polyester, en particulier du polyéthylène téréphtalate, pour contenir des boissons. Ainsi certaines boissons ne peuvent pas être conditionnées dans des bouteilles en polyéthylène téréphtalate, ou ne peuvent l'être que dans des conditions de température limitées.

30 On cherche donc toujours à élaborer des polyesters, des compositions à base de polyesters ou des procédés de mise en forme d'articles en polyesters, tels les propriétés thermomécaniques soient améliorées, en particulier tels que la température de déformation sous charge soit améliorée.

35 A cet effet, une première solution peut consister à utiliser un polyéthylène naphthalate en remplacement du polyéthylène téréphtalate, ou des copolymères comportant des unités naphthaliques et téréphtaliques. Cette solution est toutefois onéreuse, et elle n'est industriellement utilisée que pour des applications très spécifiques.

Une autre solution consiste à modifier le procédé de mise en forme des bouteilles afin de sur-cristalliser le polymère. Le procédé selon cette solution est généralement appelé "thermofixation". Brièvement, il consiste à cristalliser une bouteille en polyéthylène téréphtalate en modifiant les opérations de soufflage. La mise en œuvre de ce procédé
5 nécessite toutefois une importante modification des lignes de fabrication des bouteilles et nécessite donc d'importants investissements. Le col des bouteilles obtenues selon ce procédé est cristallisé et perd donc sa transparence. Ceci peut constituer un défaut d'aspect.

La présente invention a pour objectif de proposer des charges pouvant être
10 utilisées pour l'amélioration des propriétés thermomécaniques des polyesters, notamment des charges facilement incorporables, bien dispersées dans la matrice. Elle a également pour objectif de proposer un procédé de fabrication de compositions à base de polyester présentant des propriétés thermomécaniques améliorées.

A cet effet l'invention propose une composition à base de polyester caractérisée en
15 ce qu'elle comprend une matrice à base de polyester et des particules minérales de taille nanométrique, de facteur de forme compris entre 1 et 10, en concentration pondérale comprise entre 0,01% et 25%.

La matrice de la composition peut être à base de tout polyester. Elle peut être constituée d'un seul polymère, le polyester, ou d'un mélange de polymères dont au moins
20 un composant principal est un polyester. Elle peut aussi consister en un copolymère dont la majorité des motifs de répétition comprennent des fonctions ester.

Les polyesters convenables pour la réalisation de l'invention sont généralement obtenus par polycondensation à partir de diols et d'acides dicarboxyliques ou d'esters d'acides dicarboxyliques.

25 Parmi les diols convenables pour la réalisation de l'invention, on peut citer l'éthylène glycol, le propylène glycol, le 1,3-propanediol, le 1,4-butanediol, le 1,3-butanediol, le 2,2-diméthylpropanediol, le neopentyl-glycol, le 1,5-pentanediol, le 1,2-hexanediol, le 1,8-octanediol, le 1,10-decanediol, le 1,4-cyclohexanediméthanol, le 1,5-cyclohexanediméthanol, le 1,2-cyclohexanediméthanol, ou leurs mélanges.

30 Parmi les acides dicarboxyliques convenables pour la réalisation de l'invention on peut citer l'acide téréphtalique, l'acide isophtalique, l'acide orthophtalique, l'acide 2,5-naphtalène dicarboxylique, l'acide 2,6-naphtalène dicarboxylique, l'acide 1,3-naphtalène dicarboxylique, l'acide 2,7-naphtalène dicarboxylique, l'acide méthyle téréphtalique, l'acide 4,4'-diphényldicarboxylique, l'acide 2,2'-diphényldicarboxylique, l'acide 4,4'-
35 diphényletherdicarboxylique, l'acide 4,4'-diphénylméthanedicarboxylique, l'acide 4,4'-diphénylsulphonedicarboxylique, l'acide 4,4'-diphényl-isopropylidène-dicarboxylique, l'acide sulfo-5-isophtalique, l'acide oxallique, l'acide succinique, l'acide adiplique, l'acide

sébacique, l'acide azélaïque, l'acide dodécanedicarboxylique, l'acide dimer, l'acide maléique, l'acide fumarique et tous les diacides aliphatiques, l'acide cyclohexane dicarboxylique.

5 Les acides dicarboxyliques peuvent être introduits dans le milieu de polycondensation sous forme estérifiée, par exemple par un motif éthoxy ou par un motif méthoxy.

Les polyesters préférables pour la réalisation de l'invention sont le polyéthylène téréphtalate, le polytriméthylène téréphtalate, le polybutylène téréphtalate, le polyaphatalène téréphtalate, les copolymères et mélanges à base de ces polyesters.

10 Les particules minérales nanométriques selon l'invention confèrent à la composition des propriétés mécaniques améliorées par rapport à une composition identique ne comprenant pas lesdites particules. La température de déformation sous charge est notamment améliorée.

15 Le facteur de forme d'une particule est défini comme le rapport entre la plus grande dimension d'une particule et la plus petite dimension. Par exemple, si des particules ont une forme plaquettaire, le facteur de forme est défini par le rapport entre la longueur des plaquettes et leur épaisseur. Si des particules ont une forme d'aiguille, le facteur de forme est défini par le rapport entre la longueur de l'aiguille et le diamètre de la section transversale de l'aiguille. Si des particules ont une forme sensiblement sphérique, on considère que la grande dimension est de taille égale à la petite dimension, le facteur de
20 forme est égal à 1.

Les particules selon l'invention présentent un faible facteur de forme, compris entre 1 et 10. Le facteur de forme est de préférence compris entre 1 et 2.

25 Par particules de taille nanométrique, on entend que la petite dimension est inférieure à 200 nm, et que le grand paramètre de taille est inférieur 2000 nm, de préférence inférieur à 400 nm. Selon un mode de réalisation encore préférentiel, la petite dimension est inférieure à 100 nm et la grande dimension est inférieure à 200 nm.

30 Selon un mode de réalisation avantageux de l'invention les particules sont de forme sensiblement sphérique avec un diamètre moyen inférieur ou égal à 200 nm. Le diamètre moyen est plus préférentiellement compris entre 5 et 100 nm.

35 Les particules minérales sont de préférence choisies parmi les particules à base d'oxydes de métaux, par exemple la silice, le dioxyde de titane, l'alumine, la zircone. Elles peuvent comporter un traitement ou revêtement de surface. De tels traitements peuvent par exemple être destinés à améliorer la dispersion des particules dans le polymère, à protéger les particules d'une détérioration, ou à protéger le polymère de dégradations au contact des particules. Tous les traitements de surface et dépôts connus dans le domaine des charges pour polymères, et en particulier connus et utilisés pour des

charges de dimension supérieure à celles concernées par l'invention, peuvent être utilisés. On peut par exemple utiliser des particules de dioxyde de titane revêtues partiellement ou entièrement par un composé à base de silice.

5 Les particules à base de silice sont particulièrement adaptées à la mise en œuvre de l'invention. Tous les types de silices connus peuvent être utilisés dans les compositions à base de polyester. A titre d'exemple on peut citer les silices de pyrogénéation, les silices de combustion, les silices de précipitation, les sols de silice. L'utilisation des sols est particulièrement bien adaptée à l'obtention de composition présentant une bonne dispersion des particules.

10 La concentration pondérale en particules dans la composition est comprise entre 0,1 et 20%. Elle est de préférence comprise entre 5 et 15%.

Toutes les méthodes d'introduction d'un composé dans un polymère peuvent être utilisées. Une première méthode consiste à introduire les particules dans le milieu de synthèse du polyester, généralement avant que la polymérisation ait débuté. La polymérisation est par la suite mise en œuvre en présence des particules. Les particules
15 peuvent être introduites sous forme de poudre ou sous forme d'une dispersion dans un milieu liquide.

Une deuxième méthode consiste à introduire les particules sous forme de poudre dans du polyester fondu et à cisailier le mélange afin d'obtenir une dispersion uniforme.
20 Cette opération peut par exemple être réalisée à l'aide d'un dispositif d'extrusion, à simple ou double vis.

Une troisième méthode consiste à introduire les particules sous forme de mélange maître dans le polymère fondu. Le mélange maître peut être réalisé selon l'une des méthodes précédentes. L'introduction du mélange maître dans le polymère fondu peut
25 être réalisée à l'aide d'un dispositif d'extrusion.

Selon un mode de réalisation particulièrement avantageux de l'invention, les particules sont introduites sous forme de sol dans le milieu de synthèse du polyester. Le sol peut par exemple être un sol aqueux ou glycolique. Les sols de silices sont particulièrement adaptés à ce mode de réalisation.

30 Un procédé de préparation de compositions selon ce mode de réalisation comporte par exemple les étapes suivantes:

- a) Introduction dans un mélange d'au moins un diol avec au moins un acide dicarboxylique ou un ester d'acide dicarboxylique d'un sol de silice dont les
35 particules ont un diamètre moyen inférieur ou égal à 200 nm
- b) Estérification ou transestérification de l'acide ou de l'ester d'acide par le diol,
- c) Polycondensation sous vide du produit d'estérification,
- d) Mise en forme.

Mise a part l'introduction du sol de silice dans le mélange des monomères, le procédé de fabrication des compositions est classique. Des procédés sont par exemples décrit dans Les techniques de l'ingénieur J 6 020, 2151-2160. Le procédé ne fait l'objet d'aucune limitation à la portée de l'invention.

5 L'étape b) d'estérification ou de transestérification est une étape communément réalisée dans les procédés industriels de fabrication de polyesters. Deux voies sont par exemple principalement employées pour la fabrication de poly(éthylène téréphtalate).

10 La première voie d'obtention est la voie dite "téréphtalate de méthyle" (DMT). Il s'agit d'une réaction de transestérification. Le DMT fondu est solubilisé dans l'éthylène glycol (EG) présent en excès, le rapport molaire EG/DMT étant d'environ 1.9 à 2.2, et la réaction est menée à pression atmosphérique à des températures d'environ 130°C à 250°C. Elle nécessite la présence d'un catalyseur comme par exemple l'acétate de manganèse. Le méthanol dégagé par la réaction est éliminé par distillation. L'éthylène glycol présent en excès est éliminé par évaporation après la réaction de transestérification. Le catalyseur qui est aussi un catalyseur de la dégradation du polyester est bloqué à l'aide de composés phosphorés après la réaction. Le produit résultant de la transestérification est un mélange de bis-hydroxyéthyl-téréphtalate (BHET) et d'oligomères.

20 La deuxième voie est la voie dite "estérification directe". Il s'agit d'une réaction d'estérification de l'acide téréphtalique par l'éthylène glycol. Elle est effectuée à des températures de 130°C à 280°C. L'acide téréphtalique, fondu à ces températures, n'est pas soluble dans l'éthylène glycol mais l'est dans l'ester produit de la réaction. La solubilisation du réactif dans le milieu est donc progressive. L'éthylène glycol est présent avec un rapport molaire EG/Acide Téréphtalique d'environ 1 à 1,5. Il résulte de cette réaction un mélange d'oligomères ayant des fonctions de terminaison sous forme d'acide téréphtalique ou de téréphtalate d'hydroxyéthyle.

25 L'utilisation de ces procédés fait l'objet de nombreuses études décrites dans la littérature. Les conditions indiquées ci-dessus ne constituent pas une limitation à la portée de la présente invention.

30 Les étapes ultérieures de polycondensation sont généralement catalysées à l'aide de composés métalliques, par exemple par des composés de l'antimoine, du titane ou du germanium. Elles peuvent être catalysées par tout catalyseur de polycondensation des polyesters. Elle est généralement réalisée à pression réduite, afin de favoriser le départ de l'éthylène glycol formé au cours de la réaction de condensation.

35 Le polymère est ensuite mis en forme, par exemple par extrusion d'un jonc à travers un orifice, refroidissement, et granulation. La mise en forme est généralement précédée d'un filtrage en phase fondue. Les étapes de polycondensation en phase

fondue et de mise en forme peut être suivie d'une étape de post-condensation en phase solide.

Les compositions, par exemple sous forme de granulés, peuvent être mises en forme pour la réalisation d'articles moulés. Elles peuvent plus particulièrement être
5 utilisées sous forme de bouteilles. Tous les procédés de fabrication de bouteilles à partir de polymères thermoplastiques sont adaptés à l'invention. Le procédé de mise en forme par extrusion-soufflage est généralement préféré.

Les bouteilles ainsi réalisées peuvent être remplies par des liquides à haute température et/ou des liquides restant chaud dans la bouteille pendant un temps
10 prolongé.

D'autres détails ou avantages de l'invention apparaîtront plus clairement au vu des exemples donnés ci-dessous uniquement à titre indicatif.

On synthétise différentes compositions à base de polyester dont les caractéristiques suivantes sont mesurées:

- Indice de viscosité (IV, en ml/g): mesure selon la norme ISO 1628/5: mesure dans une solution de la composition à 0,5% dans un mélange phénol/orthodichlorobenzène 50/50 en poids, à 25°C. La concentration en polymère utilisée pour le calcul de l'indice de viscosité est la concentration réelle en polymère, tenant compte de la
15 présence des particules dans la composition.
- Masse moléculaire en poids absolue (g/mol): mesure par Chromatographie par perméation de gel (GPC)
- Coloration selon le système CIE lab: mesure de L^* , a^* , b^*
- Propriétés thermomécaniques : module à 23°C, Module à 160°C, Température de transition vitreuse (Tg). Mesure en dynamique (Dynamical mechanic analysis) sur un
20 appareil RSA, sur des éprouvettes de polymère de 40*4*2 mm, après séchage et cristallisation à 130°C sous vide pendant 16 heures.
- Température de déformation sous charge (HDT), évaluée selon la norme ISO 75-2.
- 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
25 entre 2 et 6 mm. La température des parois du moule est conditionnée à 37°C. On

note à quelle épaisseur e apparaît un léger trouble correspondant à un début de cristallisation.

Exemple 1

- 5 Dans un réacteur de polymérisation de 7,5 litres, permettant d'obtenir 3 kg de polymère par polycondensation, muni d'une agitation avec couplomètre pour suivre la viscosité du milieu réactionnel, de différents sas d'introduction, d'une colonne de distillation pour éliminer l'eau formée lors de l'estérification, ainsi que l'excès d'éthylène glycol, et d'un circuit de vide direct pour l'étape de polycondensation, on introduit:
- 10 - 2656 g d'acide téréphtalique (16,0 mol)
- 1190 g d'éthylène glycol (19,2 mol)
- 384 g d'un sol aqueux de nanoparticules de silices de 50 nm de diamètre, commercialisé par la société Hoechst sous la dénomination Klébosol® 40R50, correspondant à 143,6 g de silice.
- 15 Après purge à l'azote, le milieu réactionnel est chauffé à 275°C sous agitation et sous pression de 6,6 bar absolus.
On définit le temps d'estérification comme le temps nécessaire à la distillation de l'eau.
Le temps d'estérification est de 66 minutes.
La pression est ensuite ramenée à la pression atmosphérique en 20 minutes.
- 20 On introduit une solution d'oxyde d'antimoine dans le milieu réactionnel (250 ppm en Sb, par rapport au polymère).
La pression est maintenue pendant 20 minutes à la pression atmosphérique, avant une mise sous vide progressive de 1 bar à moins de 1 mm de mercure en 90 minutes. La colonne de distillation est ensuite by-passée pour mise sous vide direct lorsque la pression atteint 20 mm de mercure.
- 25 La masse réactionnelle est portée à 285°C lorsque la pression descend en dessous de 1 mm de mercure.
On définit le temps de polycondensation comme le temps nécessaire pour atteindre le niveau de viscosité visé à partir du moment où la pression est inférieure à 1 mm de mercure.
- 30 Le temps de polycondensation est de 32 minutes.
Une fois le niveau de viscosité visé atteint, l'agitation est arrêtée et le réacteur est mis sous pression à 3 bar pour couler et granuler le polymère obtenu.
Les granulé de polymère sont séchés sous vide pendant 15 heures à 50°C.
- 35 Des photographies prises au Microscope Electronique à Transmission sont présentées sur la planche 1. La photo 1 est prise avec un grossissement d'environ 2.10^4 , la photo 2 est prise avec un grossissement d'environ 10^5 .

Exemple 2 (exemple comparatif)

On prépare un polymère selon l'exemple 1, excepté en ce qu'on n'introduit pas de nanoparticules de silice.

- 5 Le temps d'estérification est de 54 minutes.
Le temps de polycondensation est de 67 minutes.

Exemple 3

- 10 On prépare une composition selon l'exemple 1, excepté en ce que le sol aqueux de particules de silice est introduit en même temps que la solution d'oxyde d'Antimoine.
Le temps d'estérification est de 67 minutes.
Le temps de polycondensation est de 59 minutes.

Exemple 4

- 15 On prépare une composition selon l'exemple 1, excepté en ce qu'on introduit au lieu des 2656 g d'acide téréphtalique:
- 2592 g d'acide téréphtalique
- 63,7 g d'acide isophtalique (correspondant à 2,4% en mol de la quantité d'acide)
Le temps d'estérification est de 65 minutes.
20 Le temps de polycondensation est de 42 minutes.

Exemple 5

- 25 On prépare une composition selon l'exemple 1, excepté en ce que le sol aqueux de particules de silice est un sol aqueux de nanoparticules de silices de 25 nm de diamètre, commercialisé par la société Hoechst sous la dénomination Klébosol® 40R50
Le temps d'estérification est de 68 minutes.
Le temps de polycondensation est de 32 minutes.

Exemple 6

- 30 On prépare une composition selon l'exemple 1, excepté en ce qu'on introduit les composés suivants:
- 2592 g d'acide téréphtalique
- 63,7 g d'acide isophtalique (correspondant à 2,4% en mol de la quantité d'acide)
- 37 g d'éthylène glycol
35 - 1306 g d'un sol de silice glycolique à 11,8% de silice en poids, le sol étant synthétisé par un procédé dit de type Stöber, les particules de silices ayant un diamètre de 50 nm.

Les compositions des exemples 8 et 9 sont mises en forme de bouteilles, par injection/soufflage sur une machine intégrée ABS F100. La préforme fait 32 g, les bouteilles font 600 ml.

5 On effectue sur ces bouteilles un test de remplissage à chaud: on remplit les bouteilles à différentes températures et on mesure la variation de volume de celles-ci. Plus la variation est importante, moins bonne est la composition.

Dans le tableau II sont reportées, la température de remplissage (°C) et la déformation (ml) pour une bouteille obtenue à partir de compositions selon les exemples 8 et 9.

10

Tableau II

Température	Exemple 8	Exemple 9
70	76,6	50,6
75	109,6	70,3
80	149,1	129,1
85	205,8	176,6

REVENDICATIONS

1. Composition à base de polyester présentant des propriétés thermomécaniques améliorées, caractérisée en ce qu'elle comprend une matrice à base de polyester et des particules minérales de taille nanométrique, de facteur de forme compris entre 1 et 10, en concentration pondérale comprise en 0,01 et 25 %.
2. Composition selon la revendication 1 caractérisée en ce que les particules sont de forme sensiblement sphérique avec un diamètre moyen inférieur ou égal à 200 nm.
3. Composition selon la revendication 2 caractérisée en ce que le diamètre moyen des particules est compris entre 5 et 100 nm.
4. Composition selon l'une des revendications précédentes caractérisée en ce que les particules sont à base d'oxydes métalliques.
5. Composition selon la revendication 4 caractérisée en ce que les particules sont à base d'un composé choisi parmi la silice, le dioxyde de titane, la zircone, l'alumine.
6. Composition selon la revendication 5 caractérisée en ce que les particules sont à base de silice et en ce que la composition est obtenue par introduction d'un sol de silice dans un milieu de synthèse du polyester.
7. Composition selon la revendication 6 caractérisée en ce que le sol de silice est un sol aqueux ou glycolique.
8. Composition selon l'un des revendications précédentes caractérisée en ce que le polyester est choisi parmi le polyéthylène téréphtalate, le polytriméthylène téréphtalate, le polybutylène téréphtalate, le polynaphtalène téréphtalate, les mélanges et copolymères à bases de ces polyesters.
9. Composition selon l'une des revendications précédentes, caractérisée en ce que le polyester comporte un agent amorphisant.
10. Composition ou procédé selon la revendication 9, caractérisée en ce que l'agent amorphisant est un comonomère du polyester.

Photo 1

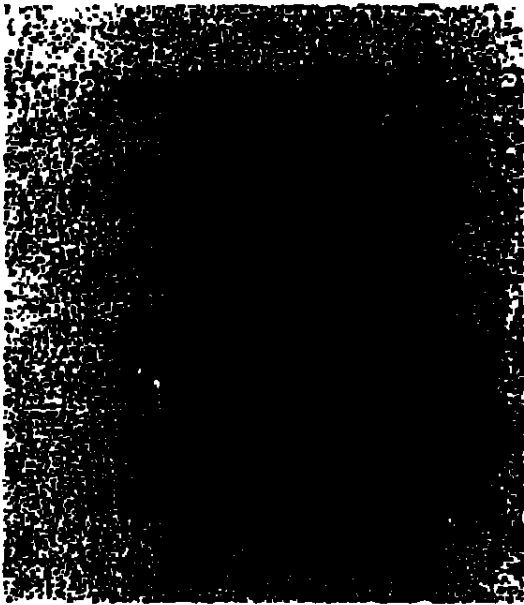


Photo 2



PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No. **01 / 0 0 0 30**International Filing Date **28 MAR 2001 28-3-01**INPI: BRAZIL - PCT INTERNATIONAL APPLICATION
Name of receiving Office and "PCT International Application"Applicant's or agent's file reference
(if desired) (12 characters maximum)

Box No. I TITLE OF INVENTION POLYESTER-BASED COMPOSITIONS HAVING IMPROVED THERMOMECHANICAL PROPERTIES AND PROCESS TO PRODUCE SAID COMPOSITIONS	
Box No. II APPLICANT ☐ This person is also inventor	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) RHODIA STER S.A. WTC - World Trade Center Avenida Das Nações Unidas, 12.551 - 8º andar 04578-903 - São Paulo - SP BRAZIL	Telephone No. (55) (11) 5502-1388 Facsimile No. (55) (11) 5502-1525 Teleprinter No. Applicant's registration No. with the Office
State (that is, country) of nationality: BR	State (that is, country) of residence: BR
This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) LEPAGE, Jean Luc Rhodia CRL 85 av des Freres Perret BP 62 69192 Saint Fons FRANCE	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: FR	State (that is, country) of residence: FR
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
☐ Further applicants and/or (further) inventors are indicated on a continuation sheet.	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) ARNAUD, Antonio M.P.; PINHEIRO, Waldemar Alvaro; NUNES, Luiz Antonio Ricco; and SCATAMBURLO, Paulo Sérgio All of Rua José Bonifácio, 93 - 7th floor 01003-901 - São Paulo - SP BRAZIL	Telephone No. (55) (11) 3106-1377 Facsimile No. (55) (11) 3106-1377 (55) (11) 3104-8037 Teleprinter No. Agent's registration No. with the Office
☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.	

Box No V DESIGNATION OF STATES

Mark the applicable check-boxes below, at least one

The following designations are hereby made under Rule 4 9(a)

PCT/BR 01/00030

Regional Patent

- ☐ AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, MZ Mozambique, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☐ EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☐ EP European Patent: AT Austria, BE Belgium, CH & LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, TR Turkey, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☐ OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Cote d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line)

- | | | |
|--|---|---|
| ☐ AE United Arab Emirates | ☐ GE Georgia | ☐ MW Malawi |
| ☐ AG Antigua and Barbuda | ☐ GH Ghana | ☐ MX Mexico |
| ☐ AL Albania | ☐ GM Gambia | ☐ MZ Mozambique |
| ☐ AM Armenia | ☐ HR Croatia | ☐ NO Norway |
| ☐ AT Austria | ☐ HU Hungary | ☐ NZ New Zealand |
| ☐ AU Australia | ☐ ID Indonesia | ☐ PL Poland |
| ☐ AZ Azerbaijan | ☐ IL Israel | ☐ PT Portugal |
| ☐ BA Bosnia and Herzegovina | ☐ IN India | ☐ RO Romania |
| | ☐ IS Iceland | ☐ RU Russian Federation |
| ☐ BB Barbados | ☐ JP Japan | ☐ SD Sudan |
| ☐ BG Bulgaria | ☐ KE Kenya | ☐ SE Sweden |
| ☒ BR Brazil | ☐ KG Kyrgyzstan | ☐ SG Singapore |
| ☐ BY Belarus | ☐ KP Democratic People's Republic of Korea | ☐ SI Slovenia |
| ☐ BZ Belize | | ☐ SK Slovakia |
| ☒ CA Canada | ☐ KR Republic of Korea | ☐ SL Sierra Leone |
| ☐ CH & LI Switzerland and Liechtenstein | ☐ KZ Kazakhstan | ☐ TJ Tajikistan |
| ☐ CN China | ☐ LC Saint Lucia | ☐ TM Turkmenistan |
| ☒ CO Colombia | ☐ LK Sri Lanka | ☐ TR Turkey |
| ☐ CR Costa Rica | ☐ LR Liberia | ☐ TT Trinidad and Tobago |
| ☐ CU Cuba | ☐ LS Lesotho | |
| ☐ CZ Czech Republic | ☐ LT Lithuania | ☐ TZ United Republic of Tanzania |
| ☐ DE Germany | ☐ LU Luxembourg | ☐ UA Ukraine |
| ☐ DK Denmark | ☐ LV Latvia | ☐ UG Uganda |
| ☐ DM Dominica | ☐ MA Morocco | ☒ US United States of America |
| ☐ DZ Algeria | ☐ MD Republic of Moldova | ☐ UZ Uzbekistan |
| ☐ EE Estonia | | ☐ VN Vietnam |
| ☐ ES Spain | ☐ MG Madagascar | ☐ YU Yugoslavia |
| ☐ FI Finland | ☐ MK The former Yugoslav Republic of Macedonia | ☐ ZA South Africa |
| ☐ GB United Kingdom | ☐ MN Mongolia | ☐ ZW Zimbabwe |
| ☐ GD Grenada | | |

(check-boxes below reserved for designating States which have become party to the PCT after issuance of this sheet)

- | | | |
|--------------------------|--------------------------|--------------------------|
| ☐ | ☐ | ☐ |
| ☐ | ☐ | ☐ |

Precautionary Designation Statement: In addition to the designations made above, the applicant hereby designates under Rule 4 9(b) all other designations which would be permitted under the PCT except any designation(s) indicated on this sheet as being excluded from the scope of this statement. The applicant declares that those additional designations are not intended to be confirmed and that any designation which is not confirmed before the expiration of 15 months from the priority date is not intended to be confirmed by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

PCT/BR 01/00030

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) March 29, 2000 (29.03.00)	0003965	FRANCE		
item (2)				
item (3)				
item (4)				
item (5)				

☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

☐ all items
 ☐ item (1)
 ☐ item (2)
 ☐ item (3)
 ☐ item (4)
 ☐ item (5)
 ☐ other, see Supplemental Box

* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)):

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / EPO

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)

Number

Country (or regional Office)

Box No. VIII DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

Number of declarations

- | | | | |
|--|--|---|----|
| ☐ Box No. VIII (i) | Declaration as to the identity of the inventor | : | |
| ☐ Box No. VIII (ii) | Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent | : | |
| ☒ Box No. VIII (iii) | Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application | : | 01 |
| ☐ Box No. VIII (iv) | Declaration of inventorship (only for the purposes of the designation of the United States of America) | : | |
| ☐ Box No. VIII (v) | Declaration as to non-prejudicial disclosures or exceptions to lack of novelty | : | |

Box No. VIII (III) DECLARATION: ENTITLEMENT TO CLAIM PRIORITY

The declaration must conform to the standardized wording provided for in Section 13 of the Rules to Box No. VIII (III) (in general) and the specific Notes to Box No. VIII (III). If this Box is not used, this sheet should not be included in the request.

Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application specified below, where the applicant is not the applicant who filed the earlier application or where the applicant's name has changed since the filing of the earlier application (Rules 4.17(iii) and 51bis.1(a)(iii)):

In relation to this international application, RHODIA STER S.A., is entitled to claim priority of earlier application No. 0003965, in the name of TERGAL FIBRES, filed in France on March 29, 2000, by virtue of the following:

(vii) transfer of entitlement from Tergal Fibres, established at rue Jules Vercuyse - 02430 Gauchy - France to RHODIA-STER S.A., established at avenida Das Nações Unidas, 12.551 - 8th floor - 04578-903, São Paulo - Brazil by way of the attached contract of assignment of all priority rights of claimed invention in the American Continent countries pertaining to the Paris Convention.

(ix) this declaration is made for the purposes of (b) the following designations for national patents: Brazil, Canada, Colombia, Mexico and the United States of America.

☐ This declaration is continued on the following sheet, "Continuation of Box No. VIII (iii)".

Box No. IX CHECK LIST; LANGUAGE OF FILING		01/00030																										
This international application contains: (a) the following number of sheets in paper form: request (including declaration sheets) : 05 description (excluding sequence listing part) : 14 claims : 02 abstract : 01 drawings : 01 Sub-total number of sheets : 23 sequence listing part of description (actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (b) below) : ---- Total number of sheets : 23 (b) sequence listing part of description filed in computer readable form (i) ☐ only (under Section 801(a)(i)) (ii) ☐ in addition to being filed in paper form (under Section 801(a)(ii)) Type and number of carriers (diskette, CD-ROM, CD-R or other) on which the sequence listing part is contained (additional copies to be indicated under item 9(ii), in right column):	This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item): <table style="width: 100%;"> <tr> <td style="width: 80%;">1. ☒ fee calculation sheet</td> <td style="width: 20%; text-align: right;">: 1</td> </tr> <tr> <td>2. ☒ original separate power of attorney</td> <td style="text-align: right;">: 1</td> </tr> <tr> <td>3. ☐ original general power of attorney</td> <td style="text-align: right;">:</td> </tr> <tr> <td>4. ☐ copy of general power of attorney; reference number, if any:</td> <td style="text-align: right;">:</td> </tr> <tr> <td>5. ☐ statement explaining lack of signature</td> <td style="text-align: right;">:</td> </tr> <tr> <td>6. ☐ priority document(s) identified in Box No. VI as item(s):</td> <td style="text-align: right;">:</td> </tr> <tr> <td>7. ☐ translation of international application into (language):</td> <td style="text-align: right;">:</td> </tr> <tr> <td>8. ☐ separate indications concerning deposited microorganism or other biological material</td> <td style="text-align: right;">:</td> </tr> <tr> <td>9. ☐ sequence listing in computer readable form (indicate also type and number of carriers (diskette, CD-ROM, CD-R or other))</td> <td style="text-align: right;">:</td> </tr> <tr> <td style="padding-left: 20px;">(i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application)</td> <td style="text-align: right;">:</td> </tr> <tr> <td style="padding-left: 20px;">(ii) ☐ (only where check-box (b)(i) or (b)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter</td> <td style="text-align: right;">:</td> </tr> <tr> <td style="padding-left: 20px;">(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing part mentioned in left column</td> <td style="text-align: right;">:</td> </tr> <tr> <td>10. ☐ other (specify):</td> <td style="text-align: right;">:</td> </tr> </table>	1. ☒ fee calculation sheet	: 1	2. ☒ original separate power of attorney	: 1	3. ☐ original general power of attorney	:	4. ☐ copy of general power of attorney; reference number, if any:	:	5. ☐ statement explaining lack of signature	:	6. ☐ priority document(s) identified in Box No. VI as item(s):	:	7. ☐ translation of international application into (language):	:	8. ☐ separate indications concerning deposited microorganism or other biological material	:	9. ☐ sequence listing in computer readable form (indicate also type and number of carriers (diskette, CD-ROM, CD-R or other))	:	(i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application)	:	(ii) ☐ (only where check-box (b)(i) or (b)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter	:	(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing part mentioned in left column	:	10. ☐ other (specify):	:	Number of items
1. ☒ fee calculation sheet	: 1																											
2. ☒ original separate power of attorney	: 1																											
3. ☐ original general power of attorney	:																											
4. ☐ copy of general power of attorney; reference number, if any:	:																											
5. ☐ statement explaining lack of signature	:																											
6. ☐ priority document(s) identified in Box No. VI as item(s):	:																											
7. ☐ translation of international application into (language):	:																											
8. ☐ separate indications concerning deposited microorganism or other biological material	:																											
9. ☐ sequence listing in computer readable form (indicate also type and number of carriers (diskette, CD-ROM, CD-R or other))	:																											
(i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application)	:																											
(ii) ☐ (only where check-box (b)(i) or (b)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter	:																											
(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing part mentioned in left column	:																											
10. ☐ other (specify):	:																											
Figure of the drawings which should accompany the abstract: 01	Language of filing of the international application: English																											

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE
<i>Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).</i>  (Antonio M.P. Arnaud - Agent)

For receiving Office use only		
1. Date of actual receipt of the purported international application:	28 MAR 2001 28-3- 01	2. Drawings: ☐ received: ☐ not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA /	6. ☐ Transmittal of search copy delayed until search fee is paid	

For International Bureau use only
Date of receipt of the record copy by the International Bureau:

PCT

FEE CALCULATION SHEET
Annex to the Request

For receiving Office use only

International Application No. **01 / 0 0 0 3 0**Applicant's or agent's
file reference

Date stamp of the receiving Office

Applicant

RHODIA STER S.A.

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE 236,00 **T**
2. SEARCH FEE . . . EUR 945 x 2,00 1.890,00 **S**

International search to be carried out by EPO
(If two or more International Searching Authorities are competent to carry out the international search, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FEE

Basic Fee

Where item (b) of Box No. IX applies, enter Sub-total number of sheets } 23
Where item (b) of Box No. IX does not apply, enter Total number of sheets }

b1 first 30 sheets . CHF 650 x 1,36 884,00 **b1**

b2 x = ... **b2**
number of sheets fee per sheet
in excess of 30

b3 additional component (only if sequence listing part of description
is filed in computer readable form under Section 801(a)(i), or
both in that form and on paper, under Section 801(a)(ii)):

400 x = ... **b3**
fee per sheet

Add amounts entered at b1, b2 and b3 and enter total at B 884,00 **B**

Designation Fees

The international application contains 05 designations.

CHF 700 x 1,36 = 952,00 **D**
number of designation fees amount of designation fee
payable (maximum 6)

Add amounts entered at B and D and enter total at I 1.836,00 **I**

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D.)

4. FEE FOR PRIORITY DOCUMENT (if applicable) **P**

5. TOTAL FEES PAYABLE 3.962,00

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

TOTAL

☐ The designation fees are not paid at this time.

MODE OF PAYMENT

☐ authorization to charge
deposit account (see below)

☐ postal money order

☐ cash

☐ coupons

☐ cheque

☐ bank draft

☐ revenue stamps

☐ other (specify):

AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT

(This mode of payment may not be available at all receiving Offices)

☐ Authorization to charge the total fees indicated above.

☐ (This check-box may be marked only if the conditions for deposit accounts
of the receiving Office so permit) Authorization to charge any deficiency
or credit any overpayment in the total fees indicated above.

☐ Authorization to charge the fee for priority document.

Receiving Office: RO/

Deposit Account No.:

Date:

Name:

Signature:

Contrat de cession de droits de priorité**DET BR 01 / 0 0030**

Entre:

La société TEGAL FIBRES, rue Jules Vercuyse - 02430 Gauchy - FRANCE, représentée par Monsieur Jean-Claude Faure, Directeur Général;

et

La société RHODIA-STER S.A., Av. das Nações Unidas, 12.551 - 8 andar - Brooklin Novo - 04578.903 - SAO PAULO - BRESIL, représentée par Messieurs José Veiga Veiga et Reinaldo Kroger.

A près avoir exposé:

- Que les parties ont cofinancé des travaux de recherches portant sur des compositions à base de polyester,
- Qu'il a été convenu entre les parties que la protection des inventions issues des travaux de recherche serait géographiquement partagée, et demandée indépendamment par chaque partie,
- Que suite aux travaux de recherche deux demandes de brevets ont été déposées en France au nom de TEGAL FIBRES,
 - "Compositions à base de polyesters présentant des propriétés thermomécaniques améliorées et procédé de fabrication de ces compositions" Demande n° 0003965 déposée le 29 mars 2000.

Il a été arrêté ce qui suit:

Article 1

La société TEGAL FIBRES cède à la société RHODIA-STER, qui accepte, les droits de priorité attachés à la première demande déposée en France le 29/03/00 sous le numéro 00/03965, pour pouvoir effectuer des dépôts de brevets sur la base de cette priorité dans les pays du continent américain appartenant à la Convention d'Union de Paris. La société TEGAL FIBRES conserve le droit de priorité attaché à la première demande mentionnée ci-dessus pour le dépôt de brevets dans les pays d'Europe, d'Afrique et d'Asie.

Article 2

En cas de décision d'abandon par l'une des parties d'un brevet ou d'une demande de brevet revendiquant la priorité de la première demande mentionnée à l'article 1, celle-ci en informera l'autre partie qui devra indiquer dans un délai de deux mois si elle reprend à sa charge les frais d'entretien du brevet ou de la demande.

Article 3

Le présent accord est régi par la loi française.

Fait à en 3 exemplaires.

TERGAL FIBRES

RHODIA STER

Jean Claude FAURE

José VEIGA VEIGA Walter CIRILLO

Contrat de cession de droits de priorité

Entre:

La société TERGAL FIBRES, rue Jules Vercuysse - 02430 Gauchy - FRANCE, représentée par Monsieur Jean-Claude Faure, Directeur Général;

et

La société RHODIA-STER S.A., Av. das Nações Unidas, 12.551-8 and.-04578-903-S.Paulo-SP - BRESIL, représentée par Messieurs José Veiga Veiga et Reinaldo Kroger.

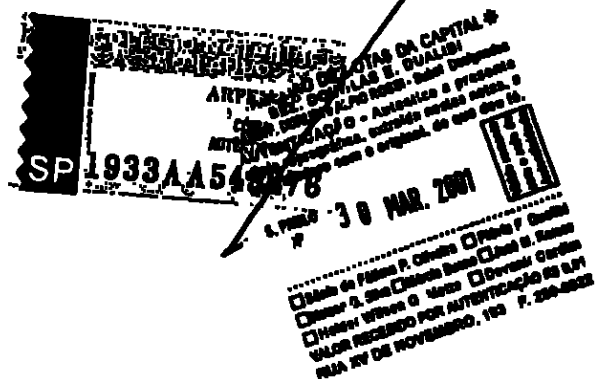
A près avoir exposé:

- Que les parties ont cofinancé des travaux de recherches portant sur des compositions à base de polyester,
- Qu'il a été convenu entre les parties que la protection des inventions issues des travaux de recherche serait géographiquement partagée, et demandée indépendamment par chaque partie,
- Que suite aux travaux de recherche ^{UNE} deux demandes de brevets ont été déposées en France au nom de TERGAL FIBRES,
 - "Compositions à base de polyesters présentant des propriétés thermomécaniques améliorées et procédé de fabrication de ces compositions" Demande n° 0003965 déposée le 29 mars 2000.

Il a été arrêté ce qui suit:

Article 1

La société TERGAL FIBRES cède à la société RHODIA-STER, qui accepte, les droits de priorité attachés à la première demande déposée en France le 29/03/00 sous le numéro 00/03965, pour pouvoir effectuer des dépôts de brevets sur la base de cette priorité dans les pays du continent américain appartenant à la Convention d'Union de Paris. La société TERGAL FIBRES conserve le droit de priorité attaché à la première demande mentionnée ci-dessus pour le dépôt de brevets dans les pays d'Europe, d'Afrique et d'Asie.



Article 2

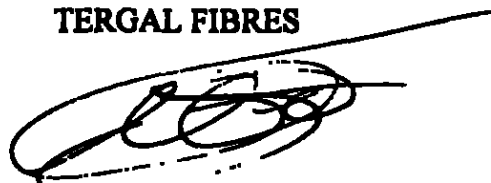
En cas de décision d'abandon par l'une des parties d'un brevet ou d'une demande de brevet revendiquant la priorité de la première demande mentionnée à l'article 1, celle-ci en informera l'autre partie qui devra indiquer dans un délai de deux mois si elle reprend à sa charge les frais d'entretien du brevet ou de la demande.

Article 3

Le présent accord est régi par la loi française.

Fait à en 3 exemplaires.

TERGAL FIBRES



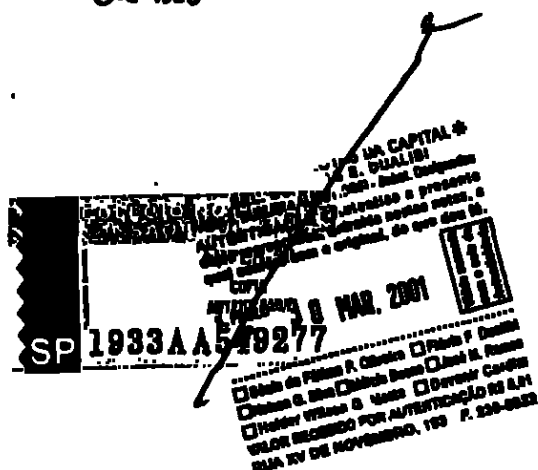
Jean Claude FAURE

RHODIA STER



José VEIGA VEIGA Reinaldo KROGER

un mot barré



Patentanwälte
HAGEMANN, BRAUN & HELD

11.10.01

our Ref.: Pat 1418/4-01-PCT

International Patent Application Nr. PCT/BR 01/00030
Appln.: Rhodia Ster S.A.

Internat. preliminary examin. fee
Handling fee

€ 1.533,00
€ 147,00
€ 1.680,00

Nur zur Verrechnung

Stadtsparkasse München

Zahlen Sie gegen diesen Scheck

Betrag in Buchstaben

eintausendsechshundertachtzig

noch Betrag in Buchstaben
an

European Patent Office
D-80298 München

* Bei zur Erfüllung des Kurses (= EUR) nur DM; danach DM oder EUR.
DM od. EUR

EUR

Betrag

1.680,00

oder Überbringer

München
Ausstellungsort

11.10.01

Datum

Lied

Unterschrift des Ausstellers

Der vorgedruckte Schecktext darf nicht geändert
oder unterschrieben werden. Bei Falschgebrauch
kann auf dem Scheck geltend gemacht werden.

Bank für Sozialleistungen

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Betrag

Barbetrag

Text

0000001531854J

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70150000J 01H

Bitte dieses Feld nicht beschriften und nicht bestempeln

PATENT COOPERATION TREATY

31 JUL 2001

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From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

ARNAUD, Antonio M.P. et al
PINHEIRO, NUNES, ARNAUD &
SCATAMBURLO
Rua José Bonifácio, 93
7th floor
01003-901 - Sao Paulo - SP
BRESIL

NOTIFICATION OF RECEIPT OF DEMAND BY COMPETENT INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rules 59.3(e) and 61.1(b), first sentence
and Administrative Instructions, Section 601(a))

Date of mailing
(day/month/year)

25.10.01

Applicant's or agent's file reference
00030

IMPORTANT NOTIFICATION

International application No.

PCT/BR 01/00030

International filing date (day/month/year)

28/03/2001

Priority date (day/month/year)

29/03/2000

Applicant

RHODIA STER S.A. et al

1. The applicant is hereby notified that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

12/10/2001

2. This date of receipt is:



the actual date of receipt of the demand by this Authority (Rule 61.1(b)).



the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).



the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

3. ☐ **ATTENTION:** That date of receipt is AFTER the expiration of 19 months from the priority date. Consequently, the election(s) made in the demand does (do) not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)). Therefore, the acts for entry into the national phase must be performed within 20 months from the priority date (or later in some Offices) (Article 22). For details, see the PCT Applicant's Guide, Volume II.



(If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on:

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

Name and mailing address of the IPEA/



European Patent Office
D-80298 Munich
Tel. (+49-89) 2399-0, Tx: 523656 epmu d
Fax: (+49-89) 2399-4465

Authorized officer

DONNELLY P P

Tel. (+49-89) 2399-2362



PATENT COOPERATION TREATY

03 OCT 2011

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PCT

INFORMATION CONCERNING ELECTED
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

From the INTERNATIONAL BUREAU

To:

ARNAUD, Antonio, M., P.
Rua José Bonifácio, 93
7th Floor
CEP-01003-901 São Paulo, SP
BRÉSIL

Date of mailing (day/month/year)

20 November 2001 (20.11.01)

Applicant's or agent's file reference

IMPORTANT INFORMATION

International application No.

PCT/BR01/00030

International filing date (day/month/year)

28 March 2001 (28.03.01)

Priority date (day/month/year)

29 March 2000 (29.03.00)

Applicant

RHODIA STER S.A. et al

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

National :CA,US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

National :BR,CO,MX

3. The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 38(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 38(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer:

Ana MENA VALENCIA

Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

83
27 FEB 2002

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

ARNAUD, Antonio M.P. et al
PINHEIRO, NUNES, ARNAUD &
SCATAMBURLO
Rua José Bonifacio, 93
7th floor
01003-901 - Sao Paulo - SP
BRASIL

NOTIFICATION OF TRANSMITTAL OF INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Applicant's or agent's file reference 00030		Date of mailing (day/month/year) 20/02/2002	
International application No. PCT/BR 01/ 00030		International filing date (day/month/year) 28/03/2001	Priority date (day/month/year) 29/03/2000
Applicant RHODIA STER S.A. et al			

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



European Patent Office
D-80298 Munich
Tel. (+49-89) 2399-0, Tx: 523656 eptmu d
Fax: (+49-89) 2399-4465

Authorized officer

DONNELLY P P
Tel. (+49-89) 2399 2828



Form PCT/IPEA/416 (July 1992) P20473

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 00030	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/BR 01/ 00030	International filing date (day/month/year) 28/03/2001	Priority date (day/month/year) 29/03/2000
International Patent Classification (IPC) or national classification and IPC G08K3/22		
Applicant RHODIA STER S.A. et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 2 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consists of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 12/10/2001	Date of completion of this report 16/02/2002
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer VAN THIELEN J B Tel. (+49-89) 2399 2828

Form PCT/IPEA/409 (cover sheet) (July 1998)



I. Basis of report

1. The basis of international preliminary examination report is the application as originally filed.

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

2. The question of whether the claimed invention appears to be novel, to involve an inventive step, or to be industrially applicable has not been and will not be the subject of the international preliminary examination (Article 34 (4) (a) (i) (ii) PCT; see also International search report) in respect of:

- 2.1 Applications having an unnecessary plurality of independent claims (generally not more than 1 independent claim in the same category is necessary; Article 6 PCT);

- 2.2 unsearched subject-matter (Article 17 (2) (a), Rule 66.1 (e) PCT).

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

3. To the extent that the international preliminary examination has been carried out (see item III above), the following is pointed out (Article 35 (2) and (3) (b) and Rule 70.7 and 70.8 (ii) PCT):

In light of the documents cited in the international search report, it is considered that the invention as claimed in the independent claims meets the criteria mentioned in Article 33 (1) PCT, i.e. it appears to be novel, to involve an inventive step and to be industrially applicable.



11 2 107 2001

Einsender / Sender / Expéditeur :

Arnaud, Antonio M.P.
PINHEIRO, NUNES, ARNAUD &
SCATAMBURLO S/C.
Rua José Bonifácio, 93 - 7th floor
01003-901 - São Paulo - SP
BRAZIL

Erhardstraße 27
W-8000 München 2
☎ 089 / 2389-0
Tx 623 958 apmu d
Fax 089 / 23 89-44 66

P.B. 6818 Potsdam 2
NL-2280 HV Rijswijk (ZH)
☎ 070 / 340-2040
Tx 31 661 ape nl
Fax 070 / 340-3018

Glöckner Straße 103
W-1000 Berlin 81
☎ 030 / 25901-0
Fax 030 / 25901-840

Bestätigung über den
Eingang nachgereichter
Unterlagen für Patentan-
meldungen/Patente beim
Europäischen Patentamt

Acknowledgement of
receipt for subsequently
filed items relating to
patent applications/patents
at the European Patent
Office

Accusé de réception à
l'Office européen des bre-
vets de pièces produites
postérieurement au dépôt
d'une demande de brevet/
à la délivrance d'un brevet
européen

Datum und Ort des Eingangs sind aus
der Perforation dieser Eingangsbestätig-
ung ersichtlich
(M + Datum = Einreichungsort München;
Datum ohne Zusatz = Einreichungsort
Den Haag; Datum + B = Einreichungsort
Berlin)

Date and place of receipt are shown by
the perforation appearing on this receipt
(M + date = Munich as place of receipt;
date alone = The Hague as place of
receipt; date + B = Berlin as place of
receipt)

La date et le lieu de réception sont indi-
qués par la perforation du présent accusé
de réception
(M + date = pièces reçues à Munich;
date seule = pièces reçues à La Haye;
date + B = pièces reçues à Berlin)

Eingereichte Unterlagen

Items filed

Pièces envoyées

Anmeldungs- (und Direktionen*) Nr./Patent Nr. Application (and Directorate*) No./Patent No. N° de la demande (et de la direction*)/n° du brevet	Ihr Zeichen Your reference Votre référence	ggfs. Art und Datum der Unterlagen** Nature and date of items (optional)** Nature et date des pièces (facultatif)**
1 PCT/BR 01/00030	RHODIA STER	Form 401
2		
3		
4		
5		
6		
7		
8		
9		
10		

* falls bereits bekannt
** Der Eingang der angegebenen Unterlagen
wird bestätigt.
Enthält diese Spalte keine Eintragungen, so
wird lediglich bestätigt, daß eine Sendung
zu dem angegebenen Adresszeichen einge-
gangen ist.

* if already known
** The receipt of the items indicated is
confirmed.
If this column does not contain any entries,
it is only confirmed that an item has been
received for the indicated file.

* si déjà connu
** La réception des pièces indiquées est
confirmée.
Faute de mention dans cette colonne, le
présent accusé de réception se rapporte à
une pièce quelconque envoyée sous la
référence indiquée.

PATENT COOPERATION TREATY 14 MAY 2001

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PCT

NOTIFICATION OF RECEIPT OF
RECORD COPY

(PCT Rule 24.2(a))

From the INTERNATIONAL BUREAU

To:

ARNAUD, Antonio, M., P.
Rua José Bonifácio, 93
7th Floor
CEP-01003-901 São Paulo, SP
BRÉSIL

Date of mailing (day/month/year) 01 May 2001 (01.05.01)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference	International application No. PCT/BR01/00030

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

RHODIA STER S.A. (for all designated States except US)
LEPAGE, Jean, Luc (for US)

International filing date : 28 March 2001 (28.03.01)
Priority date(s) claimed : 29 March 2000 (29.03.00)
Date of receipt of the record copy
by the International Bureau : 20 April 2001 (20.04.01)
List of designated Offices :

National : BR, CA, CO, MX, US

ATTENTION

The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau.

In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:

- ☒ time limits for entry into the national phase
- ☒ confirmation of precautionary designations
- ☒ requirements regarding priority documents

A copy of this Notification is being sent to the receiving Office and to the International Searching Authority.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer: R. Raisel
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

INFORMATION ON TIME LIMITS FOR ENTERING THE NATIONAL PHASE

The applicant is reminded that the "national phase" must be entered before each of the designated Offices indicated in the Notification of Receipt of Record Copy (Form PCT/IB/301) by paying national fees and furnishing translations, as prescribed by the applicable national laws.

The time limit for performing these procedural acts is 20 MONTHS from the priority date or, for those designated States which the applicant elects in a demand for international preliminary examination or in a later election, 30 MONTHS from the priority date, provided that the election is made before the expiration of 18 months from the priority date. Some designated (or elected) Offices have fixed time limits which expire even later than 20 or 30 months from the priority date. In other Offices an extension of time or grace period, in some cases upon payment of an additional fee, is available.

In addition to these procedural acts, the applicant may also have to comply with other special requirements applicable in certain Offices. It is the applicant's responsibility to ensure that the necessary steps to enter the national phase are taken in a timely fashion. Most designated Offices do not issue reminders to applicants in connection with the entry into the national phase.

For detailed information about the procedural acts to be performed to enter the national phase before each designated Office, the applicable time limits and possible extensions of time or grace periods, and any other requirements, see the relevant Chapters of Volume II of the PCT Applicant's Guide. Information about the requirements for filing a demand for international preliminary examination is set out in Chapter IX of Volume I of the PCT Applicant's Guide.

GR and ES became bound by PCT Chapter II on 7 September 1986 and 6 September 1987, respectively, and may, therefore, be elected in a demand or a later election filed on or after 7 September 1986 and 6 September 1987, respectively, regardless of the filing date of the international application. (See second paragraph above.)

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

CONFIRMATION OF PRECAUTIONARY DESIGNATIONS

This notification lists only specific designations made under Rule 4.9(a) in the request. It is important to check that these designations are correct. Errors in designations can be corrected where precautionary designations have been made under Rule 4.9(b). The applicant is hereby reminded that any precautionary designations may be confirmed according to Rule 4.9(c) before the expiration of 18 months from the priority date. If it is not confirmed, it will automatically be regarded as withdrawn by the applicant. There will be no reminder and no invitation. Confirmation of a designation consists of the filing of a notice specifying the designated State concerned (with an indication of the kind of protection or treatment desired) and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 18-month time limit.

REQUIREMENTS REGARDING PRIORITY DOCUMENTS

For applicants who have not yet complied with the requirements regarding priority documents, the following is recalled.

Where the priority of an earlier national, regional or international application is claimed, the applicant must submit a copy of the said earlier application, certified by the authority with which it was filed ("the priority document") to the receiving Office (which will transmit it to the International Bureau) or directly to the International Bureau, before the expiration of 18 months from the priority date, provided that any such priority document may still be submitted to the International Bureau before that date of international publication of the international application, in which case that document will be considered to have been received by the International Bureau on the last day of the 18-month time limit (Rule 17.1(a)).

Where the priority document is issued by the receiving Office, the applicant may, instead of submitting the priority document, request the receiving Office to prepare and transmit the priority document to the International Bureau. Such request must be made before the expiration of the 18-month time limit and may be subjected by the receiving Office to the payment of a fee (Rule 17.1(b)).

If the priority document concerned is not submitted to the International Bureau or if the request to the receiving Office to prepare and transmit the priority document has not been made (and the corresponding fee, if any, paid) within the applicable time limit indicated under the preceding paragraphs, any designated State may disregard the priority claim, provided that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity to furnish the priority document within a time limit which is reasonable under the circumstances.

Where several priorities are claimed, the priority date to be considered for the purposes of computing the 18-month time limit is the filing date of the earliest application whose priority is claimed.

From the INTERNATIONAL SEARCHING AUTHORITY

PCTNOTIFICATION OF RECEIPT
OF SEARCH COPY

(PCT Rule 25.1)

To:

PINHEIRO, NUNES, ARNAUD &
SCATAMBURLO
Attn. Arnaud, Antonio M.P.
Rua José Bonifácio, 93
7th floor
01003-901 - São Paulo - SP
BRAZIL

Date of mailing
(day/month/year)

17/05/2001

Applicant's or agent's file reference

IMPORTANT NOTIFICATION

International application No.

PCT/BR 01/ 00030

International filing date (day/month/year)

28/03/2001

Priority date (day/month/year)

29/03/2000

Applicant

RHODIA STER S.A.

1. Where the International Searching Authority and the Receiving Office are not the same office:

The applicant is hereby notified that the search copy of the international application was received by this International Searching Authority on the date indicated below.

Where the International Searching Authority and the Receiving Office are the same office:

The applicant is hereby notified that the search copy of the international application was received on the date indicated below.

23/04/2001

(date of receipt).

- 2.
- ☐
- The search copy was accompanied by a nucleotide and/or amino acid sequence listing in computer readable form.

3. Time limit for establishment of International Search Report

The applicant is informed that the time limit for establishing the International Search Report is 3 months from the date of receipt indicated above or 8 months from the priority date, whichever time limit expires later.

4. A copy of this notification has been sent to the International Bureau and, where the first sentence of paragraph 1 applies, to the Receiving Office.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

ISA/EP

PATENT COOPERATION TREATY

04 JUN 2001

90

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

ARNAUD, Antonio, M., P.
Rua José Bonifácio, 93
7th Floor
CEP-01003-901 São Paulo, SP
BRÉSIL

Date of mailing (day/month/year) 28 May 2001 (28.05.01)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference	
International application No. PCT/BR01/00030	
International publication date (day/month/year) Not yet published	
Applicant RHODIA STER S.A. et al	International filing date (day/month/year) 28 March 2001 (28.03.01) Priority date (day/month/year) 29 March 2000 (29.03.00)

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
3. An asterisk(*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(e) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
29 Marc 2000 (29.03.00)	00/03965	FR	11 May 2001 (11.05.01)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35	Authorized officer Taieb Akremi Telephone No. (41-22) 336.83.38
--	---

PATENT COOPERATION TREATY

91

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

To:

PINHEIRO, NUNES, ARNAUD &
SCATAMBURLO
Attn. Arnaud, Antonio M.P.
Rua José Bonifácio, 93
7th floor
01003-901 - Sao Paulo - SP
BRAZIL

Date of mailing
(day/month/year)

12/07/2001

Applicant's or agent's file reference

FOR FURTHER ACTION See paragraphs 1 and 4 below

International application No.

PCT/BR 01/00030

International filing date
(day/month/year)

28/03/2001

Applicant

RHODIA STER S.A.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 48):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. Further action(s): The applicant is reminded of the following:

Shortly after 18 months from the priority date, the International application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the International application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for International publication.

Within 18 months from the priority date, a demand for International preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 18 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Jan Boon

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 28, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 18, 19 and 20; new claims 21 and 22 added."

"Statement under article 19(1)" (Rule 48.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, Item 5 below.	
International application No. PCT/BR 01/00030	International filing date (day/month/year) 28/03/2001	(Earliest) Priority Date (day/month/year) 29/03/2000
Applicant RHODIA STER S.A.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the language, the International search was carried out on the basis of the International application in the language in which it was filed, unless otherwise indicated under this item.

☐ the International search was carried out on the basis of a translation of the International application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any nucleotide and/or amino acid sequence disclosed in the International application, the International search was carried out on the basis of the sequence listing:

☐ contained in the International application in written form.

☐ filed together with the International application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the International application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this International search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

NONE

☐ as suggested by the applicant.

☒ None of the figures.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 18 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/BR 01/00030

95

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0401689 A	12-12-1990	JP 2856283 B JP 3006239 A DE 69004621 D DE 69004621 T KR 9604479 B US 5096773 A	10-02-1999 11-01-1991 23-12-1993 09-06-1994 06-04-1996 17-03-1992
JP 11335542 A	07-12-1999	NONE	
WO 9801346 A	15-01-1998	US 5876812 A US 5916685 A AU 3795097 A EP 0932497 A US 5972448 A	02-03-1999 29-06-1999 02-02-1998 04-08-1999 26-10-1999

INTERNATI NAL SEARCH REPORT

International Application No

PCT/BR 01/00030

96

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08K3/22 C08K3/36 C08K7/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 401 689 A (DIAFOIL CO LTD) 12 December 1990 (1990-12-12) claims 1-6	1-16
A	----- DATABASE WPI Section Ch, Week 200008 Derwent Publications Ltd., London, GB; Class A23, AN 2000-092715 XP002152079 & JP 11 335542 A (TEIJIN LTD), 7 December 1999 (1999-12-07) abstract	1-16
A	----- WO 98 01346 A (LAURENT JACQUES ;TETRA LAVAL HOLDINGS & FINANCE (CH); FRISK PETER) 15 January 1998 (1998-01-15) claims 1-9	1-16
☐ Further documents are listed in the continuation of box C. ☒ Patent family members are listed in annex.		
* Special categories of cited documents:		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
Date of the actual completion of the international search 4 July 2001		Date of mailing of the international search report 12/07/2001
Name and mailing address of the ISA European Patent Office, P.B. 5518 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016		Authorized officer Siemens, T

AN - 2000-092715 [08]

AP - JP19990052357 19990301

CPY - TEIJ

DC - A23 E32

DR - 1966-U

FS - CPI

IC - C08J3/20 ; C08K3/22 ; C08L67/02

MC - A05-E01A2 A08-E02 E35-K02

M3 - [01]

PA - (TEIJ) TEIJIN LTD

PN - JP11335542 A 19991207 DW200008 C08L67/02 008pp

PR - JP19980050972 19980303

XA - C2000-027038

XIC - C08J-003/20 ; C08K-003/22 ; C08L-067/02

AB - JP11335542 NOVELTY - A titanium dioxide-containing polyester resin composition (I) comprises (A) titanium dioxide 0.01-5.0 wt%. DETAILED DESCRIPTION - Averaged particle size 0.1-0.5 micrometer, content of large size particles with particle size 3 μm or more 15,000/mg or less, content of large size particles with particle size 4 micrometer or more 7,500/mg or less, ratio of P_2O_5 /(A) 0.4-0.6 wt%, (e) ratio of K_2O /(B) 0.1-0.3 wt%, (f) loss of weight on heating 0.4 wt% or less, (g) ratio of rutile titanium dioxide(A1)/anatase titanium dioxide 9 x 10³ or less, (h) crystallite size 10-150 nm and (i) practically free from iron.

- USE - None given.

- ADVANTAGE - (I) is prepared without colouring and has good resistance to heat aging, gives moulded articles, fibres in which (A) is dispersed homogeneously.

- (Dwg.0/0)

IW - TITANIUM CONTAIN POLYESTER RESIN COMPOSITION PREPARATION ADD TITANIUM POLYESTER RESIN

IKW - TITANIUM CONTAIN POLYESTER RESIN COMPOSITION PREPARATION ADD TITANIUM POLYESTER RESIN

NC - 001

PD - 1998-03-03

RD - 1999-12-07

PAW - (TEIJ) TEIJIN LTD

TI - Titanium dioxide-containing polyester resin composition - prepared by addition of titanium dioxide to polyester resin

A01 - [001] 018 ; G1038-R G1025 G0997 D01 D11 D10 D50 D84 F28 F26 E21 E00

E22 G1025-R ; R00822 G1025 G0997 D01 D11 D10 D50 D82 F28 F26 ;

G1343-R G1310 G4024 D01 D60 F37 F35 E00 D18-R ; R01002 G1456 G1445

G4024 D01 D11 D10 D19 D18 D31 D50 D63 D76 D90 F41 F90 E00 E21 ;

P0839-R F41 D01 D63 ; P0884 P1978 P0839 H0293 F41 D01 D11 D10 D19 D18

D31 D50 D63 D90 E21 E00 ; P0895 P1978 P0839 H0293 F41 D01 D11 D10 D19

D18 D31 D50 D63 D92 E21 E00 ; P1989 P1978 P0839 H0293 D01 D10 D11 D18

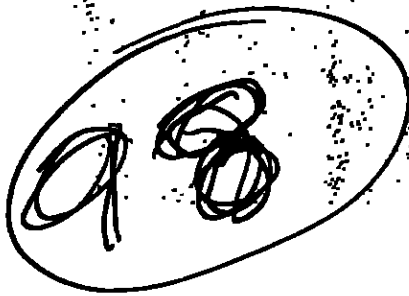
D20 D32 D50 D63 D93 D78 E00 E22 F41 F90 ; L9999 L2528 L2506 ; L9999

L2186-R ; L9999 L2197 L2186 ; H0033 H0011 ; H0293

- [002] 018 ; ND03 ; ND00 ; B9999 B4273 B4240 ; B9999 B3430 B3372 ;

B9999 B4682 B4568

- [003] 018 ; R01433 D01 D11 D10 D50 D61 D84 F36 F35 Mn 7B Tr ; R01527



G2482 D00 F20 O- 6A Sb 5A ; R01309 G3327 D01 D11 D10 D50 D63 D83 F53 ;
C999 C102 C000 ; C999 C306
- [004] 018 ; R01966 D00 F20 Ti 4B Tr O- 6A ; A999 A102 A077 ; S9999
S1456-R ; B9999 B5209 B5185 B4740 ; B9999 B4795 B4773 B4740

REQUISITOS NECESARIOS PARA PRESENTACIÓN Y AGILIZACIÓN DEL TRAMITE

USUARIO RADICADOR

PATENTE DE INVENCION [X]

MODELO DE UTILIDAD [] []

- Indicación de que se solicita la concesión de una patente [X] [X]
- Datos de identificación del solicitante o de la persona que presenta la solicitud [X] [X]
- Descripción de la invención [X] [X]
- Dibujos de ser estos pertinentes [X] [X]
- Comprobante de Pago de las tasas establecidas [X] [X]

COMPLETA [X]

INCOMPLETA [] []

DISEÑO INDUSTRIAL []

- Indicación de que se solicita el registro de Diseño Industrial. [] []
- Datos de identificación del solicitante o de la persona que presenta la solicitud. [] []
- Representación gráfica y foto gráfica del Diseño Industrial o muestra del material que incorpora el diseño. [] []
- Comprobante de pago de las tasas establecidas. [] []

COMPLETA []

INCOMPLETA [] []

ESQUEMA DE TRAZADO []

- Indicación de que se solicita el registro de un Esquema de trazado. [] []
- Datos de identificación del solicitante o de la persona que presenta la solicitud. [] []
- Representación gráfica del esquema de trazado [] []
- Comprobante de pago de las tasas establecidas. [] []

COMPLETA []

INCOMPLETA [] []

Eduardo Navarro
Firma Responsable

Fecha: 18-09-2002

Carrera 13 No. 27-00 Piso 2 mezzanina
Conmutador: 342 08 49
Fax: 350 52 20 e-mail: info@sic.gov.co
Bogotá D.C. - Colombia