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REF: Expediente No. **13-205541**
Patente de Invención: **"ESTRUCTURA A BASE DE POLIETILENO"**
Fase Nacional: **PCT/JP2012/055839**
Clasificación Int.: **B65D 1/00, C08L 23/06, 23/26, 77/06.**
Titular: **MITSUBISHI GAS CHEMICAL COMPANY, INC.**.

RESPUESTA A REQUERIMIENTO OFICIO No. 8292 NOTIFICADO POR FIJACION EN LISTA DE 15 DE JULIO DE 2014.

HUMBERTO RUBIO CAMACHO, mayor de edad, domiciliado en Bogotá, D.C., identificado con la cédula de ciudadanía número 17'192.062 de Bogotá, abogado graduado portador de la Tarjeta Profesional No. 50.007 expedida por el Consejo Superior de la Judicatura, actuando en carácter de Apoderado de **MITSUBISHI GAS CHEMICAL COMPANY, INC.,** domiciliado en 5-2, Marunouchi 2-chome, Chiyoda-ku, Tokio, Japón; encontrándome dentro de la debida oportunidad procesal para dar respuesta al auto proferido por su Despacho, mediante Oficio 8292, notificado por fijación en lista de 15 de julio de 2014 y cuya prórroga de término fue radicada ante su Despacho el 3 de octubre de 2014, me permito:

Manifestar:

I.- En el informe oficial relativo a la presente solicitud, se han emitido las objeciones que a continuación se resumen:

1. De la solicitud de patente

Reivindicaciones (Art 30 D486, Art 22 PCT)

La reivindicación 1 no es clara porque presenta dos posibilidades denominadas requisito 1 y requisito 2, lo que la hace compleja. Se sugiere que cada requisito haga parte de una reivindicación independiente.

Las reivindicaciones 1, 2 y 4 no son claras porque las expresiones *"está dispersa en forma de capa en el polietileno (A) para formar parcialmente una fase continua de la misma", "la estructura a base de polietileno de acuerdo con la reivindicación 1, caracterizada porque la estructura a base de polietileno satisface el Requisito 1", "y satisface el Requisito 2"* son resultados a alcanzar, lo que no está permitido, no define al producto y/o método porque la invención no queda definida por el resultado a alcanzar, puesto que la reivindicación incluiría no sólo la solución propuesta por el solicitante, sino todas las alternativas presentes o futuras que lleguen a ese resultado.

El capítulo reivindicatorio no es claro porque los términos "*densidad*", "*índice de fluidez MFR*" y "*viscosidad relativa*" son parámetros. Se sugiere remplazar dichos

parámetros por las características técnicas estructurales como composiciones y pesos moleculares polímeros.
La reivindicación 11 no es clara porque hace referencia a una estructura la cual es un producto, pero presenta características técnicas de un proceso/método mediante el uso de la expresión "*se forma mediante un método de soplado directo*", lo cual no es permitido. Al respecto no debe olvidarse que las reivindicaciones de producto y de procedimiento son diferentes y, por ello, deben redactarse de manera independiente en el pliego reivindicatorio. Sobre las mismas, el Tribunal Andino de Justica ha dicho lo siguiente:

"El objeto de la invención de producto está constituido por un cuerpo cierto destinado a llenar una necesidad industrial que el estado de la técnica aún no ha satisfecho. En cambio, el objeto de la invención de procedimiento se encuentra conformado por "una serie o sucesión de operaciones que inciden sobre una materia (solida, liquida o gaseosa) que se encamina a la obtención de una cosa o un resultado".

2. Determinación del Estado de la Técnica

El estado de la técnica se determinó con base en la fecha de presentación de la solicitud de prioridad invocada, es decir, el 08 de marzo de 2011.

Consultadas las fuentes de información con que se cuenta, se encontraron los siguientes documentos que anticipan el objeto de esta solicitud.

Item	Documento	Título	Fecha de Publicación
D1	JP 2008-101108	"Injection molded article excellent in barrier property"	01/Mayo/2008
D2	JP 2008-120076	"Multilayer injection molding excellent in barrier properties"	01/Mayo/2008

El documento D1 divulga una resina obtenida a partir de la mezcla de polímeros como poliamida y polietileno (Párr. 5).

El documento D2 divulga una resina obtenida a partir de la mezcla de polímeros como poliamida y poliolefinas (Párr. 7).

3. Examen de Patentabilidad (Art 14 D486)

Nivel inventivo (Art 18 D486)

La reivindicación 1 consiste en "*Una estructura a base de polietileno que comprende...*" (Ver Pág. 56 del Rad. N°13-205541 -00000-0000).

En el análisis del nivel inventivo el examinador compara las características técnicas de la invención con el estado de la técnica citado, y arriba a las siguientes conclusiones:

Los documentos D1 y D2 se consideran el estado de la técnica más cercano a la invención definida en la reivindicación 1, porque divulgan resinas a base poliamida y polietilenos y/o poliolefinas.

La diferencia entre la invención, definida en la reivindicación 1 y la estructura del documento D1 consiste en que D1 no menciona el tipo específico de poliamida con viscosidad relativa entre 2.5 a 4.5.

La diferencia entre la invención, definida en la reivindicación 1 y la estructura del documento D2 consiste en que en D2 no se menciona el polietileno.
El efecto que logra el tener la poliamida de viscosidad relativa entre 2.5 y 4.5 en la mezcla es que permite obtener estructuras con características deseadas como resistencia a combustibles e impacto de forma más eficiente.

Por lo tanto, el problema técnico objetivo que pretende resolver esta invención se puede formular así "¿cómo modificar la estructura de D1 para que se obtengan estructuras con características deseadas como resistencia a combustibles e impacto de forma más eficiente?".

Sin embargo, el empleo de poliamidas con diversas viscosidades relativas entre 2.5 y 4.5, ya está divulgado en el documento D2 que se refiere a resinas de poliamidas mezcladas con poliolefinas (Párr. 42).

En consecuencia, una persona normalmente versada en la materia incluiría mediante la realización de diversas mezclas empleando las poliamidas de D2 como materia prima de la estructura de la anterioridad D1, esperando con certeza lograr el producto, como el de la reivindicación 1 de la solicitud, lo cual es considerado obvio y, por lo tanto, sin altura inventiva.

Asimismo, el documento D1 divulga las características de las reivindicaciones dependientes así:

- Reivindicación 3: a un índice de fluidez MRF similares se esperan pesos moleculares similares por ser una propiedad derivada de esta, por lo que se está mencionando el mismo compuesto polimérico (Pág. 38).
- Reivindicación 4: Se tiene en la mezcla un polietileno no modificado entre un 40 a 90%, un polietileno modificado con ácido entre un 0 a 56% y una poliamida a base de m-xilileno entre un 10 a 60% (Párr. 5).
- Reivindicación 6: se tiene un polietileno con un índice de fluidez (MFR) de 0.05 a 0.6 (Pág. 38).
- Reivindicación 7: se tiene otro polietileno con un índice de fluidez de 0.15 a 1.8 (Párr. 38).
- Reivindicación 8: se tiene un polietileno modificado con un índice de fluidez de 0.15 a 6 (Párr. 38).
- Reivindicación 9: la unidad de m-xililendiamina en la poliamida está en una cantidad de 70 % en base mol o más (Párr. 11).
- Reivindicación 10: se tiene una estructura de contenedor o frasco (Párr. 6).

Asimismo, el documento D2 divulga las características de las reivindicaciones dependientes así:

- Reivindicación 3: a un índice de fluidez MRF similares se esperan pesos moleculares similares por ser una propiedad derivada de esta, por lo que se está mencionando el mismo compuesto polimérico (Párr. 42).
- Reivindicación 9: la unidad de m-xililendiamina en la poliamida está en una cantidad de 70 % en base mol o más (Párr. 7).
- Reivindicación 10: se tiene una estructura de contenedor o frasco (Párr. 40 y Párr. 41).
- Las reivindicaciones 2 y 5 no presentan características técnicas adicionales que otorguen nivel inventivo a la reivindicación de la cual dependen ya que están expresadas en términos de resultados a alcanzar y presentan parámetros.

4. Conclusión

Los requisitos de Patentabilidad de la presente Solicitud están afectados de la siguiente manera:

Ítem	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	JP 2008-101108	1 a 10	Nivel inventivo
D2	JP 2008-120076	1 a 10	Nivel inventivo

II.- <u>En contestación a las objeciones anteriores, manifestamos lo siguiente:</u>

1. De la solicitud de patente

Reivindicaciones (Art 30 D486, Art 22 PCT)

Con el objetivo de superar las objeciones contenidas en el informe del examen de patentabilidad, se adjunta a la presente respuesta un nuevo capítulo reivindicatorio (1-13), todas sustentadas en el contenido de la solicitud originalmente presentada, lo que es permitido según el Artículo 34 de la Decisión 486, en el cual se han realizado las siguientes modificaciones:

- Se ha seguido la sugerencia del examinador y se ha separado la reivindicación 1 original objetada en dos reivindicaciones independientes, en las cuales, en la nueva reivindicación 1 independiente se dejan únicamente las características técnicas incluidas inicialmente en el Requisito 1 y en la nueva reivindicación 3, independiente también, se incluyen las características inicialmente consideradas para Requisito 2.
- Adicionalmente, en la nueva reivindicación 1 enmendada, la expresión " *...en el cual la poliamida (C) que contiene el grupo m-xilileno está dispersa en forma de capa en el polietileno (A) para formar parcialmente una fase continua de la misma...*" se cambia por: "*...la estructura que comprende una forma de capa que está compuesta de la poliamida (C) que contiene el grupo m-xilileno en el polietileno (A), una parte de la forma de la capa que constituye una fase continua...*", como se observa en las reivindicaciones que se adjuntan.

  Esta expresión recita una característica estructural de la Figura 1. Es decir, cada una de las "líneas negras" en la Figura. 1 que se hacen a partir de la poliamida (C) deben llamarse como "capa" y las capas en plural (líneas negras plurales en la Fig. 1) están distribuidas y separados entre sí. Esta característica estructural se especifica por la expresión "*una forma de capa... dispersa en el polietileno (A)*" en la reivindicación modificada 1. Además, algunas capas se conectan con la otra capa, y esta <u>característica estructural</u> es indicada por la expresión "una parte de la forma de capa que constituye una fase continua". Por lo tanto, creemos que la expresión objetada se ha reemplazado por una expresión que describe características completamente estructurales del producto, superándose así esta objeción del examinador.

- En cuanto a la objeción de que el capítulo reivindicatorio no es claro porque los términos "*densidad*", "*índice de fluidez MFR*" y "*viscosidad relativa*" son parámetros y que por tal razón se sugiere remplazar dichos parámetros por las características técnicas estructurales como composiciones y pesos moleculares de los polímeros, queremos aclarar

que el Instructivo sobre el Examen de las Solicitudes de Patentes de Invención y Modelo de Utilidad, en su página 42 plantea:

> 2.6.5.9 Definición por parámetros
>
> Una reivindicación de producto, por ejemplo un compuesto químico, se puede caracterizar por su estructura y elementos, por su fórmula química, como un producto de un proceso, o excepcionalmente por sus parámetros.
>
> Los parámetros son valores característicos de propiedades mensurables (por ejemplo el punto de fusión), o definidos como combinaciones matemáticas de varias variables.
>
> El examinador no permitirá la caracterización de un compuesto químico solamente por sus parámetros, a menos que la invención no se pueda definir de otra manera. En cualquier caso, el parámetro tiene que poder ser determinado y medido sin ambigüedad por métodos estándar conocidos en el campo en cuestión, o descritos claramente en la solicitud.

Es decir, la posibilidad de reivindicar un producto químico por sus parámetros no está excluida según las regulaciones en materia de patentes colombianas, siempre y cuando esto se haga correctamente, como entendemos que se realiza en el presente caso.

Es bien conocido que el polietileno tiene ramas y la "densidad" del polietileno cambia de acuerdo a la cantidad y tamaño de las ramas. Es decir, la "densidad" indica el grado ramificación en el polietileno. Esto, en nuestra opinión, define una característica completamente estructural del polietileno (A).

Como se muestra en el párrafo [0048], la "viscosidad relativa" se utiliza generalmente como un índice del grado de polimerización de un polímero. El grado de polimerización define una característica estructural del polímero (poliamida (C)), ya que indica el número de unidades monoméricas en un polímero. El "índice de fluidez (MFR)" se utiliza típicamente como el índice de un peso molecular de un polímero como se muestra en el párrafo [0024]. Por consiguiente, el peso molecular también define una característica estructural del polímero (polietileno (A) y (B)).

Por lo tanto, tanto los parámetros "densidad", "viscosidad relativa" e "índice de fluidez (MFR)" definen por sí mismos características técnicas estructurales de los polímeros y por lo tanto consideramos que no es necesario de reemplazar estas palabras por otros términos.

Por otra parte, la "densidad" y el "MFR" han sido autorizados como términos que especifican las características del polietileno por muchas oficinas de patentes alrededor del mundo, tales como JPO, EPO, USPTO, y así sucesivamente. Adjuntamos a la presente respuesta dos patentes concedidas para el territorio de Estados Unidos la US.7,354,655, véase por ejemplo en particular, su reivindicación 1. Del mismo modo, la "viscosidad relativa" ha sido autorizada como un término que especifica las características de una poliamida como se muestra en la especificación de patente adjunta US 8,597,750, en particular en su reivindicación 2.

Consideramos respetuosamente que de forma consecuente, los expertos colombianos deberían asimilar estas prácticas internacionales en el examen de invenciones relativas a materias particulares, a las cuales no se pueden aplicar estándares estrictos de análisis, sino caso a caso de acuerdo a la naturaleza de la invención que se evalúa.

- En la nueva reivindicación 11 del capítulo reivindicatorio que se adjunta, se cambia la categoría de la misma de "producto" a "método". Esta enmienda se apoya en el párrafo [0054] de la solicitud internacional original. Con esta enmienda, se supera la objeción del examinador con respecto a esta reivindicación original 11.

2. **Examen de Patentabilidad** (Art 14 D486)

Nivel inventivo (Art 18 D486)

A continuación argumentaremos por qué no consideramos pertinentes las objeciones del examinador en cuanto al nivel inventivo de la presente solicitud con respecto al estado de la técnica citado, es decir, con respecto a los documentos D1 y D2 mencionados en el informe emitido por esa entidad.

En primer lugar discrepamos respetuosamente de la conclusión del examinador cuando plantea que, "....puesto que una persona normalmente versada en la materia incluiría mediante la realización de diversas mezclas empleando las poliamidas de D2 como materia prima de la estructura de la anterioridad D1, esperando con certeza lograr el producto como el de la reivindicación 1 y como consecuencia de lo cual se puede considerar que la materia para la que se busca protección es obvia y sin altura inventiva...", ya que el mero hecho de que a partir de lo divulgado en el estado de la técnica se tenga que realizar experimentación adicional para llegar a las características técnicas reivindicadas, esto involucra en sí mismo un esfuerzo inventivo adicional no derivado de forma evidente de lo previamente descrito.

Como se muestra en la nueva reivindicación 1 independiente, la relación del MFR (por ejemplo, índice de peso molecular) del polietileno modificado con ácido (B) con respecto al del polietileno (A) (en lo adelante "relación de MFR (B)/(A)") está en el intervalo de 3 a 10, mientras que las densidades (por ejemplo, grado de las ramas) del polietileno (A) y el polietileno modificado con ácido (B) se ajustan en un intervalo predeterminado, respectivamente. A partir de estas características, en la invención de la reivindicación 1, la estructura puede obtener una alta resistencia a la tensión y evitar que se formen grietas cuando se cae, mientras que mantiene una excelente propiedad de barrera cuando la estructura comprende la forma de capa que se define en la nueva reivindicación 1, como se muestra en la Tabla 1-2.

El documento D1 da a conocer un cuerpo moldeado que comprende una poliolefina no modificada (A) tal como polietileno, una poliolefina modificada (B) tal como polietileno modificado con ácido, y una poliamida (D) que contiene un grupo m-xilileno, similar a la invención de la reivindicación 1. Sin embargo, D1 no divulga que la relación de MFR (B)/(A) se controla entre "3 y 10". Más específicamente, la relación de MFR (B)/(A) en el Ejemplo 1 es de 0,9/0,35 (= 2,57), la relación MFR (B)/(A) en los Ejemplos 2-4 es 0,9/1,0 (= 0,9), y la relación de MFR (B)/(A) en los Ejemplos 5-6 es 0,9/12 (= 0,075). Es decir, las relaciones de MFR (B)/(A) de todos los Ejemplos en D1 no solo se encuentran fuera del intervalo reivindicado en la presente invención, sino incluso distantes al mismo. Además, ni las modalidades preferidas ni las reivindicaciones

de D1 anticipan la relación de MFR (B)/(A). Finalmente, D1 no anticipa que la densidad (por ejemplo, el grado de las ramas) del polietileno modificado con ácido (B) se ajusta en un intervalo predeterminado (0,90-0,935).

Por otro lado, el documento D2 describe que una capa en el artículo de múltiples capas comprende entre 10 y 70% en peso de poliamida (A) que contiene un grupo m-xilileno (correspondiente a la poliamida (C) en la reivindicación 1), 30-90% en peso de poliolefina modificada (B) (correspondiente al polietileno modificado con ácido (B)) y 0-50% en peso de poliolefina (C) (correspondiente a polietileno (A)). Sin embargo, D2 no da a conocer que la relación de MFR de poliolefina modificada/poliolefina se controla en el rango de 3 a 10, ni enseña que la densidad (por ejemplo, grado de las ramas) del polietileno modificado con ácido (B) se ajusta en un rango particular predeterminado (de 0,90 a 0,935). D2 sólo da a conocer que la densidad de la poliolefina modificada es "0,89" como se muestra en el apartado 0042.

En consecuencia, las características técnicas de la reivindicación 1 en lo concerniente a la relación de MFR y la densidad de los componentes de la estructura a base de polietileno objeto de protección no están sugeridas por la combinación de los documentos D1 y D2, por lo que podemos afirmar que la materia de la reivindicación 1 no es obvia.

Con respecto a la nueva reivindicación 3 independiente, el polietileno comprende dos tipos de polietileno (A1) y (A2) en una relación de 70/30-95 /5, el polietileno (A1) con una densidad de 0,935 a 0,965 y el otro polietileno (A2) que tiene una densidad de 0,91 a 0,93. Es decir, el polietileno comprende el polietileno (A1) con grado relativamente bajo de ramificación y el polietileno (A2) que tiene relativamente alto grado de ramificación en una relación de 70/30-95/5. Debido a estas características, la estructura resultante puede obtener una alta resistencia a la tensión y evita que se formen grietas cuando se cae, mientras mantiene una excelente propiedad de barrera cuando la estructura comprende la forma de capa que se define en la reivindicación 3, como se muestra en la Tabla 2-2.

El documento D1 da a conocer un cuerpo moldeado que comprende una poliolefina no modificada (A) tal como polietileno, una poliolefina modificada (B) tal como polietileno modificado con ácido, y poliamida que contiene un grupo m-xilileno (D), similar a la invención de la reivindicación 3. Sin embargo, D1 no da a conocer que la poliolefina no modificada (A) (que se corresponde con el polietileno (A) de la reivindicación 3 contiene dos tipos de polietileno; uno que tiene una densidad entre 0,935 y 0,965, y el otro que tiene una densidad entre 0,91 hasta 0,93 en la relación de 70/30-95/5. D2 también falla en cuanto al rasgo del polietileno (A). Por consiguiente, las características técnicas de la reivindicación 3 no se sugieren mediante la combinación de D1 y D2, y por lo tanto se puede concluir que la materia de la nueva reivindicación 3 también implica una actividad inventiva.

Finalmente, considerando que las nuevas reivindicaciones 1 y 3 del conjunto de reivindicaciones que se adjunta se pueden considerar una selección novedosa (distante en cuanto a los rangos divulgados en D1 y D2) y además esta selección demuestra provocar un efecto técnico a la estructura a base de polietileno reivindicada, podemos afirmar que

estamos en presencia de una invención de selección que satisface plenamente el requisito de nivel inventivo.

Puesto que las reivindicaciones 2 a 11 comparten el mismo concepto inventivo previamente argumentado, respetuosamente afirmamos que las mismas también son inventivas con respecto a D1 y D2.

Por todo lo argumentado anteriormente, los documentos D1 y D2 ni solos, ni combinados entre sí, trazan las pautas para llegar a las características técnicas de la presente invención, mucho menos sugieren como hacerlo, en consecuencia, la solución técnica propuesta no se deriva de manera evidente del estado de la técnica y por lo tanto es novedosa e inventiva.

Teniendo en cuenta que las nuevas reivindicaciones presentadas con esta respuesta definen la materia que se desea proteger, siendo claras, concisas y debidamente sustentadas en la descripción original, consideramos que se han superado todas y cada una de las objeciones expuestas por el examinador, por lo que el capítulo reivindicatorio cumple con los requisitos de patentabilidad conforme lo establece el artículo 14 y demás afines de la Decisión 486.

De manera atenta solicito a su Despacho, tener en cuenta todos y cada una de las consideraciones expuestas previamente, al momento de estudiar el presente caso.

III. SE ANEXA:

(i) Nuevo Capítulo reivindicatorio (1-13). (Medio magnético).
(ii) Adjuntamos documentos relacionados a dos patentes concedidas para el territorio de Estados Unidos la US.7,354,655 y la US 8,597,750, como referencia, según lo mencionado en la presente respuesta. (Medio magnético).
(iii) Comprobante de pago por concepto de excedente de dos (2) reivindicaciones adicionales.

IV. PETICIÓN:

Conforme a lo anterior, una vez atendidos los requerimientos y exigencias del examinador y al tener en cuenta el nuevo capítulo de reivindicaciones que aquí se presenta, así como los argumentos expuestos, solicito muy respetuosamente a su Despacho, continuar el trámite de rigor y de ser el caso se hagan las correspondientes observaciones con al ánimo de hacer lo pertinente dentro del presente trámite, teniendo en cuenta que la presente solicitud cumple con las exigencias establecidas en la D486.

Atentamente,

HUMBERTO RUBIO CAMACHO
C.C. 17'192.062 de Bogotá
T.P. 50.007 Consejo Superior de la Judicatura
COD. 4134

REIVINDICACIONES

1. Una estructura a base de polietileno que comprende de 60 a 90% por masa de un polietileno (A), de 5 a 35% por masa de un polietileno modificado con ácido (B) y de 5 a 35% por masa de una poliamida que contiene un grupo m-xilileno (C), en el cual la poliamida que contiene el grupo m-xilileno (C) se dispersa en forma de una capa en el polietileno (A), que parcialmente forma una fase continua del mismo, y tienen una viscosidad relativa de 2,5 a 4,5,

caracterizada porque el polietileno (A) es un polietileno de alta densidad (Aa) que tiene una densidad de 0,94 a 0,97 y un índice de fluidez (MFR) de 0,1 a 0,6, y
el polietileno modificado con ácido (B) que tiene una densidad de 0,90 a 0,935 y un índice de fluidez (MFR) que está en el rango de 3 a 10 veces el MFR del polietileno de alta densidad (Aa).

2. La estructura a base de polietileno de acuerdo con las reivindicación 1, caracterizada porque la poliamida que contiene el grupo m-xilileno (C) contiene componentes con un peso molecular promedio en número de 1,000 o menos en una cantidad de 2% por masa o menos.

3. Una estructura a base de polietileno que comprende de 60 a 90% por masa de un polietileno (A), de 5 a 35% por masa de un polietileno modificado con ácido (B) y de 5 a 35% por masa de una poliamida que contiene un grupo m-xilileno (C) , en el cual la poliamida que contiene el grupo m-xilileno (C) se dispersa en forma de una capa en el polietileno (A), que parcialmente forma una fase continua del mismo, y tiene una viscosidad relativa de 2,5 a 4,5,
caracterizada porque el polietileno (A) está en forma de una mezcla de un polietileno (A1) que tiene una densidad de 0,935 a 0,965 y un polietileno (A2) que tienen una densidad de 0,91 a 0,93, y la relación de masa del polietileno (A1) con respecto al polietileno (A2) ((A1)/(A2)) es de 70/30 a 95/5;

4. La estructura a base de polietileno de acuerdo con la reivindicación 3, caracterizada porque la estructura a base de polietileno comprende de 60 a 90% por masa del polietileno (A), de 5 a 25% por masa del polietileno modificado con ácido (B) y de 5 a 35% por masa de la poliamida que contiene el grupo m-xilileno (C).

5. La estructura a base de polietileno de acuerdo con la reivindicación 4, caracterizada porque el polietileno modificado con ácido (B) tiene una densidad de 0,90 a 0,935.

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6. La estructura a base de polietileno de acuerdo con la reivindicación 4 o 5, caracterizada porque el polietileno (A1) tiene un índice de fluidez (MFR) de 0,05 a 0,6.

7. La estructura a base de polietileno de acuerdo con cualquiera de las reivindicaciones 4 a 6, caracterizada porque el polietileno (A2) tiene un índice de fluidez (MFR) que está en el rango de 0,5 a 8 veces el MFR del polietileno (A1).

8. La estructura a base de polietileno de acuerdo con cualquiera de las reivindicaciones 4 a 7, caracterizada porque el polietileno modificado con ácido (B) tiene un índice de fluidez (MFR) que está en el rango de 3 a 10 veces el MFR del polietileno (A1).

9. La estructura a base de polietileno de acuerdo con cualquiera de las reivindicaciones 1 a 8, caracterizada porque la poliamida que contiene el grupo m-xilileno (C) contiene una unidad de m-xililendiamina en una cantidad de 70 mol% o más.

10. La estructura a base de polietileno de acuerdo con cualquiera de las reivindicaciones 1 a 9, caracterizada porque la estructura a base de polietileno está en forma de un tanque, una tubería o una botella.

11. La estructura a base de polietileno de acuerdo con cualquiera de las reivindicaciones 1 a 10, caracterizada porque la estructura a base de polietileno se forma mediante un método de soplado directo.

12. Un método para producir una estructura a base de polietileno, que comprende de 60 a 90% por masa de un polietileno (A), de 5 a 35% por masa de un polietileno modificado con ácido (B) y de 5 a 35% por masa de una poliamida que contiene un grupo m-xilileno (C), en el cual la poliamida que contiene el grupo m-xilileno (C) se dispersa en forma de una capa en el polietileno (A), que parcialmente forma una fase continua del mismo, y tienen una viscosidad relativa de 2,5 a 4,5, en el que dicho método comprende:

amasar en estado fundido un polietileno (A), un polietileno modificado con ácido (B) y una poliamida que contiene un grupo m-xilileno (C) en un extrusor;

extruir el material resultante del amasado en estado fundido en una forma tubular como un parisón;

interponer el parisón entre las partes de un troquel de metal;

soplar aire en el parisón con el fin de inflar el parisón de manera que este se ponga en estrecho contacto con el interior del troquel de metal; y

abrir el troquel de metal y luego sacar una estructura moldeada del mismo.

en el que el polietileno (A) es un polietileno de alta densidad (Aa) que tiene una densidad de 0,94 hasta 0,97 y un índice de fluidez (MFR) de 0,1 a 0,6, y

el polietileno modificado con ácido (B) tiene una densidad de 0,90 hasta 0,935 y un índice de fluidez (MFR) que está en el intervalo de 3 a 10 veces el MFR del polietileno de alta densidad (Aa).

13. Método para producir una estructura a base de polietileno, que comprende de 60 a 90% por masa de un polietileno (A), de 5 a 35% por masa de un polietileno modificado con ácido (B) y de 5 a 35% por masa de una poliamida que contiene un grupo m-xilileno (C), en el cual la poliamida que contiene el grupo m-xilileno (C) se dispersa en forma de una capa en el polietileno (A), que parcialmente forma una fase continua del mismo, y tienen una viscosidad relativa de 2,5 a 4,5, en el que dicho método comprende:

amasar en estado fundido un polietileno (A), un polietileno modificado con ácido (B) y una poliamida que contiene un grupo m-xilileno (C) en un extrusor;

extruir el material resultante del amasado en estado fundido en una forma tubular como un parisón;

interponer el parisón entre las partes de un troquel de metal;

soplar aire en el parisón con el fin de inflar el parisón de manera que este se ponga en estrecho contacto con el interior del troquel de metal; y

abrir el troquel de metal y luego sacar una estructura moldeada del mismo.

en el que el polietileno (A) es en forma de una mezcla de un polietileno (A1) que tiene una densidad de 0,935 a 0,965 y un polietileno (A2) que tiene una densidad de desde 0,91 hasta 0,93, y una relación de masa del polietileno (A1) para el polietileno (A2) ((A1) / (A2)) es de 70/30 a 95/5.

Industria y Comercio
SUPERINTENDENCIA

PLANILLA DE RADICACIÓN - DIGITALIZACIÓN DIARIA
RELACIÓN DE ANEXOS

Dependencia: 2020	Fecha: 14 (AAAA) 11 (MM) 13 (DD)	Recorrido:
Tipo de Radicación: Entrada: ☐ Salida: ☐ Traslado: ☐ Convenio: ☐		
Radicador:		Planilla:

ID	*No. Radicación*	*Consecutivo*	*Item*
1	13205541	04	
2			
3			
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11			
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14			
15			
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17			

Item	*Unidad de Conservación*
1	Bolsa
2	Caja
3	Libro
4	Sobre
5	Tomo
6	**Otro**
Item	***Soporte Documental***
7	CD X
8	Disquete
9	DVD
10	Folleto
11	Foto
12	Periódico
13	Plano
14	Publicación Periódica
15	USB
16	**Otro**

Observaciones:

El cd contiene:
3 archivos en formato pdf, procesados y subidos al sistema.

VVH

GD01-F13

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
NIT : 800.176.089-2
- / -

Industria y Comercio
SUPERINTENDENCIA

RECIBO DE CAJA

No. 14 - 121467

Bogotá D.C., Noviembre 13 de 2014 - 14:02:03

RECIBIDO DE : HUMBERTO RUBIO & CIA ABOGADOS LTDA NI 830.000.228

*** Soporte del Pago ***

TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	VR PAGO
CONSIGNACION	BANCO DE BOGOTA	062754387	636822966	13/11/2014	2.944.000.00

*** Conceptos Pagados ***

CANT.	RENTISTICO	CONCEPTO	Vr.UNDITARIO	Vr.CONCEPTO
2	50005-01-01 SOLICITUDES	1607 REIVINDICACION PATENTE UNITARIA ADICIONAL A LAS 10 INIC	31.000.00	62.000.00
				$62.000.00

SON: **SESENTA Y DOS MIL PESOS MONEDA CORRIENTE***

Responsable: _____

Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
No. 13-205541- -00004-0000
Fecha: 2014-11-13 14:17:56 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 523 RESPUESTA Folios: 13

13

REIVINDICACIONES

1. Una estructura a base de polietileno que comprende de 60 a 90% por masa de un polietileno (A), de 5 a 35% por masa de un polietileno modificado con ácido (B) y de 5 a 35% por masa de una poliamida que contiene un grupo m-xilileno (C), en el cual la poliamida que contiene el grupo m-xilileno (C) se dispersa en forma de una capa en el polietileno (A), que parcialmente forma una fase continua del mismo, y tienen una viscosidad relativa de 2,5 a 4,5,

caracterizada porque el polietileno (A) es un polietileno de alta densidad (Aa) que tiene una densidad de 0,94 a 0,97 y un índice de fluidez (MFR) de 0,1 a 0,6, y
el polietileno modificado con ácido (B) que tiene una densidad de 0,90 a 0,935 y un índice de fluidez (MFR) que está en el rango de 3 a 10 veces el MFR del polietileno de alta densidad (Aa).

2. La estructura a base de polietileno de acuerdo con las reivindicación 1, caracterizada porque la poliamida que contiene el grupo m-xilileno (C) contiene componentes con un peso molecular promedio en número de 1,000 o menos en una cantidad de 2% por masa o menos.

3. Una estructura a base de polietileno que comprende de 60 a 90% por masa de un polietileno (A), de 5 a 35% por masa de un polietileno modificado con ácido (B) y de 5 a 35% por masa de una poliamida que contiene un grupo m-xilileno (C) , en el cual la poliamida que contiene el grupo m-xilileno (C) se dispersa en forma de una capa en el polietileno (A), que parcialmente forma una fase continua del mismo, y tiene una viscosidad relativa de 2,5 a 4,5,
caracterizada porque el polietileno (A) está en forma de una mezcla de un polietileno (A1) que tiene una densidad de 0,935 a 0,965 y un polietileno (A2) que tienen una densidad de 0,91 a 0,93, y la relación de masa del polietileno (A1) con respecto al polietileno (A2) ((A1)/(A2)) es de 70/30 a 95/5;

4. La estructura a base de polietileno de acuerdo con la reivindicación 3, caracterizada porque la estructura a base de polietileno comprende de 60 a 90% por masa del polietileno (A), de 5 a 25% por masa del polietileno modificado con ácido (B) y de 5 a 35% por masa de la poliamida que contiene el grupo m-xilileno (C).

5. La estructura a base de polietileno de acuerdo con la reivindicación 4, caracterizada porque el polietileno modificado con ácido (B) tiene una densidad de 0,90 a 0,935.

6. La estructura a base de polietileno de acuerdo con la reivindicación 4 o 5, caracterizada porque el polietileno (A1) tiene un índice de fluidez (MFR) de 0,05 a 0,6.

7. La estructura a base de polietileno de acuerdo con cualquiera de las reivindicaciones 4 a 6, caracterizada porque el polietileno (A2) tiene un índice de fluidez (MFR) que está en el rango de 0,5 a 8 veces el MFR del polietileno (A1).

8. La estructura a base de polietileno de acuerdo con cualquiera de las reivindicaciones 4 a 7, caracterizada porque el polietileno modificado con ácido (B) tiene un índice de fluidez (MFR) que está en el rango de 3 a 10 veces el MFR del polietileno (A1).

9. La estructura a base de polietileno de acuerdo con cualquiera de las reivindicaciones 1 a 8, caracterizada porque la poliamida que contiene el grupo m-xilileno (C) contiene una unidad de m-xililendiamina en una cantidad de 70 mol% o más.

10. La estructura a base de polietileno de acuerdo con cualquiera de las reivindicaciones 1 a 9, caracterizada porque la estructura a base de polietileno está en forma de un tanque, una tubería o una botella.

11. La estructura a base de polietileno de acuerdo con cualquiera de las reivindicaciones 1 a 10, caracterizada porque la estructura a base de polietileno se forma mediante un método de soplado directo.

12. Un método para producir una estructura a base de polietileno, que comprende de 60 a 90% por masa de un polietileno (A), de 5 a 35% por masa de un polietileno modificado con ácido (B) y de 5 a 35% por masa de una poliamida que contiene un grupo m-xilileno (C), en el cual la poliamida que contiene el grupo m-xilileno (C) se dispersa en forma de una capa en el polietileno (A), que parcialmente forma una fase continua del mismo, y tienen una viscosidad relativa de 2,5 a 4,5, en el que dicho método comprende:

amasar en estado fundido un polietileno (A), un polietileno modificado con ácido (B) y una poliamida que contiene un grupo m-xilileno (C) en un extrusor;

extruir el material resultante del amasado en estado fundido en una forma tubular como un parisón;

interponer el parisón entre las partes de un troquel de metal;

soplar aire en el parisón con el fin de inflar el parisón de manera que este se ponga en estrecho contacto con el interior del troquel de metal; y

abrir el troquel de metal y luego sacar una estructura moldeada del mismo.

en el que el polietileno (A) es un polietileno de alta densidad (Aa) que tiene una densidad de 0,94 hasta 0,97 y un índice de fluidez (MFR) de 0,1 a 0,6, y

el polietileno modificado con ácido (B) tiene una densidad de 0,90 hasta 0,935 y un índice de fluidez (MFR) que está en el intervalo de 3 a 10 veces el MFR del polietileno de alta densidad (Aa).

13. Método para producir una estructura a base de polietileno, que comprende de 60 a 90% por masa de un polietileno (A), de 5 a 35% por masa de un polietileno modificado con ácido (B) y de 5 a 35% por masa de una poliamida que contiene un grupo m-xilileno (C), en el cual la poliamida que contiene el grupo m-xilileno (C) se dispersa en forma de una capa en el polietileno (A), que parcialmente forma una fase continua del mismo, y tienen una viscosidad relativa de 2,5 a 4,5, en el que dicho método comprende:

amasar en estado fundido un polietileno (A), un polietileno modificado con ácido (B) y una poliamida que contiene un grupo m-xilileno (C) en un extrusor;

extruir el material resultante del amasado en estado fundido en una forma tubular como un parisón;

interponer el parisón entre las partes de un troquel de metal;

soplar aire en el parisón con el fin de inflar el parisón de manera que este se ponga en estrecho contacto con el interior del troquel de metal; y

abrir el troquel de metal y luego sacar una estructura moldeada del mismo.

en el que el polietileno (A) es en forma de una mezcla de un polietileno (A1) que tiene una densidad de 0,935 a 0,965 y un polietileno (A2) que tiene una densidad de desde 0,91 hasta 0,93, y una relación de masa del polietileno (A1) para el polietileno (A2) ((A1) / (A2)) es de 70/30 a 95/5.

US007354655B2

(12) **United States Patent**
Yamaguchi et al.

(10) **Patent No.: US 7,354,655 B2**
(45) **Date of Patent: Apr. 8, 2008**

(54) **ADHESIVE RESIN COMPOSITION AND MULTI-LAYER LAMINATED STRUCTURE USING THE SAME**

(75) Inventors: **Tatsuo Yamaguchi**, Tokyo (JP); **Shinji Miwa**, Kawasaki (JP); **Fumio Asada**, Kawasaki (JP); **Kenichi Hiraki**, Shiojiri (JP); **Naoki Minorikawa**, Naka-gun (JP)

(73) Assignee: **Japan Polyolefins Co., Ltd.**, Tokyo (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **10/303,848**

(22) Filed: **Nov. 26, 2002**

(65) **Prior Publication Data**

US 2003/0175538 A1 Sep. 18, 2003

Related U.S. Application Data

(63) Continuation-in-part of application No. PCT/JP02/03083, filed on Mar. 28, 2002.

(30) **Foreign Application Priority Data**

Mar. 28, 2001 (JP) P2001-092651
Jun. 19, 2001 (JP) P2001-184835
Jun. 25, 2001 (JP) P2001-191573

(51) **Int. Cl.**
B32B 27/32 (2006.01)

(52) **U.S. Cl.** **428/516**; 428/500; 428/515; 428/518; 428/523; 525/78; 525/240

(58) **Field of Classification Search** 428/500, 428/522

See application file for complete search history.

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Primary Examiner—Monique R. Jackson
(74) *Attorney, Agent, or Firm*—Sughrue Mion, PLLC

(57) **ABSTRACT**

An object of the present invention is to provide an adhesive resin composition which displays excellent adhesive strength on bonding to a barrier material, during initial adhesion, durable adhesion, and even after soak in fuel oil, and which also has excellent moldability. Furthermore, another object of the present is to provide an adhesive resin composition which when recycled, displays good compatible in a regrind layer with polyethylene resins and barrier materials such as saponified products of ethylene-vinyl acetate copolymers or polyamide based resins, and which is consequently capable of suppressing deterioration in the low temperature impact resistance of a multi-layer vessel containing a regrind layer. In order to achieve these objects, the present invention provides an adhesive resin composition (C) comprising (A) 100 to 5% by mass of a modified polyethylene in which an unsaturated carboxylic acid and/or an unsaturated carboxylic acid derivative unit is grafted to a high molecular weight polyethylene with a melt flow rate (MFR: temperature 190° C., loading 2.16 kg) of 0.1 to 2.0 g/10 minutes, and a density of 0.91 to 0.96 g/cm^3, and (B) 0 to 95% by mass of an unmodified polyethylene with a melt flow rate (MFR: temperature 190° C., loading 2.16 kg) of 0.1 to 20 g/10 minutes, and a density of 0.86 to 0.96 g/cm^3, wherein the density of the adhesive resin composition (C) is 0.925 to 0.940 g/cm^3, the content of the unsaturated carboxylic acid and/or unsaturated carboxylic acid derivative unit incorporated therein is at least 0.09% by mass, and the melt flow rate (MFR: temperature 190° C., loading 2.16 kg) is from 0.1 to 2 g/10 minutes.

32 Claims, 5 Drawing Sheets

Fig. 1

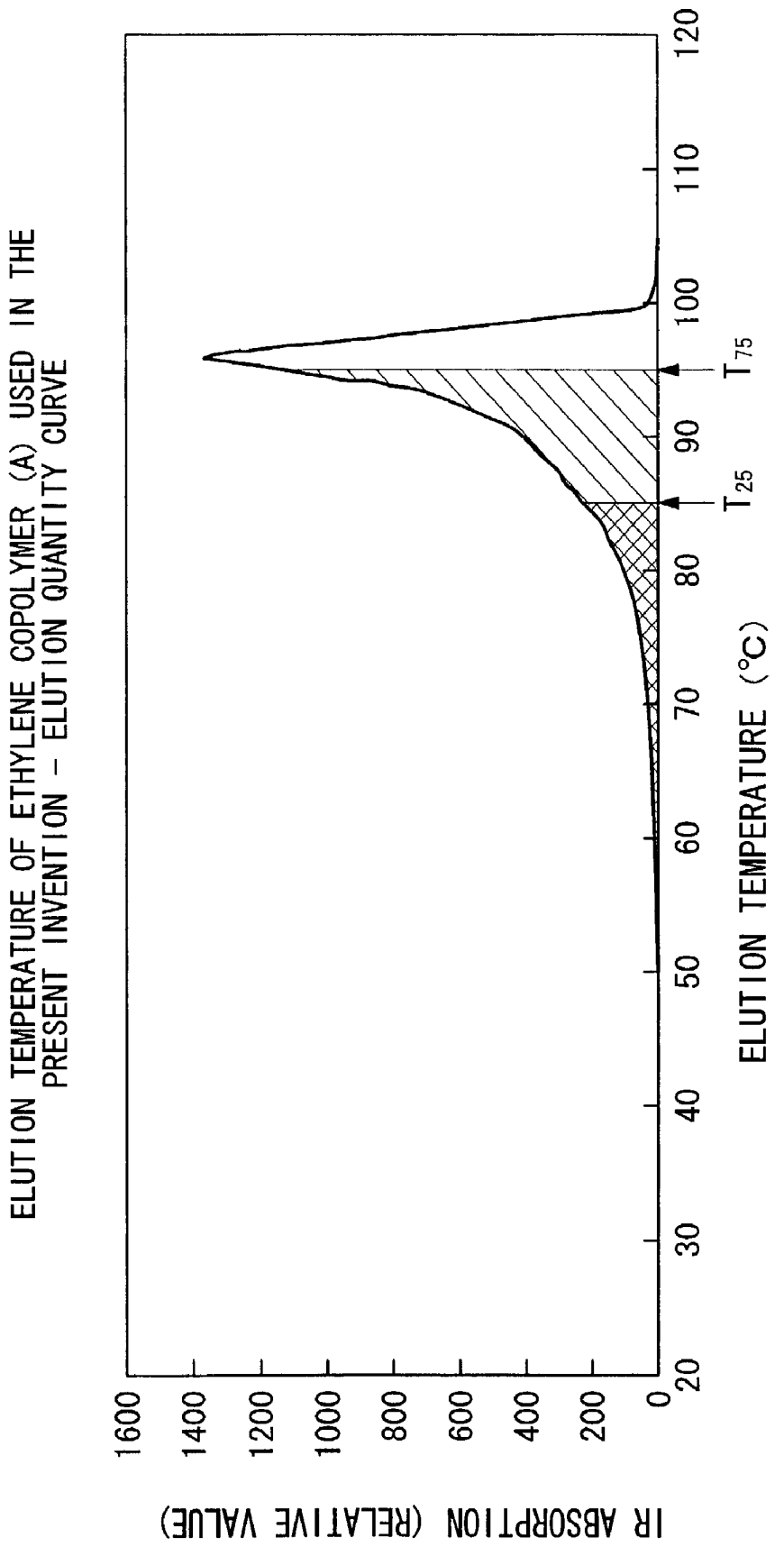
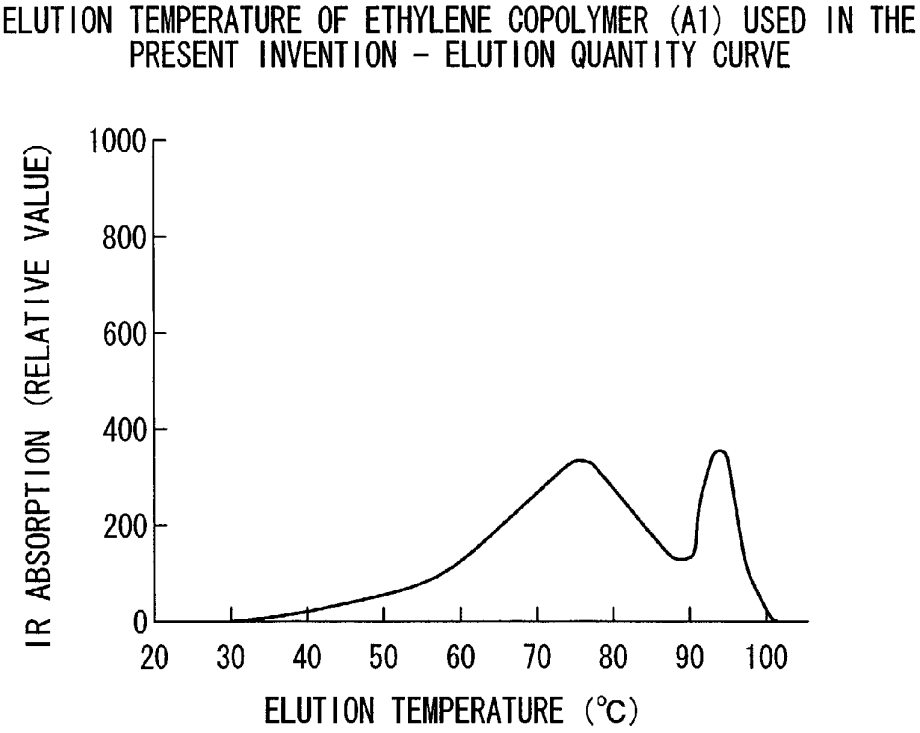

ELUTION TEMPERATURE OF ETHYLENE COPOLYMER (A) USED IN THE PRESENT INVENTION - ELUTION QUANTITY CURVE
IR ABSORPTION (RELATIVE VALUE)
1600
1400
1200
1000
800
600
400
200
0
20
30
40
50
60
70
80
90
100
110
120
T75
T25
ELUTION TEMPERATURE (°C)

Fig. 2


ELUTION TEMPERATURE OF ETHYLENE COPOLYMER (A1) USED IN THE PRESENT INVENTION - ELUTION QUANTITY CURVE
IR ABSORPTION (RELATIVE VALUE)
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800
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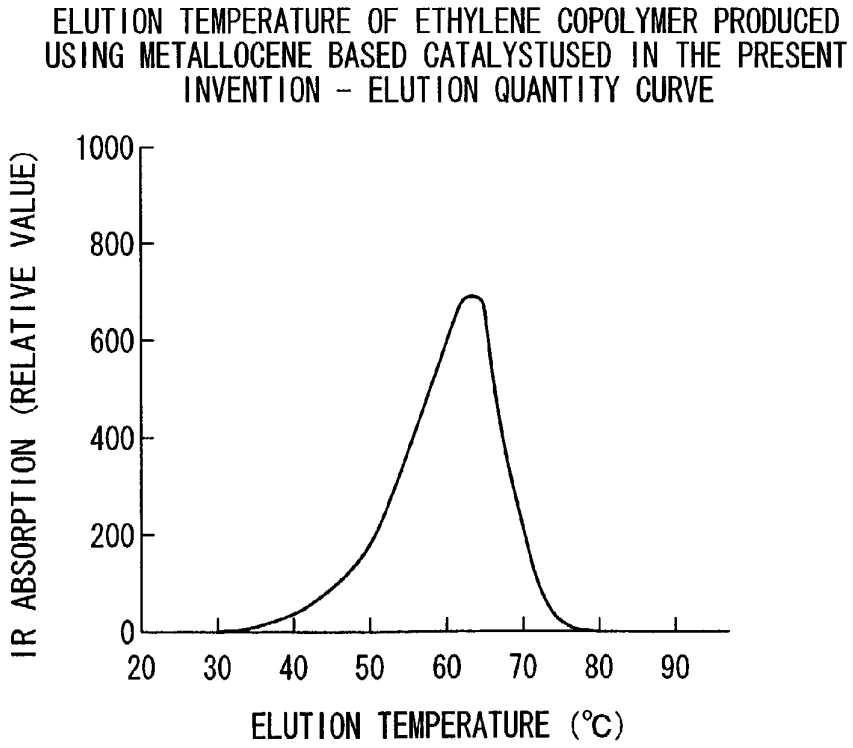
400
200
0
20
30
40
50
60
70
80
90
100
ELUTION TEMPERATURE (℃)

Fig. 3


ELUTION TEMPERATURE OF ETHYLENE COPOLYMER PRODUCED USING METALLOCENE BASED CATALYSTUSED IN THE PRESENT INVENTION - ELUTION QUANTITY CURVE
IR ABSORPTION (RELATIVE VALUE)
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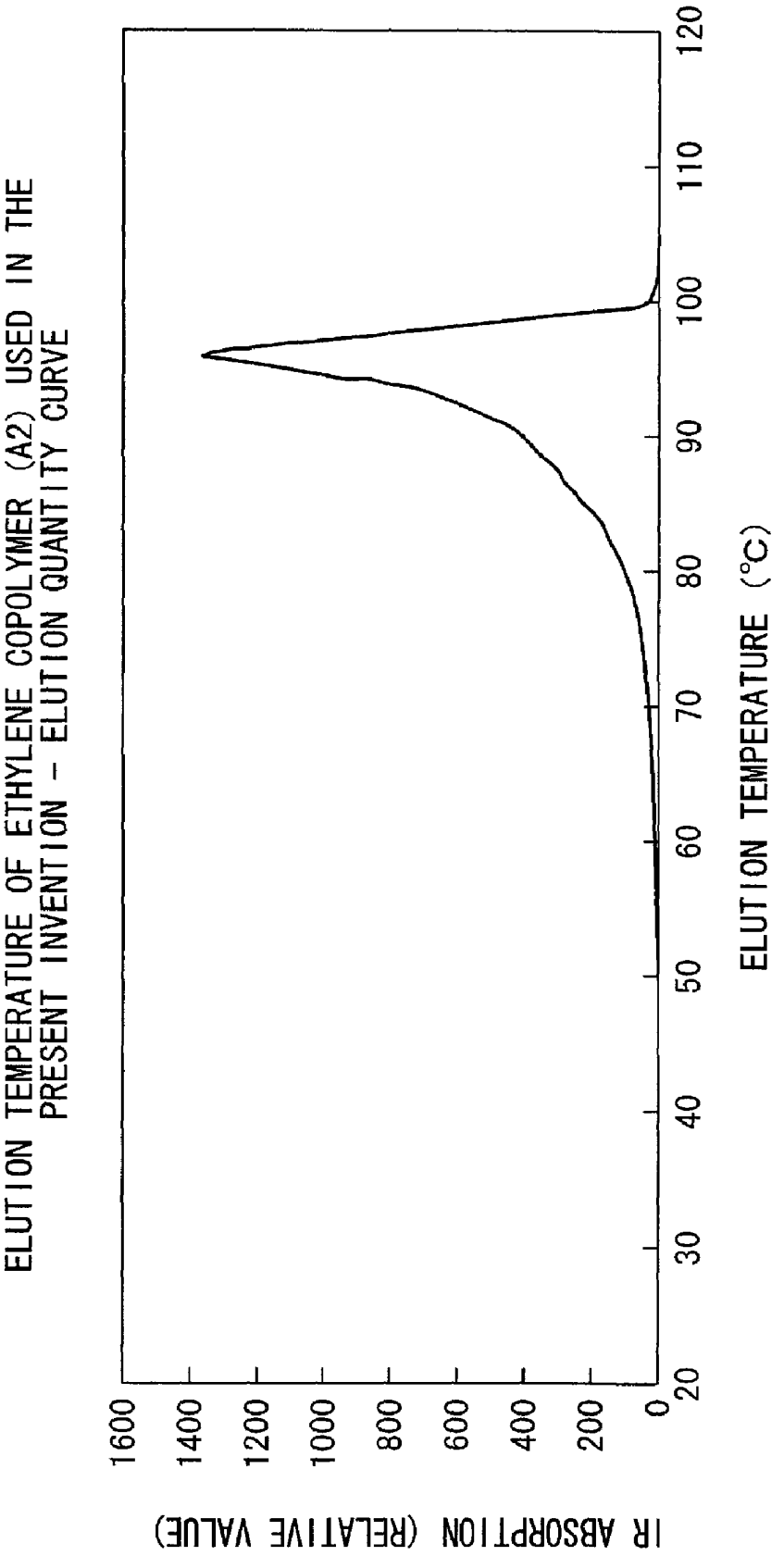
20
30
40
50
60
70
80
90
ELUTION TEMPERATURE (℃)

Fig. 4


ELUTION TEMPERATURE OF ETHYLENE COPOLYMER (A2) USED IN THE PRESENT INVENTION - ELUTION QUANTITY CURVE
IR ABSORPTION (RELATIVE VALUE)
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50
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90
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ELUTION TEMPERATURE (°C)

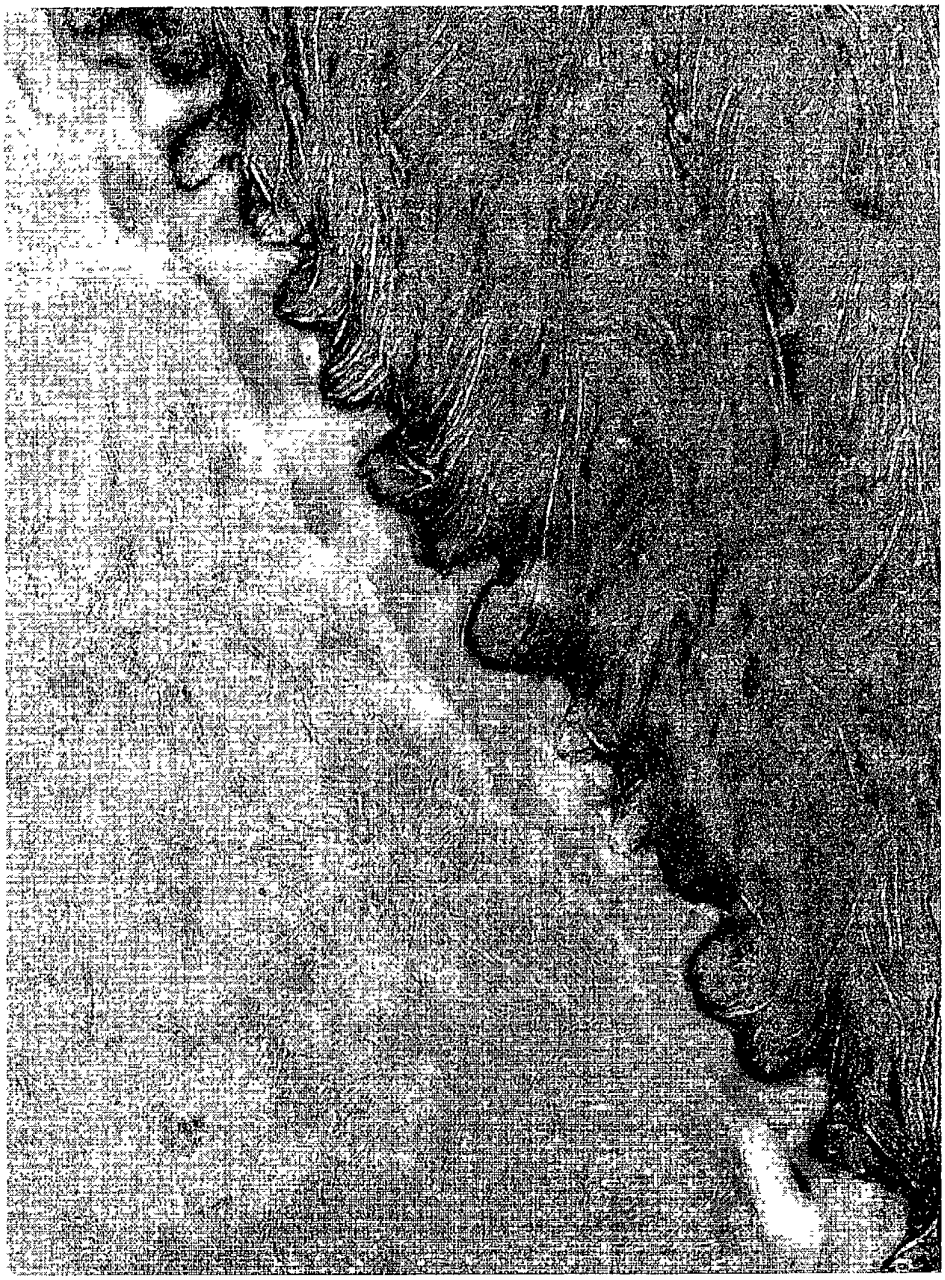

Fig. 5

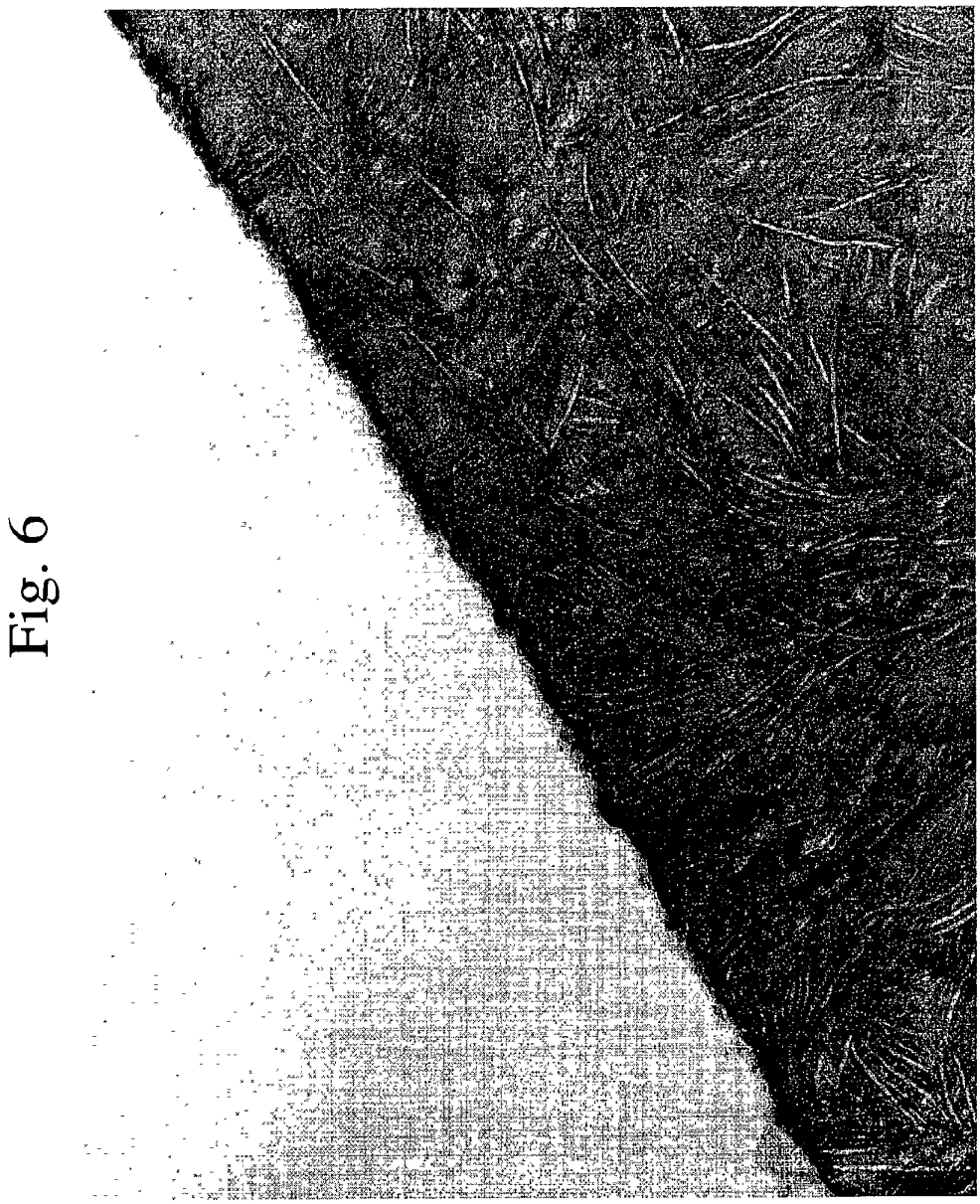

Fig. 6

ADHESIVE RESIN COMPOSITION AND MULTI-LAYER LAMINATED STRUCTURE USING THE SAME

CROSS REFERENCE TO RELATED APPLICATION

This is a Continuation-In-Part of Application No. PCT/JP02/03083 with an international filing date of Mar. 28, 2002; the complete disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

The present invention relates to an adhesive resin composition which displays excellent initial adhesion and durable adhesion to barrier materials such as saponified products of ethylene-vinyl acetate copolymers, or polyamide based resins, has excellent moldability, and for which deterioration in the physical properties during the recycling of molding by-products such as burrs and unused parison can be significantly suppressed. Furthermore, the present invention also relates to multi-layer laminated structures such as laminated vessels or laminated sheets using such an adhesive resin composition, which display good adhesive strength between layers, have good low temperature impact resistance, and display excellent resistance to fuel oil.

BACKGROUND ART

In recent years, multi-layer laminated structures such as multi-layer vessels and multi-layer sheets, which comprises saponified products of ethylene-vinyl acetate copolymers or polyamide based resins as a barrier layer, and a polyolefin as the outermost layer, are gradually being employed for applications which have conventionally used metals.

For example, in view of a lighter weight, a greater capacity, ease of molding, and rust resistance, in the case vehicle fuel vessels and drums, the change from metal tanks to synthetic resin tanks is occurring rapidly.

In particular, synthetic resin fuel vessels are required to have resistance to fuel oil, impact resistance and adhesion durability. For synthetic resin fuel vessels which satisfy these requirements, multi-layer laminated structures comprising a layer made of a barrier material such as a saponified product of an ethylene-vinyl acetate copolymer, or a polyamide resin, which provides an excellent barrier to penetration by gases or liquids, and a layer made of a high density polyethylene resin, which offers excellent mechanical characteristics, laminated together are now in widespread use.

In addition, in recent years the performance requirements for fuel vessels have been tightened even further. For example, long term maintenance of performance for the so-called "15 years, 150,000 miles" period is now required. Examples of the specifics of the performance requirements which must be maintained for this long period include no peeling of individual layers of the multi-layer laminated structure, no deterioration or layer abnormalities within the barrier layer in order to prevent volatilization of fuel components into the atmosphere, no fuel volatilization arising from peeling of the pinch off section produced by a die cutter during the blow molding process, and maintenance of the low temperature impact resistance above a certain level in order to minimize damage caused by a collision or the like.

However, barrier materials such as saponified products of ethylene-vinyl acetate copolymers or polyamide based resins and polyethylene resins display almost no natural adhesion, and consequently during lamination of these resins, an adhesive resin with good adhesion to both layers must be used.

Examples of this type of adhesive resin composition include resin compositions comprising a polyolefin based polymer modified with a solid rubber as disclosed in Japanese Unexamined Patent Application, First Publication No. Sho 50-7847 and resin compositions comprising an ethylene/α-olefin copolymer rubber modified with an unsaturated carboxylic acid as disclosed in Japanese Unexamined Patent Application, First Publication No. Sho 52-49289.

Furthermore, in order to improve thermal stability and prevent apparatus corrosion, these compositions typically also contain antioxidants and acid absorbers. Phenol based antioxidants or phosphorus based antioxidants are usually used to improve the thermal stability, and metal slats of fatty acids such as calcium stearate or the like is usually used to prevent apparatus corrosion.

However, although the above compositions provide a certain degree of adhesive strength, the adhesive strength is not entirely satisfactory for modern high speed molding or for thin film sections such as vessel pinch off sections generated during rapid deformations during molding. In addition, when soaked in fuel such as gasoline, which represents an actual potential application, there was a significant decrease in adhesive strength.

Furthermore, in those cases in which these types of adhesive resin compositions were used, if the burrs and unused parison and the like produced as by-products during the molding of a large vessel or sheet are returned to the process and used as a regrind layer, then because the compatible of these by-products with the major constituents, namely the polyethylene resin and the barrier materials such as the saponified product of an ethylene-vinyl acetate copolymer or the polyamide based resin, is unsatisfactory, the low temperature impact resistance of the multi-layer vessel itself may deteriorate.

An object of the present invention is to provide an adhesive resin composition which displays excellent adhesive strength on bonding to a barrier material, during initial adhesion, durable adhesion, and even after soak in fuel oil, and which also has excellent moldability. Furthermore, another object of the present invention is to provide an adhesive resin composition which when recycled, displays good compatible in a regrind layer with polyethylene resins and barrier materials such as saponified products of ethylene-vinyl acetate copolymers or polyamide based resins, and which is consequently capable of suppressing deterioration in the low temperature impact resistance of a multi-layer vessel comprising a regrind layer. In addition, yet another object of the present invention is to provide a multi-layer laminated structure with excellent low temperature impact resistance formed using such an adhesive resin composition.

DISCLOSURE OF INVENTION

As a result of intensive investigations aimed at improving the problems associated with conventional adhesive resin compositions, the inventors of the present invention discovered that the problems could be resolved by an adhesive resin composition described below and a multi-layer laminated structure using such an adhesive resin composition.

An adhesive resin composition of the present invention is an adhesive resin composition (C) comprising

(A) 100 to 5% by mass of a modified polyethylene in which an unsaturated carboxylic acid and/or an unsaturated

carboxylic acid derivative unit is grafted to a high molecular weight polyethylene with a melt flow rate (MFR: temperature 190° C., loading 2.16 kg) of 0.1 to 2.0 g/10 minutes, and a density of 0.91 to 0.96 g/cm^3, and

(B) 0 to 95% by mass of an unmodified polyethylene with a melt flow rate (MFR: temperature 190° C., loading 2.16 kg) of 0.1 to 20 g/10 minutes, and a density of 0.86 to 0.96 g/cm^3, wherein

the density of the adhesive resin composition (C) is 0.925 to 0.940 g/cm^3, the content of the unsaturated carboxylic acid and/or an unsaturated carboxylic acid derivative unit is 0.09% by mass or greater, and the melt flow rate (MFR: temperature 190° C., loading 2.16 kg) is 0.1 to 2 g/10 minutes.

Furthermore, the present invention also provides an adhesive resin composition, wherein the ratio MFR(A)/MFR(B), where MFR(A) represents the melt flow rate (MFR: temperature 190° C., loading 2.16 kg) of the modified polyethylene (A) and MFR(B) represents the melt flow rate (MFR: temperature 190° C., loading 2.16 kg) of the unmodified polyethylene (B), is less than 1.

Furthermore, the present invention also provides an adhesive resin composition, wherein the adhesive resin composition (C) comprises

(a) 100 to 5% by mass of a modified polyethylene with a melt flow rate of 0.1 to 2.0 g/10 minutes, and a density of 0.93 to 0.96 g/cm^3,

(b) 0 to 95% by mass of an unmodified polyethylene with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.93 to 0.96 g/cm^3,

(c) no more than 70% by mass of a modified and/or unmodified linear low density polyethylene with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.91 to 0.94 g/cm^3, and/or

(d) no more than 50% by mass of a modified and/or unmodified ultra low density polyethylene with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.86 to 0.91 g/cm^3, and (a)+(b)+(c)+(d) totals 100% by mass.

Furthermore, the present invention also provides an adhesive resin composition, wherein the modified polyethylene (a) is a high density polyethylene with a melt flow rate of 0.1 to 2.0 g/10 minutes and a density of 0.93 to 0.96 g/cm^3, and the unmodified polyethylene (b) is a high density polyethylene with a melt flow rate of 0.1 to 20 g/10 minutes and a density of 0.93 to 0.96 g/cm^3.

Furthermore, the present invention also provides an adhesive resin composition, wherein the linear low density polyethylene (c) and/or the ultra low density polyethylene (d) are resin compositions comprising an ethylene/o-olefin copolymer (A) (hereafter referred to as an ethylene copolymer) which satisfy the conditions (1) to (4) shown below:

(1) a density of 0.86 to 0.94 g/cm^3,

(2) a melt flow rate of 0.1 to 20 g/10 minutes,

(3) a molecular weight distribution (Mw/Mn) of 1.5 to 4.5, and

(4) a difference between T_{25}, representing the temperature at which 25% of the total is eluted, determined from the integrated elution curve of an elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method, and T_{75}, representing the temperature at which 75% of the total is eluted, namely $T_{75}-T_{25}$, and a density d which satisfy the relationship of an equation 1, shown below.

$$T_{75}-T_{25}\leqq -670\times d+644 \quad \text{(equation 1)}$$

Furthermore, the present invention also provides an adhesive resin composition, wherein the ethylene copolymer (A) also satisfies the relationship (5) described below:

(5) a difference between T_{25}, representing the temperature at which 25% of the total is eluted, determined from the integrated elution curve of an elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method, and T_{75}, representing the temperature at which 75% of the total is eluted, namely $T_{75}-T_{25}$, and a density d which satisfy the relationship of an equation 2, $T_{75}-T_{25}\geqq 300\times d+285$.

Furthermore, the present invention also provides an adhesive resin composition, wherein the ethylene copolymer (A) is an ethylene copolymer (A1) which satisfies the conditions (6) and (7) described below:

(6) a quantity X (% by mass) of an orthodichlorobenzene (ODCB) soluble fraction at 25° C., a density d, and a melt flow rate (MFR) which satisfy the relationships of an equation 3 and an equation 4 shown below:

$$X<2.0 \text{ in cases in which } d-0.008logMFR\geqq 0.93 \quad \text{(equation 3)}$$

$$X<9.8\times 10^3\times(0.9300-d+0.008logMFR)^2+2.0 \text{ in cases in which } d-0.008logMFR<0.93, \quad \text{(equation 4)}$$

, and

(7) an elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method which has a plurality of peaks.

Furthermore, the present invention also provides an adhesive resin composition, wherein the ethylene copolymer (A) is an ethylene copolymer (A2) which satisfies the conditions (8) and (9) described below:

(8) an elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method which has only one peak, and

(9) one, or two or more melting point peaks, wherein the highest melting point Tml and the density d satisfy the relationship of an equation 5, $Tml\geqq 150\times d-19$.

Furthermore, the present invention also provides an adhesive resin composition, wherein the ethylene copolymer (A2) also satisfies the condition (10) described below:

(10) a melt tension (MT) and a melt flow rate (MFR) which satisfy an equation 6 shown below.

$$logMT\leqq 0.572\times logMFR+0.3 \quad \text{(equation 6)}$$

Furthermore, the present invention also provides an adhesive resin composition, wherein the halogen concentration of the ethylene copolymer (A) is no more than 10 ppm.

Furthermore, the present invention also provides an adhesive resin composition, wherein the resin composition incorporating the ethylene copolymer (A) comprises substantially no additives.

Furthermore, the present invention also provides an adhesive resin composition, wherein if aliphatic metal salts exist within the adhesive resin composition, the concentration thereof is less than 100 weight ppm.

Furthermore, the present invention also provides an adhesive resin composition, wherein the unsaturated carboxylic acid is an acid anhydride.

Furthermore, the present invention also provides an adhesive resin composition, wherein the ring opening ratio of acid anhydride groups following modification is maintained at no more than 10%.

Furthermore, the present invention also provides an adhesive resin composition, wherein the acid anhydride is maleic anhydride.

Furthermore, the present invention also provides an adhesive resin composition, wherein 6.7% by mass of an adhesive resin composition, 88.3% by mass of a high density polyethylene with a density of 0.945 g/cm^3 and a high load melt flow rate (temperature 190° C., load 21.6 kg) of 6 g/10 minutes, and 5% by mass of a saponified product of an ethylene-vinyl acetate copolymer are subjected to molten kneading, and subsequent press molding of the kneaded product, at a temperature setting of 200° C. and a press pressure of 6 MPa, is used to prepare a sheet of thickness 4 mm, and when the WV notch tensile impact strength of a test specimen of a shape 1 according to JIS K7160 prepared from this sheet is measured at −40° C., the WV notch tensile impact strength is at least 120 KJ/cm^2.

Furthermore, the present invention also provides an adhesive resin composition, wherein the molten kneading utilizes a 50 mm single screw kneader in which the C1-C2-C3-head-dice temperature settings are set to 180° C.-200° C.-200° C.-200° C.-200° C. respectively, and the screw revolutions are set to 60 rpm.

Furthermore, the present invention also provides a multi-layer laminated structure comprising an adhesive layer formed from the adhesive resin composition, and at least a principal material layer formed on the outside of the adhesive layer, and a barrier layer formed on the inside of the adhesive layer.

Furthermore, the present invention also provides a multi-layer laminated structure, wherein the principal material layer is a high density polyethylene layer and/or a regrind layer using recycled material.

Furthermore, the present invention also provides a multi-layer laminated structure of a 3 type 5 layer structure comprising a principal material layer formed from a high density polyethylene layer and/or the regrind layer/the adhesive resin composition layer/the barrier layer/the adhesive resin composition layer/and the principal material layer formed from a high density polyethylene layer and/or the regrind layer.

Furthermore, the present invention also provides a multi-layer laminated structure, wherein the principal material layer is a high density polyethylene with a density of 0.93 to 0.97 g/cm^3 and a melt flow rate of 0.01 to 50 g/10 minutes.

Furthermore, the present invention also provides a multi-layer laminated structure, wherein the barrier layer is at least one material selected from a group consisting of saponified products of ethylene-vinyl acetate copolymers, polyamide based resins, polyester based resins and vinylidene chloride based resins.

Furthermore, the present invention also provides a multi-layer laminated structure, wherein the adhesion interface between the adhesive resin composition layer and/or the regrind layer, and the barrier layer is formed as an irregular surface.

Furthermore, the present invention also provides a multi-layer laminated structure, wherein viewing the interface structure of the multi-layer laminated structure with a transmission electron microscope at a magnification within a range from 20,000×to 50,000×reveals irregularities with an elevation difference of at least 100 nm.

Furthermore, the present invention also provides a multi-layer laminated structure, wherein the barrier layer is formed from a saponified product of an ethylene-vinyl acetate copolymer.

Furthermore, the present invention also provides a vessel formed from the multi-layer laminated structure.

Furthermore, the present invention also provides a vessel which is a blow vessel selected from a group consisting of a fuel tank, a food vessel, and an industrial chemical vessel.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a graph showing an elution temperature vs. elution quantity curve for an ethylene copolymer (A) used in the present invention.

FIG. **2** is a graph showing an elution temperature vs. elution quantity curve for an ethylene copolymer (A1) used in the present invention.

FIG. **3** is a graph showing an elution temperature vs. elution quantity curve for an ethylene copolymer (A3) produced using a typical metallocene based catalyst.

FIG. **4** is a graph showing an elution temperature vs. elution quantity curve for an ethylene copolymer (A2) used in the present invention.

FIG. **5** shows an electron microscope photograph 1 (captured at a magnification of 40,000×using a transmission electron microscope) of an interface structure between an adhesive resin composition of the present invention and a principal material layer.

FIG. **6** shows an electron microscope photograph 2 (captured at a magnification of 40,000×using a transmission electron microscope) of an interface structure between a conventional adhesive resin composition and a principal material layer.

BEST MODE FOR CARRYING OUT THE INVENTION

As follows is a more detailed description of the present invention.

[Modified Polyethylene (A)]

A modified polyethylene (A) of the present invention is a polyethylene to which an unsaturated carboxylic acid and/or an unsaturated carboxylic acid derivative unit has been grafted, and has a density from 0.91 to 0.96 g/cm^3, and preferably from 0.915 to 0.96 g/cm^3, and even more preferably from 0.93 to 0.96 g/cm^3.

It is extremely important that the polyethylene is a high molecular weight polyethylene with a melt flow rate (MFR: temperature 190° C., loading 2.16 kg) of 0.1 to 2.0 g/10 minutes, and preferably from 0.1 to 1.5 g/10 minutes, and the unsaturated carboxylic acid and/or an unsaturated carboxylic acid derivative unit is then grafted to this high molecular weight polyethylene.

Examples of suitable raw material polyethylenes include homopolymers formed solely from ethylene, and copolymers formed from ethylene and an α-olefin of 3 to 12 carbon atoms.

Examples of this type of α-olefin include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene. Specific examples of the polyethylene include high density polyethylenes and linear low density polyethylenes, although high density polyethylenes with a density of 0.93 to 0.96 g/cm^3 are preferred.

These polymers can be produced using a typical Ziegler system catalyst or a chromium based catalyst, or may also be produced using a so-called single site catalyst.

In the present invention, by modifying the type of high molecular weight polyethylene, an adhesive resin composition can be obtained which displays excellent adhesive strength during initial adhesion, durable adhesion, and even after soak in a fuel (fuel oil resistance).

Furthermore, an adhesive resin composition can be obtained which when recycled, displays good compatible in a regrind layer with polyethylene resins and barrier materials such as saponified products of ethylene-vinyl acetate copolymers or polyamide based resins, and which is consequently capable of suppressing deterioration in the low temperature impact resistance of a multi-layer vessel containing a regrind layer. If the MFR of the polyethylene is less than 0.1 g/10 minutes or exceeds 2.0 g/10 minutes, then the interlayer adhesion, the moldability, the impact strength and the fuel oil resistance of the final multi-layer laminated structure deteriorate, and the object of the present invention cannot be achieved.

Furthermore, if the density of the polyethylene is less than 0.91 g/cm^3, then not only is the adhesive strength of the final multi-layer laminated structure unsatisfactory, but the resistance to fuel oil and the like (resistance to swelling) is also insufficient. In contrast, if the density of the polyethylene exceeds 0.96 g/cm^3, then the impact resistance and the interlayer adhesion of the final multi-layer laminated structure are unsatisfactory.

When this type of polyethylene undergoes graft modification, preferably 0.1 to 2.0 parts by weight, and even more preferably 0.1 to 1.5 parts by weight, and most preferably 0.1 to 1.0 parts by weight of an unsaturated carboxylic acid and/or an unsaturated carboxylic acid derivative, and a radical initiator are added to 100 parts by weight of the polyethylene.

If the content of the unsaturated carboxylic acid and/or unsaturated carboxylic acid derivative added is less than 0.1 parts by weight, then the graft modification is insufficient, and the adhesiveness of the product adhesive resin composition may be unsatisfactory. In contrast, if the content exceeds 2.0 parts by weight, then not only is there a risk of the product modified polyethylene (A) gelling, deteriorating or coloring, but the adhesive strength and the mechanical strength of the final multi-layer laminated structure may also deteriorate.

Furthermore, the content of radical initiator added should preferably be from 0.001 to 0.5 parts by weight, and more preferably from 0.005 to 0.3 parts by weight, and even more preferably from 0.010 to 0.3 parts by weight. If the proportion of the radical initiator is less than 0.001 parts by weight, then a considerable length of time is required to achieve complete graft modification. Furthermore, the graft modification of the polyethylene may be insufficient, leading to unsatisfactory adhesive strength. In contrast, if the content exceeds 0.5 parts by weight, then the radical initiator may cause excessive decomposition or cross linking reactions.

Examples of the unsaturated carboxylic acid and/or unsaturated carboxylic acid derivative used in the modification include monobasic unsaturated carboxylic acids and dibasic unsaturated carboxylic acids, as well as metal salts, amides, imides, esters and acid anhydrides thereof.

The number of carbon atoms of such monobasic unsaturated carboxylic acids and monobasic unsaturated carboxylic acid derivatives should be no more than 20, and preferably no more than 15. Furthermore, the number of carbon atoms of such dibasic unsaturated carboxylic acids and dibasic unsaturated carboxylic acid derivatives should be no more than 30, and preferably no more than 25.

Specific examples of these unsaturated carboxylic acids and unsaturated carboxylic acid derivatives include acrylic acid, methacrylic acid, glycidyl methacrylate, maleic acid and the anhydride thereof, and 5-norbornene-2,3-dicarboxylic acid and the anhydride thereof.

Of these compounds, acid anhydrides are particularly preferred. Specific examples of such anhydrides include maleic anhydride, 5-norbornene acid anhydride, chlorendic anhydride, pyromellitic anhydride and phthalic anhydride, and of these maleic anhydride is particularly preferred. Adhesive resin compositions obtained using these types of acid anhydrides display extremely good adhesive performance.

Examples of the radical initiator include organic peroxides such as dicumyl peroxide, benzoyl peroxide, di-t-butyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane-3, lauroyl peroxide, t-butylperoxy benzoate, and dicumyl peroxide.

Examples of suitable graft modification methods include molten kneading methods in which a polyethylene such as the high density polyethylene resin (a), an unsaturated carboxylic acid and/or an unsaturated carboxylic acid derivative, and a radical initiator are kneaded together in a molten state using a kneading device such as an extruder, a Banbury mixer or a kneader; solution methods in which a polyethylene, an unsaturated carboxylic acid and/or an unsaturated carboxylic acid derivative, and a radical initiator are dissolved in a suitable solvent; and slurry methods in which an unsaturated carboxylic acid and/or an unsaturated carboxylic acid derivative, and a radical initiator act upon particles of a high density polyethylene (a) suspended in a slurry. In addition, in order to improve the physical properties of the modified polyethylene (A), the product may be heated or washed following the graft modification, so as to remove any unreacted unsaturated carboxylic acid and/or unsaturated carboxylic acid derivative monomers as well as any by-products. The actual method employed can be selected in accordance with the intended use of the final product multi-layer laminated structure.

The temperature during modification is determined taking into consideration factors such as deterioration of the polyethylene, decomposition of the unsaturated carboxylic acid and/or the unsaturated carboxylic acid derivative, and the decomposition temperature of the radical initiator used.

For example, in the molten kneading method, the temperature is typically from 200 to 350° C., and preferably from 220 to 300° C., and even more preferably from 250 to 300° C.

In the present invention, during the modification, other resins may also be incorporated provided such addition does not result in a deviation from the intent of the invention.

Examples of other synthetic resins include high pressure low density polyethylene resins, and copolymers of ethylene and other vinyl monomers, such as ethylene-vinyl acetate copolymers, ethylene-acrylic acid copolymers, ethylene-methacrylic acid copolymers, ethylene-methylacrylate copolymers, ethylene-ethylacrylate copolymers, ethylene-butylacrylate copolymers, and ethylene-methylmethacrylate copolymers.

Examples of other elastomers include ethylene-α-olefin type copolymer rubbers such as ethylene-propylene copolymer rubber, ethylene-propylene-diene three component copolymer rubber, and ethylene-butene-1 copolymer rubber; synthetic rubbers such as polyisobutylene rubber, polyurethane rubber, styrene-butadiene copolymer rubber and polybutadiene rubber; as well as natural rubber.

These other synthetic resins and elastomers (rubbers) can be used in proportions of no more than 10% by mass, and preferably no more than 5% by mass, relative to the combined total weight of the high density polyethylene resin for modification (a), and the linear low density polyethylene (c)

which is the raw material for a modified linear low density polyethylene described below. If the content of other synthetic resins and elastomers (rubbers) used exceeds 10% by mass, then there is a risk of a deterioration in the basic characteristics of the high density polyethylene resin (a) or the linear low density polyethylene (c).

[Unmodified Polyethylene (B)]

The unmodified polyethylene (B) is used to dilute the modified polyethylene (A) described above. Examples of this unmodified polyethylene (B) include homopolymers formed solely from ethylene, and copolymers formed from ethylene and an α-olefin of 3 to 12 carbon atoms. Examples of the α-olefin include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene. Specific examples of the polyethylene include high density polyethylenes, linear low density polyethylenes, and ultra low density polyethylenes, although high density polyethylenes with a density of 0.93 to 0.96 g/cm are preferred.

These polymers can be produced using a typical Ziegler system catalyst or a chromium based catalyst, or may also be produced using a so-called single site catalyst.

Furthermore, the unmodified polyethylene (B) has a MFR at a temperature of 190° C. and a loading of 2.16 kg of 0.1 to 20 g/10 minutes, and a density within a range from 0.86 to 0.96 g/cm^3, and preferably from 0.91 to 0.96 g/cm^3, and even more preferably from 0.93 to 0.96 g/cm^3. If the MFR is less than 0.1 g/10 minutes, then the compatible with the modified polyethylene (A) and the other resins deteriorates, whereas if the MFR exceeds 20 g/10 minutes, then there is a risk of a deterioration in the adhesive strength and the moldability. Furthermore, if the density is less than 0.86 g/cm^3, then not only is there a risk that the adhesive strength of the final multi-layer laminated structure will be unsatisfactory, but the resistance to fuel oil and the like is also insufficient, whereas if the density exceeds 0.96 g/cm^3, then a there is a risk of a deterioration in the adhesiveness of the final adhesive resin composition.

An adhesive resin composition (C) of the present invention should preferably also comprise up to 70% by mass of a linear low density polyethylene (c) with a density of 0.91 to 0.94 g/cm^3 and a melt flow rate of 0.1 to 20 g/10 minutes, and/or up to 50% by mass of an ultra low density polyethylene (d) with a density of 0.86 to 0.91 g/cm^3 and a melt flow rate of 0.1 to 20 g/10 minutes. The linear low density polyethylene (c) and/or the ultra low density polyethylene (d) may be either modified or unmodified materials.

[Linear Low Density Polyethylene (c)]

A linear low density polyethylene (c) according to the present invention can utilize any polyethylene, provided the density is from 0.91 to 0.94 g/cm^3 and the melt flow rate is from 0.1 to 20 g/10 minutes. Specific examples include copolymers formed from ethylene and an α-olefin of 3 to 12 carbon atoms. Examples of the α-olefin include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

The density of the linear low density polyethylene (c) should be within a range from 0.91 to 0.94 g/cm^3, and preferably from 0.915 to 0.935 g/cm^3, and even more preferably from 0.92 to 0.93 g/cm^3. If the density is less than from 0.91 g/cm^3 or greater than 0.940 g/cm^3, then there is a risk the degree of improvement in the adhesive strength and the low temperature impact strength of the product adhesive resin composition will be unsatisfactory.

Furthermore, the MFR of the linear low density polyethylene (c) should be within a range from 0.1 to 20 g/10 minutes, and preferably from 0.1 to 15 g/10 minutes, and even more preferably from 0.1 to 10 g/10 minutes. If the MFR is less than 0.1 g/10 minutes, then the compatible during blending deteriorates, whereas if the MFR exceeds 20 g/10 minutes, then there is a risk of a deterioration in the moldability, the adhesive strength and the mechanical strength and the like.

The linear low density polyethylene (c) should preferably comprise from 5 to 30, and even more preferably from 5 to 25 short chain branches for every 1,000 carbon atoms of the principal chain. If the number of short chain branches falls outside the above range, then problems can arise with the adhesiveness and the impact resistance.

Here, a short chain refers essentially to an alkyl chain of 1 to 10 carbon atoms, and preferably 1 to 6 carbon atoms.

The melting point of the linear low density polyethylene (c) as determined by a differential scanning calorimetry method (a DSC method) should preferably be from 115 to 130° C. At melting points less than 115° C. the adhesiveness is unsatisfactory, whereas if the melting point exceeds 130° C., the impact resistance is unfavorable.

Here, melting points according to a DSC method are measured by forming a sheet of thickness 0.2 mm using a hot press method, punching out an approximately 5 mg sample from the sheet, and then holding the sample at a temperature of 200° C. for 5 minutes, cooling the temperature to 30° C. at a rate of 10° C. per minute, and then raising the temperature to 200° C. again at a rate of 10° C. per minute, with the melting point (Tml) then being defined as the temperature at the apex of the highest temperature peak.

[Ultra Low Density Polyethylene (d)]

An ultra low density polyethylene (d) used in the present invention is an ethylene-α-olefin copolymer with a density of 0.86 to 0.91 g/cm^3 and a MFR of 0.1 to 20 g/10 minutes. Specific examples include copolymers formed from ethylene and an α-olefin of 3 to 12 carbon atoms. Examples of the α-olefin include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

The density of the ultra low density polyethylene (d) should be within a range from 0.86 to 0.91 g/cm^3, and preferably from 0.89 to 0.91 g/cm^3, and even more preferably from 0.90 to 0.91 g/cm^3. If the density is less than from 0.86 g/cm^3, then there is a possibility of problems remaining with respect to fuel oil resistance of the product adhesive resin composition, whereas in contrast, if the density exceeds 0.91 g/cm^3, then there is a possibility that the degree of improvement in the low temperature impact resistance and the like will be unsatisfactory.

Furthermore, the MFR of the ultra low density polyethylene (d) should be within a range from 0.1 to 20 g/10 minutes, and preferably from 0.1 to 15 g/10 minutes, and even more preferably from 0.1 to 10 g/10 minutes.

If the MFR is less than 0.1 g/10 minutes, then the compatible during blending deteriorates, whereas if the MFR exceeds 20 g/10 minutes, then there is a risk that the degree of improvement in the moldability, the adhesive strength and the mechanical strength and the like will be insufficient.

The melting point of the ultra low density polyethylene (d) as determined by a differential scanning calorimetry method (a DSC method) should preferably be from 90 to 125° C. At melting points less than 90° C. the heat resistance of the product adhesive resin composition is unsatisfactory, whereas if the melting point exceeds 125° C., the impact resistance and the adhesiveness are unfavorable.

The linear low density polyethylene (c) and the ultra low density polyethylene (d) can be distinguished on the basis of density range. There are no particular restrictions on the

method of producing the linear low density polyethylene (c) and the ultra low density polyethylene (d), and suitable methods include copolymerization of ethylene and the α-olefin via a gas phase method, a solution method or a slurry (suspension) method, using either a so-called Ziegler catalyst, a chromium based catalyst, a single site catalyst or a metallocene based catalyst, although a specific ethylene-α-olefin copolymer (A) (hereafter referred to as an ethylene copolymer (A)) which satisfies the conditions (1) to (4) listed below is preferred:

(1) a density of 0.86 to 0.94 g/cm^3,

(2) a melt flow rate of 0.1 to 20 g/10 minutes,

(3) a molecular weight distribution (Mw/Mn) of 1.5 to 4.5, and

(4) a difference between T_{25}, representing the temperature at which 25% of the total is eluted, determined from the integrated elution curve of an elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method, and T_{75}, representing the temperature at which 75% of the total is eluted, namely $T_{75}-T_{25}$, and a density d which satisfy the relationship of an equation 1, shown below.

$$T_{75}-T_{25}\leqq -670\times d+644 \quad \text{(equation 1)}$$

An ethylene copolymer (A) used in the present invention is an ethylene-α-olefin copolymer obtained by copolymerization of ethylene and an α-olefin of 3 to 20 carbon atoms, and preferably 3 to 12 carbon atoms.

Specific examples of the α-olefin of 3 to 20 carbon atoms include propylene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene and 1-dodecene. Furthermore, the content of these α-olefins should typically total no more than 30% by mol, and should preferably be selected from within a range from 3 to 20% by mol.

An ethylene copolymer (A) according to the present invention includes the linear low density polyethylenes (c) and the ultra low density polyethylenes (d), and (1) has a density within a range from 0.86 to 0.94 g/cm^3, and preferably from 0.89 to 0.935 g/cm^3, and even more preferably from 0.90 to 0.93 g/cm^3. If the density is less than 0.86 g/cm^3, then the adhesive strength (the break strength), the heat resistance and the fuel oil resistance deteriorate. In contrast, if the density exceeds 0.94 g/cm^3, then there is a risk of the low temperature impact resistance and the like being unsatisfactory.

The melt flow rate (hereafter abbreviated as MFR) of the condition (2) in the present invention is within a range from 0.1 to 20 g/110 minutes, and preferably from 0.1 to 15 g/10 minutes, and even more preferably from 0.1 to 10 g/10 minutes. If the MFR is less than 0.1 g/10 minutes, then the molding workability deteriorates, whereas if the MFR exceeds 20 g/10 minutes, then there is a risk of a deterioration in the impact resistance and the fuel oil resistance and the like.

The molecular weight distribution (Mw/Mn) of the condition (3) in the present invention is within a range from 1.5 to 4.5, and preferably from 2.0 to 4.0, and even more preferably from 2.5 to 3.0. At Mw/Mn values of less than 1.5 the molding workability deteriorates, whereas if Mw/Mn exceeds 4.5, then there is a risk of a deterioration in the adhesive strength and the low temperature impact resistance.

Here, the molecular weight distribution (Mw/Mn) of an ethylene copolymer can be determined by calculating the ratio (Mw/Mn) between the weight average molecular weight (Mw) and the number average molecular weight (Mn) as determined by gel permeation chromatography (GPC).

An ethylene copolymer (A) according to the present invention should preferably satisfy the condition (4), as shown in FIG. **1**, that the difference between T_{25}, representing the temperature at which 25% of the total is eluted, determined from the integrated elution curve of an elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method, and T_{75}, representing the temperature at which 75% of the total is eluted, namely $T_{75}-T_{25}$, and the density d satisfy the relationship

$$T_{75}-T_{25}\leqq -670\times d+644 \quad \text{(equation 1)}$$

In those cases in which $T_{75}-T_{25}$ and the density d do not satisfy the equation 1, there is a risk of a deterioration in the adhesive strength and the low temperature impact strength.

The TREF measurement method is performed in the manner described below. First, the sample is added to ODCB containing an antioxidant (such as butylhydroxytoluene) so that the sample concentration is 0.05% by mass, and the mixture is then heated to 140° C. and the sample dissolved. 5 ml of this sample solution is then injected into a column filled with glass beads, and is cooled to 25° C. at a cooling rate of 0.1° C./minute, so that the sample is deposited on the surface of the glass beads. Next, ODCB is passed through the column at a constant flow rate, while the column temperature is raised at a constant rate of 50° C./hour, and the sample is gradually eluted. During this process, the concentration of the sample eluted within the solvent is continuously detected by using an infrared detector to measure the absorption at wave number 2925 cm^{-1} by the asymmetric stretching vibration of methylene. The concentration of ethylene copolymer within the solvent can be determined from this value by quantitative analysis, and the relationship between elution temperature and elution rate can then be determined. According to TREF analysis, the variation in elution rate relative to variations in temperature can be analyzed continuously using an extremely small content of a sample, and consequently it becomes possible to detect comparatively minor peaks which are not detectable by fractionation methods.

An ethylene copolymer (A) according to the present invention should preferably also satisfy a condition (5) that the difference between T_{25}, representing the temperature at which 25% of the total is eluted, determined from the integrated elution curve of an elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method, and T_{75}, representing the temperature at which 75% of the total is eluted, namely $T_{75}-T_{25}$, and the density d satisfy the relationship of an equation 2, $T_{75}-T_{25}\geqq -300\times d+285$. If the values of $T_{75}-T_{25}$ and the density d satisfy the equation 2, then the performance of factors such as the heat resistance can be improved.

An ethylene copolymer (A) according to the present invention is preferably either an ethylene copolymer (A1) which in addition, also satisfies the conditions (6) and (7) listed below, or an ethylene copolymer (A2) which in addition, also satisfies the conditions (8) and (9) listed below.

(6) The quantity X (% by mass) of the ODCB soluble fraction at 25° C., the density d, and the melt flow rate (MFR) of an ethylene copolymer (A1) according to the

present invention satisfy the relationships of equation 3 and equation 4 shown below,

$$X<2.0 \text{ in cases in which } d-0.008logMFR\geqq 0.93 \quad \text{(equation 3)}$$

$$X<9.8\times10^3\times(0.9300-d+0.008logMFR)^2+2.0 \text{ in cases in which } d-0.008logMFR<0.93 \quad \text{, (equation 4)}$$

and preferably satisfy the relationships:

X<1.0 in cases in which d−0.008 logMFR≧0.93, and

$X<7.4\times10^3\times(0.9300-d+0.008\ \text{logMFR})^2+2.0$ in cases in which d−0.008 logMFR<0.93, and even more preferably satisfy the relationships:

X<0.5 in cases in which d−0.008 logMFR≧0.93, and

$X<5.6\times10^3\times(0.9300-d+0.008\ \text{logMFR})^2+2.0$ in cases in which d−0.008 logMFR<0.93

Here, the quantity X (% by mass) of the ODCB soluble fraction at 25° C. is measured by the method described below. 0.5 g sample in 20 ml of ODCB is heated at 135° C. for 2 hours, and following complete dissolution of the sample, the solution is cooled to 25° C. The solution is then left to stand overnight at 25° C., and is then filtered through a Teflon filter and the filtrate collected. Using this filtrate, which represents a solution of the sample, the absorption peak strength of the asymmetric stretching vibration of methylene at a wave number of approximately 2925 cm^{-1} is measured with an infrared spectrometer, and the sample concentration is then calculated from a previously prepared calibration curve. This value determines the content of the ODCB soluble fraction at 25° C.

The ODCB soluble fraction at 25° C. represents the highly branched constituents and the low molecular weight constituents incorporated within the ethylene copolymer, which are responsible for a reduction in heat resistance and a stickiness on the surface of a molded product, and are also the cause of hygiene problems and blocking on the internal surface of a molded product, and consequently smaller ODCB soluble fractions are preferred. The content of the ODCB soluble fraction is affected by the content and the molecular weight of the α-olefin within the copolymer, in other words, the density and the MFR. Accordingly, if these indicators, namely the density, the MFR and the content of the ODCB soluble fraction, satisfy the above equation, then this indicates that uneven distribution of the α-olefin within the copolymer is limited.

Furthermore, an ethylene copolymer (A1) according to the present invention is a copolymer for which (7) the elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method has a plurality of peaks. Copolymers in which the peak temperature of the highest temperature peak amongst the plurality of peaks is within a range from 85° C. to 100° C. are particularly preferred. The existence of this peak raises the melting point, increases the degree of crystallization and improves the heat resistance and the rigidity of a molded product.

Furthermore, an ethylene copolymer (A2) according to the present invention is a copolymer which (8) has one, or two or more melting point peaks, and moreover of these peaks, (9) the highest melting point Tml and the density d satisfy the relationship of an equation 5 shown below.

$$Tml\geqq 150\times d-19 \quad \text{(equation 5)}$$

If the melting point Tml and the density d satisfy the relationship of the equation 5 above, then the heat resistance improves.

Furthermore, amongst ethylene copolymers (A2), ethylene copolymers which also satisfy the condition (10) shown below are preferred.

(10) a melt tension (MT) and a melt flow rate (MFR) which satisfy the relationship of an equation 6 shown below:

$$logMT\leqq -0.572\times logMFR+0.3 \quad \text{(equation 6)}$$

If the MT and the MFR values satisfy the relationship of the equation 6 above, then the molding workability in extrusion molding or the like is very favorable.

Here, an ethylene copolymer (A1) is a special ethylene-α-olefin copolymer for which, as is shown in FIG. **2**, the elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method has a plurality of peaks. In contrast, an ethylene copolymer of FIG. **3** is an ethylene copolymer for which the elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method has essentially a single peak, and corresponds with a conventional ethylene copolymer produced using a typical metallocene based catalyst.

Furthermore, as shown in FIG. **4**, although the ethylene copolymer (A2) has a single TREF peak, a conventional ethylene copolymer produced using a typical metallocene based catalyst does not satisfy the equation 2. Consequently, the ethylene copolymer (A2) can be clearly distinguished from a conventional ethylene copolymer (FIG. **3**) produced using a typical metallocene based catalyst.

Provided an ethylene copolymer (A) used in the present invention satisfies the above parameters, then there are no particular restrictions on factors such as the catalyst or the production method, and production can be performed using a typical metallocene based catalyst or a CGC catalyst or the like, although a linear low density ethylene copolymer prepared by copolymerization of ethylene and an α-olefin in the presence of a catalyst incorporating an organic cyclic compound with at least a conjugated double bond and a transition metal compound from group IV of the periodic table is preferred. This type of linear low density ethylene copolymer has a narrow molecular weight distribution and a narrow compositional distribution, and consequently is a superior product with excellent mechanical characteristics, which displays excellent initial adhesive strength, durable adhesive strength, and adhesive strength following soak in fuel oil, and also has excellent heat resistance.

It is particularly desirable if this type of linear low density ethylene copolymer is polymerized with a catalyst obtained by mixing the compounds a1 to a4 described below.

a1: a compound represented by a general formula Me1R1pR2q(OR3)rX14-p-q-r wherein, Me1 represents zirconium, titanium or hafnium; R1 and R3 each represent a hydrocarbon group of 1 to 24 carbon atoms; R2 represents a 2,4-pentanedionato ligand or a derivative thereof, a benzoylmethanato ligand, or a benzoylacetonato ligand or a derivative thereof; X1 represents a halogen atom, and p, q and r each represent integers which satisfy the ranges 0≦p≦4, 0≦q≦4, 0≦r≦4, and 0≦p+q+r≦4.

a2: a compound represented by a general formula Me2R4m(OR5)nX2z-m-n wherein, Me2 represents an element from group 1 to group 3 of the periodic table; R4 and R5 each represent a hydrocarbon group of 1 to 24 carbon atoms; X2 represents a halogen atom or a hydrogen atom (although if X2 is a hydrogen atom, then Me2 can only be an element from group 3 of the periodic table); z represents the valency of Me2, and m and n each represent integers which satisfy the ranges 0≦m≦z, 0≦n≦z, and moreover 0≦m+n≦z.

a3: an organic cyclic compound with a conjugated double bond.

a4: a modified organic aluminum oxy compound incorporating a Al—O—Al linkage and/or a boron compound.

These compounds are described below in further detail.

In the formula of the catalyst constituent compound al represented by the general formula Me1R1pR2q(OR3)rX14-p-q-r, Me1 represents zirconium, titanium or hafnium, and the variety of these transition metals is not restricted, and a plurality of metals may be used, although zirconium is particularly preferred as it produces a copolymer with superior weather resistance. R1 and R3 each represent a hydrocarbon group of 1 to 24 carbon atoms, and preferably 1 to 12 carbon atoms, and even more preferably 1 to 8 carbon atoms. Specific examples include alkyl groups such as methyl groups, ethyl groups, propyl groups, isopropyl groups and butyl groups; alkenyl groups such as vinyl groups and allyl groups; aryl groups such as phenyl groups, tolyl groups, xylyl groups, mesityl groups, indenyl groups and naphthyl groups; and aralkyl groups such as benzyl groups, trityl groups, phenethyl groups, styryl groups, benzhydryl groups, phenylbutyl groups and neophyl groups.

These hydrocarbon groups may contain branches. R2 represents a 2,4-pentanedionato ligand or a derivative thereof, a benzoylmethanato ligand, or a benzoylacetonato ligand or a derivative thereof. X1 represents a halogen atom such as a fluorine atom, an iodine atom, a chlorine atom or a bromine atom. p, q, and r each represent integers which satisfy the ranges $0 \leqq p \leqq 4$, $0 \leqq q \leqq 4$, $0 \leqq r \leqq 4$, and $0 \leqq p+q+r \leqq 4$.

Examples of compounds represented by the general formula of the catalyst constituent a1 include tetramethylzirconium, tetraethylzirconium, tetrabenzylzirconium, tetrapropoxyzirconium, tripropoxymonochlorozirconium, tetraethoxyzirconium, tetrabutoxyzirconium, tetrabutoxytitanium and tetrabutoxyhafnium, and of these Zr(OR)4 compounds such as tetrapropoxyzirconium and tetrabutoxyzirconium are preferred, and two or more of these compounds may also be used in combination. Furthermore, specific examples of the 2,4-pentanedionato ligand or a derivative thereof, benzoylmethanato ligand, or benzoylacetonato ligand or a derivative thereof include tetra(2,4-pentanedionato)zirconium, tri(2,4-pentanedionato)zirconium chloride, di(2,4-pentanedionato)zirconium dichloride, (2,4-pentanedionato)zirconium trichloride, di(2,4-pentanedionato) zirconium diethoxide, di(2,4-pentanedionato)zirconium di-n-propoxide, di(2,4-pentanedionato)zirconium di-n-butoxide, di(2,4-pentanedionato)dibenzylzirconium, di(2,4-pentanedionato)dineophylzirconium, tetra (dibenzoylmethanato)zirconium, di(dibenzoylmethanato) zirconium diethoxide, di(dibenzoylmethanato)zirconium di-n-propoxide, di(dibenzoylmethanato)zirconium di-n-butoxide, di(benzoylacetonato)zirconium diethoxide, di(benzoylacetonato)zirconium di-n-propoxide, and di(benzoylacetonato)zirconium di-n-butoxide.

In the formula of the catalyst constituent compound a2 represented by the general formula Me2R4m(OR5)nX2z-m-n, Me2 represents an element from group 1 to group 3 of the periodic table, such as lithium, sodium, potassium, magnesium, calcium, zinc, boron and aluminum. R4 and R5 each represent a hydrocarbon group of 1 to 24 carbon atoms, and preferably 1 to 12 carbon atoms, and even more preferably 1 to 8 carbon atoms. Specific examples include alkyl groups such as methyl groups, ethyl groups, propyl groups, isopropyl groups and butyl groups; alkenyl groups such as vinyl groups and allyl groups; aryl groups such as phenyl groups, tolyl groups, xylyl groups, mesityl groups, indenyl groups and naphthyl groups; and aralkyl groups such as benzyl groups, trityl groups, phenethyl groups, styryl groups, benzhydryl groups, phenylbutyl groups and neophyl groups. These hydrocarbon groups may contain branches. X2 represents a halogen atom such as a fluorine atom, an iodine atom, a chlorine atom or a bromine atom, or alternatively, a hydrogen atom. However, if X2 is a hydrogen atom then Me2 can only be an element from group 3 of the periodic table such as boron or aluminum or the like. Furthermore, z represents the valency of Me2, and m and n each represent integers which satisfy the ranges $0 \leqq m \leqq z$, $0 \leqq n \leqq z$, and moreover $0 \leqq m+n \leqq z$.

Examples of compounds represented by the general formula of the catalyst constituent a2 include organic lithium compounds such as methyllithium and ethyllithium; organic magnesium compounds such as dimethylmagnesium, diethylmagnesium, methylmagnesium chloride and ethylmagnesium chloride; organic zinc compounds such as dimethylzinc and diethylzinc; organic boron compounds such as trimethylboron and triethylboron; and organic aluminum compounds such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisobutylaluminum, trihexylaluminum, tridecylaluminum, diethylaluminum chloride, ethylaluminum dichloride, ethylaluminum sesquichloride, diethylaluminum ethoxide and diethylaluminum hydride.

The organic cyclic compound with a conjugated double bond of the catalyst constituent compound a3 includes cyclic hydrocarbon compounds with one, or two or more rings with at least two, and preferably 2 to 4, and even more preferably 2 to 3 conjugated double bonds, and with a total number of carbon atoms from 4 to 24, and preferably from 4 to 12; cyclic hydrocarbon compounds similar to those above but partially substituted with 1 to 6 hydrocarbon residues (typically alkyl groups or aralkyl groups of 1 to 12 carbon atoms); organic silicon compounds incorporating a cyclic hydrocarbon group with one, or two or more rings with at least two, and preferably 2 to 4, and even more preferably 2 to 3 conjugated double bonds, and with a total number of carbon atoms from 4 to 24, and preferably from 4 to 12; and organic silicon compounds in which the above cyclic hydrocarbon group is partially substituted with 1 to 6 hydrocarbon residues or alkali metal salts (sodium or lithium salts). Molecules which incorporate a cyclopentadiene structure are particularly preferred.

Specific examples of preferred compounds include cyclopentadiene, indene and azulene, as well as alkyl, aryl, aralkyl, alkoxy and aryloxy derivatives thereof. Furthermore, compounds in which the above compounds are linked (bridged) via an alkylene group (with 2 to 8, and preferably 2 to 3 carbon atoms) can also be used favorably.

Organic silicon compounds with a cyclic hydrocarbon group can be represented by a general formula shown below.

$$ALSiR4-L$$

Here, A represents the cyclic hydrocarbon group such as a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group or a substituted indenyl group; R represents either a hydrogen atom or a hydrocarbon residue of 1 to 24 carbon atoms, and preferably 1 to 12 carbon atoms, including alkyl groups such as methyl groups, ethyl groups, propyl groups, isopropyl groups and butyl groups; alkoxy groups such as methoxy groups, ethoxy groups, propoxy groups and butoxy groups; aryl groups such as phenyl groups; aryloxy groups such as phenoxy groups; and aralkyl groups such as benzyl groups; and L represents a number wherein $1 \leqq L \leqq 4$, and preferably $1 \leqq L \leqq 3$.

Specific examples of organic cyclic hydrocarbon compounds of the constituent a3 include cyclopolyenes and substituted cyclopolyenes of 5 to 24 carbon atoms such as cyclopentadiene, methylcyclopentadiene, ethylcyclopentadiene, propylcyclopentadiene, butylcyclopentadiene, 1,3-dimethylcyclopentadiene, 1-methyl-3-ethylcyclopentadiene, 1-methyl-3-propylcyclopentadiene, 1-methyl-3-butylcyclopentadiene, 1,2,4-trimethylcyclopentadiene, pentamethylcyclopentadiene, indene, 4-methyl-1-indene, 4,7-dimethylindene, cycloheptatriene, methylcycloheptatriene, cyclooctatetraene, azulene, fluorene and methylfluorene, as well as monocyclopentadienyl silane, biscyclopentadienyl silane, triscyclopentadienyl silane, monoindenyl silane, bisindenyl silane and trisindenyl silane.

A modified organic aluminum oxy compound incorporating a Al—O—Al linkage of the catalyst constituent compound a4 is a modified organic aluminum oxy compound, typically called an aluminoxane, obtained by reacting an alkylaluminum compound with water, and usually comprises 1 to 100, and preferably 1 to 50 Al—O—Al linkages within each molecule. Furthermore, these modified organic aluminum oxy compounds may be either linear type structures or cyclic structures.

The reaction between organic aluminum and water is usually conducted within an inert hydrocarbon. Examples of preferred inert hydrocarbons include aliphatic, alicyclic and aromatic hydrocarbons such as pentane, hexane, heptane, cyclohexane, benzene, toluene and xylene.

The reaction ratio between water and the organic aluminum compound (the water/A1 molar ratio) is usually from 0.25/1 to 1.2/1, and preferably from 0.5/1 to 1/1.

Examples of boron compounds include triethylaluminum tetra(pentafluorophenyl)borate, triethylammonium tetra(pentafluorophenyl)borate, dimethylanilinium tetra(pentafluorophenyl)borate, dimethylanilinium tetra(pentafluorophenyl)borate, butylammonium tetra(pentafluorophenyl)borate, N,N-dimethylanilinium tetra(pentafluorophenyl)borate, N,N-dimethylanilinium tetra(3,5-difluorophenyl)borate, trityltetrakispentafluoroborate, ferrocenium tetrakispentafluoroborate, and trispentafluoroborane. Of these, N,N-dimethylanilinium tetra(pentafluorophenyl)borate, trityltetrakispentafluoroborate, ferrocenium tetrakispentafluoroborate, and trispentafluoroborane are preferred.

The above catalyst constituents a1 to a4 can be mixed together prior to use, although preferably they should be supported on an inorganic support and/or a particulate polymer support (a5) prior to use.

The inorganic support and/or a particulate polymer support (a5) refers to a carbonaceous material, a metal, a metal oxide, a metal chloride, a metal carbonate or a mixture of such materials, or alternatively a thermoplastic resin or a thermosetting resin. Examples of suitable metals for use as this type of inorganic support include iron, aluminum, and nickel and the like.

Specific examples of suitable materials include SiO_2, Al_2O_3, MgO, ZrO_2, TiO_2, B_2O_3, CaO, ZnO, BaO, ThO_2, or mixtures thereof such as SiO_2—Al_2O_3, SiO_2—V_2O_5, SiO_2—TiO_2, SiO_2—MgO, and SiO_2—Cr_2O_3. Of these, materials comprising at least one material selected from the group consisting of SiO_2 and Al_2O_3 as a primary constituent are preferred.

Furthermore, in terms of organic compounds, both thermoplastic resins and thermosetting resins can be used, and specific examples include particulate polyolefins, polyesters, polyamides, polyvinyl chlorides, poly methyl (meth)acrylates, polystyrenes, polynorbornenes and the various natural macromolecules, as well as mixtures thereof.

The inorganic support and/or a particulate polymer support can be used as is, although preferably a pretreatment should be performed wherein the support is contacted with an organic aluminum compound or a modified organic aluminum compound comprising Al—O—Al linkages prior to being used as the constituent a5.

An ethylene copolymer (A) according to the present invention can be produced by a gas phase polymerization method with essentially no solvent, a slurry polymerization method, or a solution polymerization method, in the presence of the catalyst. Specifically, the ethylene copolymer (A) is produced in an environment free of oxygen and water, either in the presence of an inert hydrocarbon solvent including aliphatic hydrocarbons such as butane, pentane, hexane or heptane, aromatic hydrocarbons such as benzene, toluene or xylene, and alicyclic hydrocarbons such as cyclohexane or methylcyclohexane, or alternatively may be produced without such a solvent. There are no particular restrictions on the production conditions, although the polymerization temperature is typically from 15 to 350° C., and preferably from 20 to 200° C., and even more preferably from 50 to 110° C., the polymerization pressure in the case of a low or medium pressure method is typically from atmospheric pressure to 70 kg/cm^2G, and preferably from atmospheric pressure to 20 kg/cm^2G, and in the case of a high pressure method is preferably no more than 1500 kg/cm^2G. The polymerization time in the case of a low or medium pressure method is typically from 3 minutes to 10 hours, and preferably from 5 minutes to approximately 5 hours, and in the case of a high pressure method is typically from 1 minute to 30 minutes, and preferably from 2 minutes to approximately 20 minutes. Furthermore, the polymerization may be performed via a one stage polymerization, or via a multi-stage polymerization with two or more stages in which polymerization conditions such as the hydrogen concentration, the monomer concentration, the polymerization pressure, the polymerization temperature and the catalyst differ between stages. The method disclosed in Japanese Unexamined Patent Application, First Publication No. Hei 5-132518 represents a particularly preferred production method.

In producing an ethylene copolymer (A) used in the present invention, by using a catalyst in which the catalyst constituents contain no halogens such as chlorine, a product can be obtained in which the halogen concentration is no more than 10 ppm, and preferably no more than 5 ppm, and even more preferably is essentially halogen free (ND: no more than 2 ppm). By using this type of chlorine or halogen free ethylene copolymer (A), the need for a conventional acid neutralizing agent (halogen absorbing agent) such as calcium stearate or hydrotalcite disappears. Consequently, the reduction in adhesive strength caused by the inclusion of these additives can be avoided.

[Adhesive Resin Composition (C)]

An adhesive resin composition (C) is formed from the modified polyethylene (A) and an unmodified polyethylene (B), and comprises from 100 to 5% by mass of the modified polyethylene (A), and from 0 to 95% by mass of the unmodified polyethylene (B). Preferred ratios (A)/(B) for the modified polyethylene (A) and the unmodified polyethylene (B) are from 10/90 to 90/10 (mass ratios), with ratios from 15/85 to 85/15 being even more desirable. Provided the ratio (A)/(B) is within the range from 10/90 to 90/10, then the concentration of the product adhesive resin composition can be adjusted, and the low impact resistance of a regrind layer during recycling can be balanced.

Furthermore, the ratio MFR(A)/MFR(B), where MFR(A) represents the MFR for the modified polyethylene (A) at a temperature of 190° C. and a loading of 2.16 kg, and MFR(B) represents the MFR for the unmodified polyethylene (B) at a temperature of 190° C. and a loading of 2.16 kg, should preferably be less than 1, and even more preferably less than 0.6. If the ratio MFR(A)/MFR(B) exceeds 1, then the adhesive strength initially, and following soak in fuel, may deteriorate.

A preferred state for the adhesive resin composition (C) comprises 100 to 5% by mass of a modified polyethylene (a), and in particular a high density polyethylene with a MFR of 0.1 to 2 g/10 minutes and a density of 0.93 to 0.96 g/cm^3, 0 to 95% by mass of an unmodified polyethylene (b), and in particular a high density polyethylene with a MFR of 0.1 to 20 g/10 minutes and a density of 0.93 to 0.96 g/cm^3, no more than 70% by mass, and preferably 5 to 60% by mass, and even more preferably 10 to 50% by mass of a linear low density polyethylene (c) with a MFR of 0.1 to 2 g/10 minutes and a density of 0.91 to 0.94 g/cm^3. Furthermore, the content of an ultra low density polyethylene (d) with a MFR of 0.1 to 2 g/10 minutes and a density of 0.86 to 0.91 g/cm^3 should be no more than 50% by mass, and preferably from 5 to 40% by mass, and even more preferably from 10 to 35% by mass. By forming an adhesive resin composition from this type of mixture, the compatible with the modified polyethylene (A) and the unmodified polyethylene (B) is good, and a composition with balanced properties can be achieved including good initial adhesion, durable adhesion, low temperature impact resistance and fuel oil swelling resistance, and good compatible with a low temperature impact resistant regrind composition of a regrind layer produced on recycling of the adhesive resin composition.

A production method for the adhesive resin composition (C) involves molten mixing of a raw material mixture incorporating a modified polyethylene (A) and an unmodified polyethylene (B). There are no particular restrictions on the molten mixing method, and for example, the raw materials can be mixed in a conventional mixer such as a Henschel mixer, followed by molten mixing using either a single screw or a double screw extruder. Furthermore, solution methods in which the mixture is dissolved in a solvent and modification is then conducted are also effective methods.

The thus obtained adhesive resin composition (C) has a density of 0.925 to 0.940 g/cm^3, an unsaturated carboxylic acid and unsaturated carboxylic acid derivative content of at least 0.09% by mass, and a MFR at a temperature of 190° C. and a loading of 2.16 kg of 0.1 to 2.0 g/10 minutes, and preferably 0.1 to 1.5 g/10 minutes.

If the density is less than 0.925 g/cm^3, then the degree of swelling relative to fuel oil and the like increases, and consequently the long term durability (the adhesive strength following soak in fuel oil) deteriorates. In contrast, if the density exceeds 0.940 g/cm^3, then the contraction during solidification following the molding of a multi-layer laminated structure increases, leading to a decrease in the adhesive strength.

Furthermore, if the content of the unsaturated carboxylic acid and unsaturated carboxylic acid derivative is less than 0.09% by mass, then the adhesive strength of the final product multi-layer laminated structure deteriorates. Furthermore, in cases in which molding burrs and unused parison is recycled and used as a regrind layer, the compatible of the regrind layer and the barrier material such as a saponified product of an ethylene-vinyl acetate copolymer, or a polyamide resin also deteriorates, and consequently the low temperature impact resistance of the final product multi-layer laminated structure falls.

Furthermore, if the MFR is less than 0.1 g/10 minutes or exceeds 2 g/10 minutes, then the moldability of the obtained adhesive resin composition (C) deteriorates.

A characteristic of the present invention is the fact that in the adhesive resin composition (C), the rate of ring opening of acid anhydride groups following modification should preferably be maintained at a value of no more than 10%. By ensuring that the rate of ring opening of acid anhydride groups following graft modification of the adhesive resin composition is maintained at no more than 10%, it was discovered that the reaction with the saponified product of an ethylene-vinyl acetate copolymer or the like of the barrier resin can be promoted, thereby improving the initial adhesive strength and the adhesive strength following soak in fuel oil, as well as the degree of swelling following soak in fuel oil. Furthermore, in the case of subsequent use as a regrind layer during recycling, the compatible with the barrier materials such as saponified products of ethylene-vinyl acetate copolymers, or polyamide resins also improves.

Where necessary, additives and other resins may be combined with an adhesive resin composition (C). Examples of additives include phenol based and phosphorus based antioxidants, antiblocking agents such as talc, and slipping agents such as fatty acid amides and the like.

However, fatty acid metal salts such as calcium stearate or zinc stearate which are typically used as acid absorbers inhibit the reaction between unsaturated carboxylic acids and unsaturated carboxylic acid derivatives such as succinic acid which modify the polyethylene, and polyamides or saponified products of ethylene-vinyl acetate copolymers. Accordingly, in those cases in which a fatty acid metal salt is used, the amount added should preferably be no more than 100 ppm.

Quantities of no more than 50 ppm are even more preferred, and amounts less than the detection limit of quantitative analysis using X-ray fluorescence analysis are particularly preferred. If the content of fatty acid metal salts added is less than 100 ppm, then the adhesive strength of the adhesive resin composition can be further improved, and the mechanical characteristics of a multi-layer laminated structure can also be further improved. Furthermore, synthetic or natural hydrotalcite can also be used as an acid absorber instead of stearate based compounds.

Examples of other resins include homopolymers formed from ethylene, copolymers formed from ethylene and an α-olefin of 3 to 12 carbon atoms, and copolymers formed from ethylene and other vinyl monomers such as ethylene-vinyl acetate copolymers, ethylene-acrylic acid copolymers, ethylene-methacrylic acid copolymers, ethylene-methylacrylate copolymers, ethylene-ethylacrylate copolymers, ethylene-butylacrylate copolymers, and ethylene-methylmethacrylate copolymers. Examples of the above α-olefin include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

These polymers may be produced by high pressure radical methods, by using a typical Ziegler catalyst or a chromium catalyst, or by using a so-called single site catalyst.

Furthermore, a preferred form of an adhesive resin composition (C) of the present invention should preferably satisfy the following conditions.

Namely, 6.7% by mass of an adhesive resin composition (C), 88.3% by mass of a high density polyethylene (Japan Polyolefins Co. Ltd., KBY47C) with a density of 0.945

g/cm^3 and a high load melt flow rate (temperature 190° C., load 21.6 kg) of 6 g/10 minutes, and 5% by mass of a saponified product of an ethylene-vinyl acetate copolymer (Kuraray Co. Ltd., EVAL F101B) are subjected to molten kneading, and press molding of the kneaded product thus obtained, at a temperature setting of 230° C. and a press pressure of 6 MPa, is then used to prepare a sheet of thickness 4 mm, and when the WV notch tensile impact strength of a test specimen of a shape 1 according to JIS K7160 prepared from this sheet is measured at −40° C., the WV notch tensile impact strength should preferably be at least 120 KJ/cm^2.

The proportions described above represent the proportions of a typical recycled composition (regrind composition) during recycling. During recycling, by using an adhesive resin composition, the low temperature impact resistance of multi-layer laminated structures such as 4 type 6 layer structures and 3 type 5 layer structures using recycled burrs from multi-layer molding and unused parison can be improved.

In the molten kneading, the C1-C2-C3-head-dice temperature settings should preferably be set to 180° C.-200° C.-200° C.-200° C.-200° C. respectively, and a 50 mm single screw kneader with the screw revolutions adjusted to 60 rpm should preferably be used.

Evaluation of the low temperature impact resistance includes a method in which an actual molded product is dropped within a low temperature environment, although the measurement operation in this method is quite demanding, and consequently measurements are typically conducted as −40° C. Charpy impact strength measurements on a flat specimen.

[Multi-Layer Laminated Structure]

A multi-layer laminated structure which represents another aspect of the present invention is produced using an adhesive resin composition of the type described above. In other words, the multi-layer laminated structure comprises an adhesive layer formed from an adhesive resin composition, and at least a principal material layer formed on the outside of the adhesive layer, and a barrier layer formed on the inside of the adhesive layer.

There are no particular restrictions on the thickness of the adhesive layer, although thickness values from 50 to 300 μm are preferred, and values of 100 to 200 μm are even more desirable. At thickness values less than 50 μm, the adhesiveness with the barrier layer and the principal material layer may be unsatisfactory, whereas at values exceeding 300 μm, the rigidity of the multi-layer laminated structure itself deteriorates.

[Principal Material Layer]

There are no particular restrictions on the material of the principal material layer provided sufficient impact resistance is imparted to the final product multi-layer laminated structure, and suitable materials include layers of a high density polyethylene or a linear low density polyethylene, although a high density polyethylene should preferably be used. This high density polyethylene is selected from materials with a density of 0.93 to 0.97 g/cm^3, and a melt flow rate of 0.01 to 50 g/10 minutes and preferably 0.1 to 10 g/10 minutes.

In another form, the principal material layer can use a regrind material produced from recycled burrs and rejected products produced during molding of the molded product such as a fuel vessel or the like. Depending on the situation, this regrind material may be used as is, or may also be blended with the high density polyethylene.

The thickness of the principal material layer will vary depending on the intended use of the final product, although will typically be selected from within a range from 50 to 1,000 μm.

[Barrier Layer]

The barrier layer is a layer for preventing penetration of fuel oil or the like. Examples of resins used for barrier layers include a variety of synthetic resin materials including various polyamide resins such as nylon 6 and nylon 6,6, various hydroxy group containing resins such as saponified products of ethylene-vinyl acetate copolymers, various polyester resins such as polyethylene terephthalate resins and polybutylene terephthalate resins, and various halogen containing resins such as polyvinyl chloride resins and polyvinylidene chloride resins. In addition, metal materials such as aluminum and iron may also be used.

Of these materials, polyamide based resins and saponified products of ethylene-vinyl acetate copolymers are used in preference due to their high barrier properties.

There are no particular restrictions on the thickness of the barrier layer, although thickness values from 50 to 300 μm are preferred. At thickness values less than 50 μm, there is a risk of fuel oil or the like penetrating through the layer when the multi-layer laminated structure is filled with the fuel oil or the like, whereas at values exceeding 300 μm, the amount of the highly priced barrier resin used increases, causing an increase in the cost of the multi-layer laminated structure.

[Layer Configuration]

A multi-layer laminated structure of the present invention may utilize recycled material produced by grinding up burrs and unmolded parison generated during the molding of laminated vessels and the like, other than the barrier layer, the adhesive layer and the principal material layer, with this recycled material being mixed with the material of the principal material layer. Furthermore, recycled material produced by grinding up burrs and unmolded parison may also be used as a regrind layer formed between the principal material layer and the adhesive layer.

The multi-layer laminated structure should preferably be of a sandwich type structure with at least a layer comprising a polyethylene based resin as the main constituent provided on the outside of the adhesive resin composition, and a layer formed from a polyamide resin or a saponified product of an ethylene-vinyl acetate copolymer (hereafter abbreviated as EVOH) formed on the inside of the adhesive resin composition.

Examples of layer configurations of the multi-layer laminated structure, listed in sequence from the innermost layer, include 3 type 3 layer structures comprising principal material layer/adhesive layer/principal material layer; 3 type 5 layer structures comprising principal material layer/adhesive layer/barrier layer/adhesive layer/principal material layer, barrier layer/adhesive layer/principal material layer/adhesive layer/barrier layer, or (principal material layer+regrind layer)/adhesive layer/barrier layer/adhesive layer/(principal material layer+regrind layer); and 4 type 6 layer structures comprising principal material layer/adhesive layer/barrier layer/adhesive layer/regrind layer/principal material layer, or principal material layer/regrind layer/adhesive layer/barrier layer/adhesive layer/principal material layer.

In particular 3 type 5 layer structures comprising a high density polyethylene layer and/or a regrind layer/an adhesive resin composition layer/a saponified product of an ethylene-vinyl acetate copolymer layer/an adhesive resin

composition layer/and a high density polyethylene layer and/or a regrind layer are preferred.

[Production Method for Multi-Layer Laminated Structure]

There are no particular restrictions on the production method used for producing a multi-layer laminated structure of the present invention, and following formation of a multi-layer laminate via coextrusion molding, the multi-layer laminate is molded to form a multi-layer laminated structure.

Examples of suitable methods for forming a multi-layer laminate and converting this to a multi-layer laminated structure include blow molding methods, vacuum molding methods, injection molding methods, compression molding methods, and extrusion molding methods, and of these, blow molding is the most preferred method for large scale fuel vessels and the like.

A characteristic of a multi-layer laminated structure of the present invention, is that when an adhesive resin composition layer, and a high density polyethylene and/or a regrind layer of a principal material layer are subjected to coextrusion molding using the multi-layer blow molding device to form a 3 type 5 layer material, because a high molecular weight modified high density polyethylene (a) is used, the adhesion interface with the saponified product of an ethylene-vinyl acetate copolymer of the barrier layer is formed as an irregular surface. As shown in an electron microscope photograph (1) in FIG. **5**, when the structure of this interface between the adhesive resin composition and the barrier layer is viewed with a transmission electron microscope at a magnification within a range from 20,000× to 50,000× (40,000× in this case), irregularities with an elevation difference of at least 100 nm are visible.

In the present invention the adhesion interface adopts this type of irregular structure. This phenomenon is believed to be due to the fact that because the ring opening ratio of the anhydride, and preferably maleic anhydride, is small, the reaction with hydroxyl groups of the EVOH at the interface is accelerated, and because the molecular weight of the adhesive resin is large, the fluid viscosity changes rapidly, and the accompanying contraction causes distortions and irregularities to form in the interface structure. It is thought that as a result of this irregular structure, the adhesive resin and the EVOH generate an anchoring effect at the interface, causing a synergic increase in the initial adhesive strength, the durable adhesive strength (the adhesive strength following soak in fuel oil), and the resistance to swelling following soak in fuel oil.

In contrast, in a conventional structure using an adhesive resin composition, these types of irregularities with an elevation difference of at least 100 nm are not visible (using a transmission electron microscope at a magnification of 40,000), and the interface is essentially linear as shown in the electron microscope photograph (1) of FIG. **6**, and as a result there is no improvement in the adhesive strength.

In molding via a multi-layer blow molding method, the two layers, namely a molten barrier layer formed from a saponified product of an ethylene-vinyl acetate copolymer, a polyamide based resin, a polyester based resin or a polyvinylidene chloride based resin or the like, and a similarly molten adhesive resin composition layer, are brought in contact inside the die of a multi-layer blow molding device, and subsequently blown. The adhesion between the two layers is essentially concluded during this period of molten contact. The adhesive material used in the present invention has a considerably large molecular weight, and similarly the high density polyethylene of the principal material layer also has a large molecular weight. Furthermore, the adhesion mechanism is also a phenomenon of mass transfer. Accordingly, if there is no movement of acid modified resin molecules at the adhesion interface, then no adhesion will be exhibited between the two layers. As a result, ensuring a molten contact which lasts for at least a certain length of time is favorable in terms of producing good adhesive strength. When an adhesive resin composition of the present invention is used in a large scale multi-layer hollow molded product such as the fuel tank or the like, this length of time is defined as being the time from when the adhesive resin layer and the barrier layer come into molten state contact inside the die, until a multi-layer parison coextruded therefrom is blown, contacts a blow mold, and begins to cool. Specifically, this molten contact time should be at least 10 seconds, and preferably at least 15 seconds, and even more preferably at least 20 seconds. There are no particular restrictions on the upper limit for this time, although very long contact times offer little in terms of further increases in adhesive strength, and simply result in an equivalent reduction in production efficiency. Typically, the upper limit is set at 2 to 3 minutes. Needless to say, when a plurality of interfaces exist between adhesive resin composition layers and barrier layers, the above relationship should preferably be established at each of the interfaces. The same can be assumed for the interface between the adhesive material layer and the principal material layer, although in the case of the present invention, the base resin in both layers is a polyolefin, and consequently the mutual adhesion itself is comparatively good. As a result, it is preferable that the above relationship is established for contact between different materials, namely the adhesive resin layer and the barrier layer.

[Applications]

This type of multi-layer laminated structure according to the present invention can be used favorably for fuel tanks (vessels) such as gasoline tanks for filling with fuel oil, tanks for holding chemicals and solvents and the like, vessels such as tanks for holding industrial chemicals, and foodstuff vessels for holding cooking oils or detergents or the like.

In particular, a multi-layer laminated structure of the present invention displays excellent resistance to swelling on soak in fuel oil and also displays excellent adhesive strength following soak in fuel oil, and is consequently very useful as a fuel tank (vessel).

EXAMPLES

As follows is a more detailed description of the present invention based on a series of examples. The resins used are described below.

A [linear low density polyethylene (c) produced using a single site catalyst] and an [ultra low density polyethylene (d)] utilized materials prepared by polymerization in the following manner.

An ethylene copolymer (A1) of the present invention was polymerized using the method below.

[Solid Catalyst Preparation]

To a catalyst preparation device equipped with an electromagnetic induction stirrer, 1000 ml of toluene purified under an nitrogen atmosphere, 26 g of tetrapropoxyzirconium ($Zr(OPr)_4$), 22 g of indene, and 88 g of methylbutylcyclopentadiene were placed, and with the temperature maintained at 90° C., 100 g of tripropylaluminum was added dropwise over a period of 100 minutes, and the mixture was then reacted for 2 hours at the same temperature. Following

cooling to 40° C., 2,424 ml of a toluene solution of methylalumoxane (concentration: 3.3 mol/l) was added and stirred for 2 hours. Next, 2,000 g of silica (surface area: 300 m^2/g) which had been subjected, in advance, to 5 hours baking at 450° C. was added, and following stirring for one hour at room temperature, the mixture was blown with nitrogen and dried under reduced pressure at 40° C., yielding a solid catalyst (i) with good fluidity.

[Gas Phase Polymerization]

Using a continuous fluidized bed gas polymerization device, copolymerization of ethylene and 1-hexene was conducted at a polymerization temperature of 65° C. and with a total pressure of 20 kgf/cm^2G. The polymerization was performed by supplying the solid catalyst (i) continuously, while ethylene, 1-hexene and hydrogen were supplied so as to maintain a predetermined molar ratio, and yielded an ethylene copolymer (A1). The results of measurements of the physical properties of this copolymer are shown in Table 1.

An ethylene copolymer (A2) was prepared by polymerization using the following method.

[Solid Catalyst Preparation]

[Solid Catalyst (ii)]

To a catalyst preparation device equipped with an electromagnetic induction stirrer, 1,000 ml of toluene purified under an nitrogen atmosphere, 26 g of tetrapropoxyzirconium ($Zr(OPr)_4$), 74 g of indene, and 78 g of methylpropylcyclopentadiene were placed, and with the temperature maintained at 90° C., 100 g of tripropylaluminum was added dropwise over a period of 100 minutes, and the mixture was then reacted for 2 hours at the same temperature. Following cooling to 40° C., 2,133 ml of a toluene solution of methylalumoxane (concentration: 3.3 mol/l) was added and stirred for 2 hours. Next, 2,000 g of silica (surface area: 300 m^2/g) which had been subjected, in advance, to 5 hours baking at 450° C. was added, and following stirring for one hour at room temperature, the mixture was blown with nitrogen and dried under reduced pressure at 40° C., yielding a solid catalyst (ii) with good fluidity.

[Gas Phase Polymerization]

Using a continuous fluidized bed gas polymerization device, copolymerization of ethylene and 1-hexene was conducted at a polymerization temperature of 80° C. and with a total pressure of 20 kgf/cm^2G. The polymerization was performed by supplying the solid catalyst (ii) continuously, while ethylene, 1-hexene and hydrogen were supplied so as to maintain a predetermined molar ratio, and yielded an ethylene copolymer (A2). The results of measurements of the physical properties of this copolymer are shown in Table 1.

[Test Methods]

Methods for the aforementioned tests are as described below.

[Density]

Measured in accordance with JIS K6760.

[MFR]

Measured in accordance with JIS K6760

[Mw/Mn]

Measured using a GPC (model 150C, manufactured by Waters Corporation), and using ODCB at 135° C. as the solvent. The column used was a HT806M, manufactured by Shodex Co., Ltd.

[TREF]

With a column maintained at 140° C., a sample was injected into the column, and the temperature was then lowered to 25° C. at a cooling rate of 0.1° C./minute, causing the polymer to become deposited on the glass beads. The temperature of the column was then raised under the following conditions, and the polymer concentration eluted at each temperature was detected by an infrared detector (solvent: ODCB, flow rate: 1 ml/minute, rate of temperature increase: 50° C./hour, detector: infrared spectrometer (wavelength 2,925 cm^{-1}), column: 0.8 cmϕ×12 cmL (filled with glass beads), sample concentration: 0.05% by mass).

[Halogen Concentration]

Halogen concentration was measured using an X-ray fluorescence method, and in cases in which at least 10 ppm of chlorine was detected, the detected value was used as the analysis result. In the case of a result less than 10 ppm, measurement was performed using a chlorine and sulfur analysis device, model TOX-100 manufactured by Dyer Instruments (Ltd.), and results less than 2 ppm were recorded as ND, indicating an essentially halogen free material.

(Amount X of ODCB soluble fraction)

0.5 g of sample in 20 ml of ODCB was heated at 135° C. for 2 hours, and following complete dissolution of the sample, the solution was cooled to 25° C. The solution was then left to stand overnight at 25° C., and was then filtered through a Teflon filter and the filtrate collected. The absorption peak strength of the asymmetric stretching vibration of methylene at a wave number of approximately 2925 cm^{-1} of the filtrate which is sample solution was measured with an infrared spectrometer. Then, the sample concentration was then calculated from a previously prepared calibration curve. This value determined the content of the ODCB soluble fraction at 25° C.

(T_{ml} by DSC)

A sheet of thickness 0.2 mm was prepared using a hot press method, punching out an approximately 5 mg sample from the sheet, and then holding the sample at a temperature of 230° C. for 10 minutes, cooling the temperature to 0° C. at a rate of 2° C. per minute, and then raising the temperature to 70° C. again at a rate of 10° C. per minute, with the melting point (T_{ml}) then being defined as the temperature of the apex of the highest temperature peak.

(Melt tension: MT)

MT was determined by measuring the stress using a strain gauge when a melt resin was elongated with a fixed rate. A polymer in a pellet shape which is obtained by pelletization was used as a test sample, and MT measuring machine marketed by Toyo Seiki Seisaku-Sho, Ltd was used as the strain gauge. The orifice used for measuring has a diameter of 2.09 mm ø and a length of 8 mm. The stress was measured under conditions in that a temperature of resin was 190° C., a cylinder descending rate was 20 mm/mm., and a winding rate was 15 m/mm.

TABLE 1

		Type of Resin	
		A1 sLLDPE	A2 sLLDPE
		Type of Catalyst	
		single site	single site
(1)	Density (g/cm^3)	0.906	0.930
(2)	MFR (g/10 min.)	1.1	1.0
(3)	Mw/Mn	2.5	2.8
(4)	T75 − T25	24.2	13.2
(4)	(equation 1) − 670 × d + 644	37.0	20.9
(5)	(equation 2) − 300 × d + 285	13.2	6.0
(6)	ODCB soluble fraction (% by mass)	3.1	0.3
(6)	(equation 3) d − 0.008LogMFR	0.906	0.930
(6)	(equation 4) 9.8 × 10^3 × (0.9300 − d + 0.008logMFR)^2 + 2.0	7.8	2.0
(7)	number of TREF peaks	3	2
(7)	TREF peak temperatures (° C.)	59, 81, 94	88, 97
(8)	Number of DSC peaks	3	1
(8)	DSC melting points (° C.) T1	91.2	124.4
	T2	119.4	
	T3	122.7	
(8)	Tml (° C.)	122.7	124.4
(8)	(equation 5) 150 × d − 19	118.9	122.5
(9)	MT	0.70	0.70
(9)	LogMT	−0.15	−0.15
(9)	(equation 6) − 0.572 × LogMFR + 0.3	0.276	0.300
(10)	halogen concentration (ppm)	ND	ND
(11)	additives included (antioxidants, neutralizers)	none	none

The resins used in the present invention are listed in the Table 2 below.

TABLE 2

[Resins Used]

No	Resin used	*) Catalyst type	Abbreviated name	Density g/cm^3	MFR g/10 min.	Brand	Manufacturer
1	high density polyethylene	Z type	HDPE1	0.956	0.80	J-Rex-HD	Japan Polyolefins Co. Ltd
2	high density polyethylene	Z type	HDPE2	0.951	0.73	J-Rex-HD	Japan Polyolefins Co. Ltd
3	linear low density polyethylene	Z type	LLDPE1	0.928	0.80	J-Rex-LL	Japan Polyolefins Co. Ltd
4	linear low density polyethylene	Z type	LLDPE2	0.923	2.00	J-Rex-LL	Japan Polyolefins Co. Ltd
5	linear low density polyethylene	Z type	LLDPE3	0.923	0.80	J-Rex-LL	Japan Polyolefins Co. Ltd
6	linear low density polyethylene	Z type	LLDPE4	0.930	4.00	J-Rex-LL	Japan Polyolefins Co. Ltd
7	linear low density polyethylene	Z type	LLDPE5	0.923	8.00	J-Rex-LL	Japan Polyolefins Co. Ltd
8	linear low density polyethylene	Z type	LLDPE6	0.927	0.90	J-Rex-LL	Japan Polyolefins Co. Ltd
9	linear low density polyethylene	Z type	LLDPE7	0.921	30.0	J-Rex-LL	Japan Polyolefins Co. Ltd
10	linear low density polyethylene	S type	sLLDPE (A2)	0.930	1.0	Polymerized	
11	ultra low density polyethylene	M type	mLLDPE	0.908	1.00	Affinity PL1840	Dow Plastics Ltd
12	ultra low density polyethylene	Z type	zVLDPE	0.904	0.89	J-Rex-VL	Japan Polyolefins Co. Ltd
13	ultra low density polyethylene	S type	sVLDPE (A1)	0.902	1.00	Polymerized	
14	ultra low density polyethylene	S type	sVLDPE (A1)	0.906	1.10	Polymerized	

Z type: Ziegler type catalyst,
S type: single site catalyst,
M type: metallocene catalyst)

[Production of Modified Polyethylene]

The modified polyethylenes used in the examples and the comparative examples (hereafter also referred to as modified resins) were prepared in the manner described below.

(Modified Resin 1)

To 100 parts of a high density polyethylene (HDPE1) with a density of 0.956 g/cm^3 and a MFR at temperature 190° C. and loading 2.16 kg of 0.80, 0.015 parts of 2,5-dimethyl-2,5-t-butylperoxyhexane was added, and the mixture was then dry blended for one minute in a Henschel mixer. Subsequently, 0.375 parts of maleic anhydride was added, and following a further 2 minutes of dry blending, the mixture was subjected to molten kneading at 260° C. using a 50 mm single screw extruder manufactured by Modern Machinery (Ltd.), and yielded a modified polyethylene (modified resin 1). In this modified polyethylene, the content of grafted maleic anhydride was 0.30% by mass. The density and MFR of the original polyethylene, and the content of grafted maleic anhydride (labeled MAH content in the table) are shown in Table 3.

(Modified Resin 2, Modified Resin 3)

With the exception of altering the raw material polyethylene to the polyethylenes shown in Table 3, production was performed under identical conditions to the modified resin 1. The density and MFR of the original polyethylenes, and the content of grafted maleic anhydride are shown in Table 3.

(Modified Resin 4)

To 100 parts of a high density polyethylene (HDPE1) with a density of 0.956 g/cm^3 and a MFR of 0.80, 0.015 parts of 2,5-dimethyl-2,5-t-butylperoxyhexane was added, and the

mixture was then dry blended for one minute in a Henschel mixer. Subsequently, 0.60 parts of maleic anhydride was added, and the mixture was dry blended for a further 2 minutes. The mixture was then subjected to molten kneading at 290° C. using a 50 mm single screw extruder manufactured by Modern Machinery (Ltd.), and yielded a modified polyethylene (modified resin 4). In this modified polyethylene, the content of grafted maleic anhydride was 0.43% by mass. The density and MFR of the original polyethylene, and the content of grafted maleic anhydride are shown in Table 3.

(Modified Resin 5, Modified Resin 6, and Modified Resin 10 to Modified Resin 11)

With the exception of altering the raw material polyethylene to the polyethylenes shown in Table 3, production was performed under identical conditions to the modified resin 4. The density and MFR of the original polyethylenes, and the content of grafted maleic anhydride are shown in Table 3.

The raw material polyethylene used in a modified resin 7, a modified resin 8 and a modified resin 9, utilized a pre-blended mixture of two types of polyethylene shown in Table 3.

Examples 1 to 13 and Comparative Examples 1 to 12

The antioxidants and acid absorbers shown in Table 6 were added to the compositions shown in Table 4 to Table 5, and adhesive resin compositions were then produced by molten kneading at 200° C. using a 50 mm single screw extruder manufactured by Modern Machinery (Ltd.). The antioxidants and acid absorbers were added in accordance with an additives recipe 1 shown below for the examples 1 to 13 and the comparative examples 1 to 10, in accordance with an additives recipe 2 shown below for the comparative example 11, an in accordance with an additives recipe 3 shown below for the comparative example 12.

TABLE 3-1

	Raw material resin				Raw material resin				Maleic anhydride (MAH)	Organic peroxide	Adhesive resin composition		
Modified resin	type (1)	density (g/cm^3)	MFR (g/10 min)	content (% by mass)	type (2)	density (g/cm^3)	MFR (g/10 min)	content (% by mass)	content (parts by mass)	content (parts by mass)	Grafted MAH content (% by mass)	MFR (g/10 min)	Ring opening ratio (%)
1	HDPE1	0.956	0.80	100	—	—	—	—	0.375	0.015	0.30	0.30	1
2	LLDPE1	0.928	0.80	100	—	—	—	—	0.375	0.015	0.30	0.28	2
3	LLDPE2	0.923	2.0	100	—	—	—	—	0.375	0.015	0.30	0.28	5
4	HDPE1	0.956	0.80	100	—	—	—	—	0.60	0.015	0.43	0.20	2
5	LLDPE1	0.928	0.80	100	—	—	—	—	0.60	0.015	0.43	0.20	3
6	LLDPE3	0.923	0.80	100	—	—	—	—	0.60	0.015	0.45	0.18	3
7	HDPE2	0.952	0.80	85	LLDPE1	0.928	0.80	15	0.375	0.015	0.30	0.30	3
8	HDPE2	0.952	0.80	56	LLDPE1	0.928	0.80	44	0.60	0.015	0.43	0.21	1
9	HDPE2	0.952	0.80	44	LLDPE1	0.928	0.80	56	0.60	0.015	0.43	0.19	3
10	LLDPE4	0.930	4.0	100	—	—	—	—	0.60	0.015	0.45	2.0	3
11	LLDPE5	0.923	8.0	100	—	—	—	—	0.60	0.015	0.45	3.2	3
12	HDPE1	0.956	0.80	85	LLDPE1	0.928	0.80	15	0.375	0.015	0.30	0.30	2
13	HDPE1	0.956	0.80	56	LLDPE1	0.928	0.80	44	0.375	0.015	0.30	0.25	3
14	HDPE1	0.956	0.80	67	LLDPE1	0.928	0.80	33	0.375	0.015	0.30	0.27	2
15	HDPE1	0.956	0.80	15	LLDPE1	0.928	0.80	85	0.375	0.015	0.31	0.23	2

TABLE 3-2

	Raw material resin				Raw material resin				Maleic anhydride (MAH)	Organic peroxide	Adhesive resin composition		
Modified resin	type (1)	density (g/cm^3)	MFR (g/10 min)	content (% by mass)	type (2)	density (g/cm^3)	MFR (g/10 min)	content (% by mass)	content (parts by mass)	content (parts by mass)	Grafted MAH content (% by mass)	MFR (g/10 min)	Ring opening ratio (%)
16	HDPE1	0.956	0.80	100	—	—	—	—	0.375	0.015	0.29	0.33	2
17	LLDPE1	0.928	0.80	100	—	—	—	—	0.375	0.015	0.32	0.20	1
18	HDPE2	0.951	0.73	100	—	—	—	—	0.375	0.015	0.29	0.32	3
19	LLDPE6	0.927	0.90	100	—	—	—	—	0.370	0.010	0.28	0.40	3
20	HDPE2	0.952	0.80	85	LLDPE1	0.928	0.80	15	0.375	0.015	0.30	0.30	30
21	HDPE1	0.956	0.80	85	LLDPE1	0.928	0.80	15	0.375	0.015	0.30	0.30	29

TABLE 4-1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Modified resin 1	41						
Modified resin 2					41		
Modified resin 3						41	
Modified resin 5							
Modified resin 6							
Modified resin 7		41	41	41			
Modified resin 8							30
Modified resin 9							
HDPE1 0.956/0.80			5		5	15	
LLDPE2 0.923/2.00							
LLDPE3 0.923/0.80	59	59	54		54	44	70
LLDPE5 0.923/8.00				59			
Additives recipe	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1
MFR (g/10 minutes)	0.5	0.5	0.5	0.6	0.5	0.5	0.5
MAH content (% by mass)	0.12	0.12	0.12	0.12	0.12	0.12	0.13
MAH ring opening ratio (%)	1.0	1.0	1.0	1.0	1.0	3.0	1.0
Density (g/cm^3)	0.937	0.935	0.937	0.931	0.927	0.928	0.929
MFR A/B ratio	0.38	0.38	0.38	0.38	0.31	0.31	0.26
Moldability	○	○	○	○	○	○	○
Tensile impact strength of a nominal regrind composition at −40° C. (KJ/m^2)	128	127	128	128	127	128	128
Charpy impact strength of a 4 type 6 layer vessel at −40° C. (KJ/m^2)		5.3				1.2	
Degree of fuel oil swelling (% by mass)	17	18	17	22	28	26	25
Initial adhesive strength (MPa)	16	16	16	16	15	16	15
Adhesive strength following soak in fuel oil (MPa)	14	14	15	14	13	15	14
Measurement and observation of transmission electron microscope photograph	○	—	○	—	—	○	○

TABLE 4-2

	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13
Modified resin 1						
Modified resin 2						
Modified resin 3						
Modified resin 5					30	
Modified resin 6						30
Modified resin 7						
Modified resin 8	30	30	30			
Modified resin 9				30		
HDPE1 0.956/0.80	10		10	10		10
LLDPE2 0.923/2.00		70				
LLDPE3 0.923/0.80	60				70	60
LLDPE5 0.923/8.00			60	60		
Additives recipe	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1
MFR (g/10 minutes)	0.5	0.7	0.5	0.5	0.5	0.6
MAH content (% by mass)	0.13	0.13	0.13	0.13	0.13	0.13
MAH ring opening ratio (%)	1.0	1.0	1.0	1.0	1.0	1.0
Density (g/cm^3)	0.933	0.929	0.928	0.927	0.925	0.925
MFR A/B ratio	0.26	0.11	0.26	0.24	0.25	0.23
Moldability	○	○	○	○	○	○
Tensile impact strength of a nominal regrind composition at −40° C. (KJ/m^2)	129	130	130	130	131	130
Charpy impact strength of a 4 type 6 layer vessel at −40° C. (KJ/m^2)			5.4			
Degree of fuel oil swelling (% by mass)	20	25	26	28	30	29
Initial adhesive strength (MPa)	15	15	15	15	15	15
Adhesive strength following soak in fuel oil (MPa)	14	13	13	14	13	14
Measurement and observation of transmission electron microscope photograph	—	—	—	—	—	—

TABLE 5-1

	Co. Ex. 1	Co. Ex. 2	Co. Ex. 3	Co. Ex. 4	Co. Ex. 5	Co. Ex. 6
Modified resin 1	17	24			35	35
Modified resin 2	3	3			6	6
Modified resin 4						
Modified resin 5						
Modified resin 7						
Modified resin 10			30			
Modified resin 11				30		
HDPE1 0.956/0.80			10	10		
LLDPE1 0.928/0.80		13				10
LLDPE2 0.923/2.00						
LLDPE3 0.923/0.80	80	60	60	60		
LLDPE4 0.930/4.00					59	49
LLDPE5 0.923/8.00						
sVLDPE 0.902/1.00						
Additives recipe	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1
MFR (g/10 minutes)	0.5	0.5	0.5	0.5	4.2	3.0
MAH content (% by mass)	0.06	0.08	0.13	0.13	0.12	0.12
MAH ring opening ratio (%)	1.0	1.0	1.0	1.0	1.0	1.0
Density (g/cm^3)	0.929	0.932	0.928	0.926	0.934	0.934
MFR A/B ratio	0.36	0.36	2.5	4.0	0.01	0.02
Moldability	○	○	○	○	X	X
Tensile impact strength of a nominal regrind composition at −40° C. (KJ/m^2)	90	105	130	131	128	128
Charpy impact strength of a 4 type 6 layer vessel at −40° C. (KJ/m^2)	3.6	4.2				
Degree of fuel oil swelling (% by mass)	25	21	26	29	19	19
Initial adhesive strength (MPa)	13	14	8	8	13	13
Adhesive strength following soak in fuel oil (MPa)	12	13	6	6	12	11
Measurement/observation of transmission electron microscope photograph	—	—	—	—	—	—

TABLE 5-2

	Co. Ex. 7	Co. Ex. 8	Co. Ex. 9	Co. Ex. 10	Co. Ex. 11	Co. Ex. 12
Modified resin 1		6	60	60	41	41
Modified resin 2		35	11	11		
Modified resin 4	13					
Modified resin 5	17					
Modified resin 7						
Modified resin 10						
Modified resin 11						
HDPE1 0.956/0.80						
LLDPE1 0.928/0.80				29		
LLDPE2 0.923/2.00			29			
LLDPE3 0.923/0.80					59	59
LLDPE4 0.930/4.00						
LLDPE5 0.923/8.00	70	59				
sVLDPE 0.902/1.00						
Additives recipe	recipe 1	recipe 1	recipe 1	recipe 1	recipe 2	recipe 3
MFR (g/10 minutes)	0.6	0.6	0.6	0.6	0.5	0.4
MAH content (% by mass)	0.13	0.12	0.21	0.21	0.11	0.11
MAH ring opening ratio (%)	1.0	1.0	1.0	1.0	1.0	1.0
Density (g/cm^3)	0.923	0.923	0.943	0.945	0.937	0.937
MFR A/B ratio	0.25	0.38	0.15	0.38	0.38	0.38
Moldability	○	○	○	○	○	○
Tensile impact strength of a nominal regrind composition at −40° C. (KJ/m^2)	129	127	140	140	128	128
Charpy impact strength of a 4 type 6 layer vessel at −40° C. (KJ/m^2)						
Degree of fuel oil swelling (% by mass)	34	34	13	13	17	17
Initial adhesive strength (MPa)	14	14	10	10	12	10
Adhesive strength following soak in fuel oil (MPa)	12	12	8	8	10	7

TABLE 5-2-continued

	Co. Ex. 7	Co. Ex. 8	Co. Ex. 9	Co. Ex. 10	Co. Ex. 11	Co. Ex. 12
Measurement/observation of transmission electron microscope photograph	—	—	—	X	X	—

TABLE 6

Additive Type	Brand	Additives recipe 1	Additives recipe 2	Additives recipe 3
Phenol based antioxidant	Irganox 1330 (Ciba Specialty Chemicals Ltd.)	0.15	0.15	0.15
	Irganox 1076 (Ciba Specialty Chemicals Ltd.)	0.05	0.05	0.05
Phosphoric acid based antioxidant	Irgafos 168 (Ciba Specialty Chemicals Co., Ltd.)	0.10	0.10	0.10
Acid absorber	Hydrotalcite DHT4A (Kyowa Chemical Industry Co., Ltd.)	0.05	—	—
	Calcium stearate (NOF Corporation)	—	0.03	0.10

Units: parts by mass

[Formation of a 3 Type 5 Layer Tank]

First, parison was formed from the adhesive resin composition. Then, using a 3 type 5 layer small multi-layer blow molding machine at a molding temperature of 210° C., this parison was used to form a 3 type 5 layer laminated vessel with a total thickness of 6 mm, an internal capacity of 10 L, and a layer configuration comprising a high density polyethylene (HDPE) layer (principal material layer)/an adhesive resin composition layer (adhesive layer)/a saponified product of an ethylene-vinyl acetate copolymer (barrier layer)/an adhesive resin composition layer (adhesive layer)/and a high density polyethylene layer (principal material layer) formed in a ratio of 45.5/3/3/3/45.5 respectively.

In this process, the high density polyethylene utilized a product KBY47C manufactured by Japan Polyolefins Co. Ltd. with a density of 0.947 g/cm^3 and a 190° C. MFR at a loading of 21.6 kg of 6 g/10 minutes, whereas the saponified product of an ethylene-vinyl acetate copolymer used a product EVAL F101B manufactured by Kuraray Co., (Ltd.).

[Moldability Evaluation]

The moldability evaluations were performed by slicing samples out of the intermediate region of the parison used in the formation of the 3 type 5 layer laminated tank, and then visually inspecting the samples for irregularities in the lamination of the adhesive layer/barrier layer/adhesive layer. 5 parison samples were inspected, and if an irregularity was observed in even one sample, the evaluation result was recorded as X. These evaluation results are shown in Table 4 to Table 5.

[Initial Adhesive Strength]

The initial adhesive strength was measured by cutting a 10 mm wide sample in the MD direction from the flat section in the base of the 3 type 5 layer vessel, and then measuring the adhesive strength between the outermost adhesive layer and the barrier layer using a T-peel method. This measurement was performed twice and the average value was recorded. The results are shown in Table 4 to Table 5.

[Adhesive Strength Following Soak in Fuel Oil]

The adhesive strength following soak in fuel oil was measured in a similar manner to the initial adhesive strength evaluation, by cutting a strip sample of width 10 mm and length 150 mm in the MD direction from the flat section in the base of the 3 type 5 layer vessel, soaking the sample in commercially available regular gasoline at 65° C. for a period of 2,000 hours, and then measuring the adhesive strength between the outermost adhesive layer and the barrier layer using a T-peel method. This measurement was performed twice and the average value was recorded. The results are shown in Table 4 to Table 5.

[Degree of Fuel Oil Swelling]

Fuel oil swelling was determined by cutting a 80 mm×10 mm sample from a pressed sheet of thickness 4 mm, soaking the sample in commercially available regular gasoline at 65° C. for a period of 2,000 hours, and then measuring the weight increase from the weight prior to soak, thereby determining a weight proportion due to fuel oil swelling. This measurement was performed twice and the average value was recorded. The results are shown in Table 4 to Table 5.

[Measurement of Maleic Anhydride Quantity]

The content of added maleic anhydride (MAH) (the degree of maleination) was determined by using infrared absorption spectroscopy to measure the absorption of A1: 1,790 cm^{-1} anhydride group (C═O), A2: 1,710 to 1,720 cm^{-1} carboxylic acid group (C═O), and A3: 4,250 cm^{-1} methylene group (—CH_2—), and then calculating the following content:

MAH content=A1 (anhydride group) absorption+A2 (carboxylic acid group) absorption/*A*3 (methylene group) absorption×0.265 (% by mass)

[Maleic Anhydride Ring Group Opening Ratio]

Using infrared absorption spectroscopy, the absorption was measured for A1: 1,790 cm^{-1} anhydride group (C═O), and A2: 1,710 to 1,720 cm^{-1} carboxylic acid group (C═O), and the maleic anhydride group ring opening ratio was then determined in the following manner:

Ring opening ratio=(A2: carboxylic acid group absorption/A1: anhydride group absorption+A2: carboxylic acid group absorption)×100 (% by mass)

[Nominal Regrind Layer Composition]

A mixture of 6.7% by mass of an adhesive resin composition from examples 1 to 13 and comparative examples 1 to 12, 88.3% by mass of a high density polyethylene (KBY47C, manufactured by Japan Polyolefins Co. Ltd.) with a density of 0.945 g/cm^3 and a MFR at temperature 190° C. and loading 21.6 kg of 6 g/10 minutes, and 5% by mass of a saponified product of an ethylene-vinyl acetate copolymer (EVAL F101B, manufactured by Kuraray Co., Ltd.) was subjected to molten kneading under the conditions shown below.

Extruder: Modern Machinery (Ltd.), 50 mm single screw extruder,

Screw revolutions: 60 rpm,

Temperature: cylinder 1-cylinder 2-cylinder 3-H-dice temperature settings of 180° C.-200° C.-200° C.-200° C.-200° C.

[Sheet Molding Conditions]

A sheet of thickness 4 mm was prepared in a press molding device using a temperature setting of 200° C., a press pressure of 6 MPa, a preheating period of 7 minutes, a press time of 5 minutes, and a cooling period of 10 minutes, and a test specimen of a shape 1 according to JIS K7160 was then punched out of this sheet.

[WV Notch Tensile Impact Strength]

Subsequently, the above test specimen was used to measure the WV notch tensile impact strength at −40° C. (JIS K7160 (ISO8256)). The measurement was performed with n=5, and the average of these results was recorded. The results are shown in Table 4 to Table 5.

[Formation of a 4 Type 6 Layer Tank with a Regrind Layer]

A 4 type 6 layer vessel with a total thickness of 4 to 7 mm, an internal capacity of 70 L, and a layer configuration comprising an outer layer/regrind layer/outer adhesive layer/barrier layer/inner adhesive layer/and an inner layer was formed in a ratio of 15/45/2/3/2/33 respectively. In this process, the outer layer and the inner layer utilized a high density polyethylene (brand: KBY47C manufactured by Japan Polyolefins Co. Ltd.) with a density of 0.945 g/cm^3 and a MFR at a temperature 190° C. and a loading 21.6 kg of 6 g/10 minutes, whereas the barrier layer used a saponified product of an ethylene-vinyl acetate copolymer (brand: EVAL F101B manufactured by Kuraray Co., (Ltd.)).

Observation of this multi-layer blow molding revealed that the time taken from when the adhesive resin layer and the barrier layer came into molten state contact inside the die, until air was blown into the parison and the swelling parison contacted the blow mold and began to cool was approximately 30 seconds.

[Evaluation of Low Temperature Impact Resistance Strength]

A sample was cut from the flat section in the base of the regrind layer containing 4 type 6 layer vessel formed in the manner described above, and this sample was evaluated in accordance with JIS K7111, by measuring the −40° C. Charpy impact strength (KJ/m2) for a notched test specimen. The results are shown in Table 4 to Table 5.

[Measurement of Transmission Electron Microscope Photographs]

While freezing the interface of a laminate (adhesive resin composition/EVOH) with liquid N_2 gas, a mirror surface was formed, this mirror surface was dyed with an osmium tetroxide solution, and following washing and subsequent dyeing with ruthenium tetroxide, the interface was used to prepare a 70 to 80 nm section using an ultramicrotome, and this section was then observed under a transmission electron microscope at a magnification of 20,000× to 50,000×.

O: Irregularities with an elevation difference of at least 100 nm were visible

X: Irregularities with an elevation difference of at least 100 nm were not visible

[Evaluation Results]

3 type 5 layer vessels were prepared using the compositions shown in the examples 1 to 13 and the comparative examples 1 to 12 as the adhesive layer, and the moldability, the initial adhesive strength, the adhesive strength following soak in fuel oil, the degree of fuel oil swelling, and the WV notch tensile impact strength at −40° C. of a nominal regrind composition was evaluated for each vessel, and then for representative examples, the low temperature impact resistance of a 4 type 6 layer vessel was also measured. The results of these evaluations shown in Table 4 to Table 5 reveal that the examples 1 to 13 satisfy the conditions of the present invention, and consequently showed good results for all of the evaluations.

In contrast, the comparative example 1 and the comparative example 2, for which the maleic anhydride content in the final adhesive resin composition was low, displayed an inferior low temperature impact resistance of the vessel with a regrind layer, as well as an inferior low temperature impact resistance of the associated 4 type 6 layer laminated vessel.

Furthermore, the comparative example 3 and the comparative example 4, for which the melt flow rate of the modified raw material resin was outside the range specified by the present invention (MFR=4.0 for the comparative example 3, and MFR 8.0 for the comparative example 4), and moreover for which the ratio between the melt flow rates at a temperature of 190° C. and a loading of 2.16 kg for the modified polyethylene (A) and the unmodified polyethylene (B) was greater than 1, displayed a lower adhesive strength.

Furthermore, the comparative example 5 and the comparative example 6, for which the MFR of the final adhesive resin composition was a high value outside the range specified by the present invention, displayed inferior moldability.

Furthermore, the comparative example 7 and the comparative example 8, for which the density of the final adhesive resin composition was a low value outside the range specified by the present invention, displayed a large degree of fuel oil swelling.

The comparative example 9 and the comparative example 10, for which the density of the final adhesive resin composition was very high, displayed an inferior adhesive strength.

In addition, the comparative example 11 and the comparative example 12, which used calcium stearate as an acid absorber, displayed an inferior adhesive strength.

Examples 14 to 33

The modified polyethylenes (modified resin 12 to modified resin 21 described below) were produced in the following manner.

(Modified Resin 12)

To a high density polyethylene (HDPE1) with a density of 0.956 g/cm^3 and a MFR of 0.80 g/10 minutes produced using a Ziegler catalyst, or alternatively to a mixture of this polyethylene with a linear low density polyethylene, 0.015 parts of 2,5-dimethyl-2,5-t-butylperoxyhexane was added, and the mixture was then dry blended for one minute in a Henschel mixer. Subsequently, 0.375 parts of maleic anhy-

dride was added, and following a further 2 minutes of dry blending, the mixture was subjected to molten kneading at a temperature of 260° C. using a 50 mm single screw extruder manufactured by Modern Machinery (Ltd.), yielding the modified resin. The content of grafted maleic anhydride (MAH content) and the like are shown in Table 3.

(Modified Resin 13)

Production was performed under identical conditions to the modified resin 12, but with two different types of raw material polyethylene pre-blended in the composition shown in Table 3. The density and MFR of the original polyethylenes, and the content of grafted maleic anhydride are summarized in Table 3.

(Modified Resin 14 to Modified Resin 17)

Production was performed under identical conditions to the modified resin 13, using a linear low density polyethylene (LLDPE1) with a density of 0.928 g/cm^3 and a MFR of 0.80 g/10 minutes produced using a Ziegler catalyst. 0.015 parts of 2,5-dimethyl-2,5-t-butylperoxyhexane were added, and the mixture was dry blended for one minute in a Henschel mixer, and the content of subsequently grafted maleic anhydride was 0.32% by mass (refer to Table 3).

(Modified Resin 18)

To a high density polyethylene (HDPE2) with a density of 0.951 g/cm^3 and a MFR of 0.73 g/10 minutes produced using a Ziegler catalyst, 0.012 parts of 2,5-dimethyl-2,5-t-butylperoxyhexane was added, and the mixture was then dry blended for one minute in a Henschel mixer. Subsequently, 0.375 parts of maleic anhydride was added, and following a further 2 minutes of dry blending, the mixture was subjected to molten kneading at a temperature of 260° C. using a 50 mm single screw extruder manufactured by Modern Machinery (Ltd.), yielding the modified resin. The content of grafted maleic anhydride was 0.29% by mass (refer to Table 3).

(Modified Resin 19)

To a linear low density polyethylene (LLDPE2) with a density of 0.927 g/cm^3 and a MFR of 0.9 g/10 minutes produced using a Ziegler catalyst, 0.01 parts of 2,5-dimethyl-2,5-t-butylperoxyhexane was added, and the mixture was then dry blended for one minute in a Henschel mixer. Subsequently, 0.375 parts of maleic anhydride was added, and following a further 2 minutes of dry blending, the mixture was subjected to molten kneading at a temperature of 260° C. using a 50 mm single screw extruder manufactured by Modern Machinery (Ltd.), yielding the modified resin. The content of grafted maleic anhydride was 0.28% by mass (refer to Table 3).

(Modified Resin 20)

To a mixture of 85% by mass of a high density polyethylene (HDPE2) with a density of 0.952 g/cm^3 and a MFR of 0.80 g/10 minutes, and 15% by mass of a linear low density polyethylene (LLDPE1) with a density of 0.928 g/cm^3 and a MFR of 0.80 g/10 minutes, 0.015 parts of 2,5-dimethyl-2,5-t-butylperoxyhexane was added, and the mixture was then dry blended for one minute in a Henschel mixer. Subsequently, 0.375 parts of maleic anhydride was added, and following a further 2 minutes of dry blending, the mixture was subjected to molten kneading at 290° C. using a 50 mm single screw extruder manufactured by Modern Machinery (Ltd.), yielding a modified polyethylene (the modified resin 20). The content of grafted maleic anhydride in this modified polyethylene was 0.30% by mass.

This modified resin 20 was left sitting in the open air at room temperature for 3 months, and the ring opening ratio of the maleic anhydride was then measured. Furthermore, the density and MFR of the original polyethylenes, and the content of grafted maleic anhydride are shown in Table 3.

(Modified Resin 21)

To a mixture of 85% by mass of a high density polyethylene (HDPE1) with a density of 0.956 g/cm^3 and a MFR of 0.80 g/10 minutes, and 15% by mass of a linear low density polyethylene (LLDPE1) with a density of 0.928 g/cm^3 and a MFR of 0.80 g/10 minutes, was added 0.015 parts of 2,5-dimethyl-2,5-t-butylperoxyhexane, and the mixture was then dry blended for one minute in a Henschel mixer. Subsequently, 0.375 parts of maleic anhydride was added, and following a further 2 minutes of dry blending, the mixture was subjected to molten kneading at 290° C. using a 50 mm single screw extruder manufactured by Modem Machinery (Ltd.), yielding a modified polyethylene (the modified resin 21). The content of grafted maleic anhydride in this modified polyethylene was 0.30% by mass.

This modified resin 21 was left sitting in the open air at room temperature for 3 months, and the ring opening ratio of the maleic anhydride was then measured. Furthermore, the density and MFR of the original polyethylenes, and the content of grafted maleic anhydride are shown in Table 3.

Examples 14 to 21

To a composition produced by combining the modified resins shown in Table 7 with an ultra low density polyethylene (sVLDPE) produced using a single site catalyst, which represents an ethylene copolymer (A1), were added antioxidants and an acid absorber (recipe 1), and the mixture was then subjected to molten kneading at a temperature of 220° C. using a 50 mm single screw extruder manufactured by Modern Machinery (Ltd.), yielding an adhesive resin composition. A 3 type 5 layer vessel was produced using the adhesive resin composition, and the moldability, the initial adhesive strength, the adhesive strength following soak in fuel oil, and the degree of fuel oil swelling were measured and evaluated. The results are shown in Table 7.

Examples 22 to 29

The results of evaluations for adhesive resin compositions in which the ethylene copolymer (A1) was replaced with an ultra low density polyethylene (mVLDPE) produced using a metallocene catalyst are also shown in Table 7.

Example 30

The results of evaluations for an adhesive resin composition in which the ethylene copolymer (A1) was replaced with a linear low density polyethylene (sLLDPE) produced using a single site catalyst, which represents an ethylene copolymer (A2), and a Ziegler based ultra low density polyethylene (zVLDPE) are also shown in Table 7.

Examples 31 to 32

The results of evaluations for adhesive resin compositions using the modified resins 20, 21, for which the ring opening ratio of the maleic anhydride group is high, are also shown in Table 7.

Example 33

The results of evaluations for an adhesive resin composition prepared in the same manner as the example 15, with the exception of replacing the single site ultra low density polyethylene (sVLDPE) of the example 15 with a Ziegler based ultra low density polyethylene, are also shown in Table 7.

Comparative Examples 13 to 17

The modified resins and other used resins shown in Table 8 were combined, and 3 type 5 layer vessels were produced using the compositions shown in the comparative examples 13 to 17 as the adhesive layer. The moldability, the initial adhesive strength, the adhesive strength following soak in fuel oil, and the degree of fuel oil swelling were measured for each vessel, and the results of the evaluations are shown in Table 8.

[Evaluation Results]

The examples 14 to 33, which correspond with the present invention, displayed good values for all the evaluations. In contrast, the comparative example 13, for which the content of unsaturated carboxylic acid and derivatives thereof in the final composition was low, displayed an inferior adhesive strength and a poor low temperature impact strength for the nominal regrind composition, whereas the comparative examples 14 to 16, displayed a large degree of fuel swelling. The comparative example 17 displayed a MFR value outside the range specified by the present invention, and the moldability was poor.

TABLE 7-1

	Example 14	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20
Modified resin 12		41			41	41	41
Modified resin 13				41			
Modified resin 14							
Modified resin 15							
Modified resin 16	41						
Modified resin 17			41				
Modified resin 19							
Modified resin 20							
Modified resin 21							
HDPE1 0.956/0.80	5	5	15	5			
HDPE2 0.951/0.73					1	1	1
LLDPE1 0.928/0.80	29	29	19	29	33		33
LLDPE3 0.923/0.80						33	10
sLLDPE (A2) 0.930/1.00							
zVLDPE 0.904/0.89							
sVLDPE (A1) 0.906/1.10	25	25	25	25	25	25	15
mVLDPE 0.908/1.00							
Additives recipe	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1
MFR (g/10 minutes)	0.5	0.5	0.6	0.5	0.5	0.5	0.5
MAH content (% by mass)	0.12	0.12	0.13	0.12	0.12	0.12	0.12
MAH ring opening ratio (%)	1	1	1	1	1	1	1
Density (g/cm^3)	0.935	0.934	0.927	0.930	0.933	0.931	0.934
MFR A/B ratio	0.34	0.31	0.21	0.26	0.33	0.33	0.34
Moldability	○	○	○	○	○	○	○
Tensile impact strength of a nominal regrind composition at −40° C. (KJ/m^2)	127	128	129	128	128	129	128
Charpy impact strength of a 4 type 6 layer vessel at −40° C. (KJ/m^2)		5.3					5.2
Degree of fuel oil swelling (% by mass)	18	19	28	23	21	22	19
Initial adhesive strength (MPa)	15	16	17	16	16	15	16
Adhesive strength following soak in fuel oil (MPa)	13	14	16	15	13	13	14
Observation of transmission electron microscope photograph	○	—	—	—	—	—	—

TABLE 7-2

	Example 21	Example 22	Example 23	Example 24	Example 25	Example 26	Example 27
Modified resin 12	41	41				41	41
Modified resin 13					41		
Modified resin 14							
Modified resin 15							
Modified resin 16			41				
Modified resin 17				41			
Modified resin 19							
Modified resin 20							
Modified resin 21							
HDPE1 0.956/0.80	5	5	5	15	5		
HDPE2 0.951/0.73						1	1

TABLE 7-2-continued

	Example 21	Example 22	Example 23	Example 24	Example 25	Example 26	Example 27
LLDPE1 0.928/0.80	24	29	29	19	29	33	
LLDPE3 0.923/0.80							33
sLLDPE (A2) 0.930/1.00							
zVLDPE 0.904/0.89							
sVLDPE (A1) 0.906/1.10	30						
mVLDPE 0.908/1.00		25	25	25	25	25	25
Additives recipe	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1
MFR (g/10 minutes)	0.7	0.5	0.5	0.6	0.5	0.5	0.5
MAH content (% by mass)	0.12	0.12	0.12	0.13	0.12	0.12	0.12
MAH ring opening ratio (%)	1	1	1	1	1	1	1
Density (g/cm^3)	0.933	0.934	0.936	0.927	0.931	0.933	0.931
MFR A/B ratio	0.33	0.33	0.35	0.22	0.26	0.36	0.36
Moldability	○	○	○	○	○	○	○
Tensile impact strength of a nominal regrind composition at −40° C. (KJ/m^2)	127	128	128	130	128	128	128
Charpy impact strength of a 4 type 6 layer vessel at −40° C. (KJ/m^2)						5.3	
Degree of fuel oil swelling (% by mass)	20	19	17	28	22	20	22
Initial adhesive strength (MPa)	15	15	14	16	16	15	15
Adhesive strength following soak in fuel oil (MPa)	13	13	13	15	15	13	13
Observation of transmission electron microscope photograph	○	○	—	—	—	—	—

TABLE 7-3

	Example 28	Example 29	Example 30	Example 31	Example 32	Example 33
Modified resin 12	41	41	41			41
Modified resin 13						
Modified resin 14						
Modified resin 15						
Modified resin 16						
Modified resin 17						
Modified resin 19						
Modified resin 20				41		
Modified resin 21					41	
HDPE1 0.956/0.80		5	5	5	5	5
HDPE2 0.951/0.73	1					
LLDPE1 0.928/0.80	33	24		29	29	29
LLDPE3 0.923/0.80	10					
sLLDPE (A2) 0.930/1.00			29			
zVLDPE 0.904/0.89			25			25
sVLDPE (A1) 0.906/1.10				25		
mVLDPE 0.908/1.00	15	30			25	
Additives recipe	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1
MFR (g/10 minutes)	0.5	0.7	0.7	0.5	0.5	0.6
MAH content (% by mass)	0.12	0.12	0.12	0.12	0.12	0.12
MAH ring opening ratio (%)	1	1	1	18	17	1
Density (g/cm^3)	0.935	0.933	0.932	0.933	0.933	0.933
MFR A/B ratio	0.38	0.36	0.34	0.34	0.34	0.34
Moldability	O	O	O	O	O	O
Tensile impact strength of a nominal regrind composition at −40° C. (KJ/m^2)	127	128	126	125	126	128
Charpy impact strength of a 4 type 6 layer vessel at −40° C. (KJ/m^2)						
Degree of fuel oil swelling (% by mass)	19	20	19	18	18	20
Initial adhesive strength (MPa)	15	15	17	13	13	12
Adhesive strength following soak in fuel oil (MPa)	13	13	16	11	11	10
Observation of transmission electron microscope photograph	O	—	O	—	—	—

TABLE 8

	Comparative Example 13	Comparative Example 14	Comparative Example 15	Comparative Example 16	Comparative Example 17
Modified resin 12					41
Modified resin 13		41			
Modified resin 14	15				
Modified resin 15				41	
Modified resin 17			41		
Modified resin 18					
Modified resin 19					
Modified resin 21					
HDPE1 0.956/0.80	11		5	5	
HDPE2 0.951/0.73		1			
LLDPE1 0.928/0.80	49				
LLDPE2 0.923/2.00		19	29	29	
LLDPE3 0.923/0.80					
LLDPE7 0.921/30.0					34
zVLDPE 0.904/0.89		45	25	25	
sVLDPE 0.906/1.00	25				25
Additives recipe	recipe 1	recipe 1	recipe 1	recipe 1	recipe 1
MFR (g/10 minutes)	0.8	0.6	0.6	0.6	2.2
MAH content (% by mass)	0.05	0.12	0.13	0.12	0.12
MAH ring opening ratio (%)	1	1	1	1	1
Density (g/cm^3)	0.928	0.923	0.922	0.923	0.930
MFR A/B ratio	0.34	0.29	0.26	0.27	0.03
Moldability	O	O	O	O	X
Tensile impact strength of a nominal regrind composition at −40° C. (KJ/m^2)	92	128	130	128	128
Charpy impact strength of a 4 type 6 layer vessel at −40° C. (KJ/m^2)	3.7				
Degree of fuel oil swelling (% by mass)	26	33	36	33	23
Initial adhesive strength (MPa)	8	16	15	15	15
Adhesive strength following soak in fuel oil (MPa)	6	14	13	13	13
Observation of transmission electron microscope photograph	X	—	—	X	—

[Effect of the Ring Opening Ratio of the Maleic Anhydride Group of an Adhesive Resin Composition]

The results of considering the effect of the ring opening ratio of the maleic anhydride group of an adhesive resin composition following modification are shown in Table 9 below.

TABLE 9

Reference Example	Example	Modified resin type	Ring opening ratio of acid anhydride group (%)	*) Tensile impact strength (KJ/m^2)	Degree of fuel oil swelling (% by mass)	Initial adhesive strength (MPa)	Adhesive strength following soak in fuel oil (MPa)
1	1	Modified resin 1	1.0	128	17	16	14
2	6	Modified resin 3	3.0	128	26	16	15
3	31	modified resin 20	18	125	18	13	11
4	32	Modified resin 21	17	126	18	13	11

*) Tensile impact strength at −40° C. of nominal regrind composition

[Evaluation Results]

Although there are no practical problems with the examples 31 and 32, for which the ring opening ratio of the maleic anhydride group of the adhesive resin composition following modification is large, the initial adhesive strength and the adhesive strength following soak in fuel oil tended to be slightly lower.

INDUSTRIAL APPLICABILITY

A characteristic of the present invention is the use of a high molecular weight graft modified polyethylene with a MFR of 0.1 to 2 g/10 minutes, and the use of an adhesive resin composition produced by combining such a modified polyethylene with an unmodified polyethylene of a specific

type, and in particular the production of a resin composition in which the MFR ratio of the modified polyethylene and the unmodified polyethylene falls within a specific range.

Furthermore, yet another characteristic of the present invention is the combining of a linear low density polyethylene and an ultra low density polyethylene in an adhesive resin composition.

Furthermore, yet another characteristic of the present invention is the control of the ring opening ratio of the acid anhydride group of an adhesive resin composition following graft modification.

This type of adhesive resin composition of the present invention has excellent moldability, displays excellent adhesion to barrier materials such as saponified products of ethylene-vinyl acetate copolymers or polyamide resins, and moreover is capable of suppressing any deterioration in physical properties when molding by-products such as burrs and unused parison are recycled and reused within the process. Furthermore, products such as laminated vessels and laminated sheets comprising such an adhesive resin composition, and having at least an adhesive layer formed from the adhesive resin composition, a barrier layer formed from a barrier material such as a saponified product of an ethylene-vinyl acetate copolymer or a polyamide resin, a principal material layer formed from a polyethylene based resin, and where necessary a regrind layer formed from recycled burrs or unused parison, display good adhesive strength between each of the layers, and offer excellent low temperature impact resistance for the regrind layer. In particular, the initial adhesive strength and the adhesive strength following soak in fuel oil are high, and the adhesion durability of sections such as pinch off sections generated during rapid deformations during molding (the adhesive strength following soak in fuel oil) is also excellent.

Furthermore, because the degree of fuel oil swelling is low, such vessels are more than capable of enduring extended use with fuel contained therein.

In addition, in a so-called internal recycling process, in which burrs and unused parison generated as by-products during blow molding are ground up and returned to the production process, the low temperature impact resistance of the layer comprising the recycled burrs can be maintained at a high level, and consequently the low temperature impact resistance of the overall vessel is excellent.

Accordingly, a composition of the present invention can be used in a wide variety of applications requiring good adhesive strength, including gasoline tanks for holding fuel oil, and vessels and sheets containing recycled burrs.

The invention claimed is:

1. An adhesive resin composition (III) comprising:

(I) 10 to 90% by mass of a modified polyethylene in which an unsaturated carboxylic acid and/or an unsaturated carboxylic acid derivative unit is grafted to a high molecular weight polyethylene with a melt flow rate (MFR: temperature 190° C., loading 2.16 kg) of 0.1 to 2.0 g/10 minutes, and a density of 0.91 to 0.96 g/cm^3, which is at least one of (a) a modified high density polyethylene with a melt flow rate of 0.1 to 2.0 g/10 minutes, and a density of 0.93 to 0.96 g/cm^3, and (c) a modified linear low density polyethylene with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.91 or greater and less than 0.93 g/cm^3, and

(II) 10 to 90% by mass of an unmodified polyethylene with a melt flow rate (MFR: temperature 190° C., loading 2.16 kg) of 0.1 to 20 g/10 minutes, and a density of 0.86 to 0.96 g/cm^3, which is at least one of (b') an unmodified high density polyethylene with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.93 to 0.96 g/cm^3, (c') an unmodified linear low density polyethylene with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.91 or greater and less than 0.93 g/cm^3, and (d') an unmodified ultra low density polyethylene with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.86 to 0.91 g/cm^3, and

wherein a ratio MFR(I)/MFR(II), where MFR(I) represents a melt flow rate (MFR: temperature 190° C., loading 2.16 kg) of said modified polyethylene (I) and MFR(II) represents a melt flow rate (MFR: temperature 190° C., loading 2.16 kg) of said unmodified polyethylene (II), is less than 1,and

wherein at least one of (c) the modified linear low density polyethylene, (c') the unmodified linear low density polyethylene, and (d') the unmodified ultra low density polyethylene is produced using a single site catalyst,

wherein said at least one of (c) a modified linear low density polyethylene, (c') an unmodified linear low density polyethylene, and (d') an unmodified ultra low density polyethylene produced using a single site catalyst is present in said composition, and

wherein a density of said adhesive resin composition (III) is 0.925 to 0.940 g/cm^3, a content of said unsaturated carboxylic acid and/or unsaturated carboxylic acid derivative unit incorporated therein is at least 0.09% by mass, and a melt flow rate (MFR: temperature 190° C., loading 2.16 kg) is from 0.1 to 2 g/10 minutes.

2. An adhesive resin composition according to claim **1**, wherein said modified polyethylene (I) is a high density polyethylene with a melt flow rate of 0.1 to 2.0 g/10 minutes and a density of 0.93 to 0.96 g/cm^3, and said unmodified polyethylene (II) is an unmodified high density polyethylene with a melt flow rate of 0.1 to 20 g/10 minutes and a density of 0.93 to 0.96 g/cm^3.

3. An adhesive resin composition according to claim **1**, wherein said unmodified linear low density polyethylene (c') and/or said unmodified ultra low density polyethylene (d') are resin compositions comprising an ethylene/α-olefin copolymer (A) which satisfy conditions (1) to (4) shown below:

(1) a density of 0.86 to 0.94 g/cm^3,

(2) a melt flow rate of 0.1 to 20 g/10 minutes,

(3) a molecular weight distribution (Mw/Mn) of 1.5 to 4.5, and

(4) a difference between T_{25}, representing a temperature at which 25% of a total content is eluted, determined from an integrated elution curve of an elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method, and T_{75}, representing a temperature at which 75% of said total content is eluted, namely $T_{75}-T_{25}$, and a density d which satisfy a relationship of an equation 1, shown below:

$$T_{75}-T_{25}\leqq -670\times d+644 \quad \text{(equation 1).}$$

4. An adhesive resin composition according to claim **3**, wherein said ethylene copolymer (A) also satisfies a relationship (5) described below:

(5) a difference between T_{25}, representing a temperature at which 25% of a total content is eluted, determined from an integrated elution curve of an elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method, and T_{75}, representing a temperature at which 75% of said

total content is eluted, namely $T_{75}-T_{25}$, and a density d which satisfy a relationship of an equation 2, shown below:

$$T_{75}-T_{25}-300\times d+285 \quad \text{(equation 2).}$$

5. An adhesive resin composition according to claim **3**, wherein said ethylene copolymer (A) is an ethylene copolymer (A1) which satisfies conditions (6) and (7) described below:

(6) a quantity X (% by mass) of an orthodichlorobenzene (ODCB) soluble fraction at 25° C., a density d, and a melt flow rate (MFR) which satisfy relationships of an equation 3 and an equation 4 shown below:

$$X<2.0 \text{ in cases in which } d-0.0081 \log MFR\geqq 0.93 \quad \text{(equation 3)}$$

$$X<9.8\times 10^3\times(0.9300-d+0.008 \log MFR)^2+2.0 \text{ in cases in which } d-0.008 \log MFR<0.93, \quad \text{(equation 4)}$$

and

(7) an elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method which has a plurality of peaks.

6. An adhesive resin composition according to claim **4**, wherein said ethylene copolymer (A) is an ethylene copolymer (A2) which also satisfies conditions (8) and (9) described below:

(8) an elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method which has only one peak, and

(9) one, or two or more melting point peaks, wherein a highest melting point Tml and a density d satisfy a relationship of an equation 5, shown below:

$$Tml\geqq 150\times d-19 \quad \text{(equation 4).}$$

7. An adhesive resin composition according to claim **6**, wherein said ethylene copolymer (A2) also satisfies a condition (10) described below:

(10) a melt tension (MT) and a melt flow rate (MFR) which satisfy an equation 6 shown below:

$$\log MT\leqq 0.572\times \log MFR+0.3 \quad \text{(equation 6).}$$

8. An adhesive resin composition according to claim **3**, wherein a halogen concentration of said ethylene copolymer (A) is no more than 10 ppm.

9. An adhesive resin composition according to claim **3**, wherein said resin composition incorporating said ethylene copolymer (A) comprises substantially no additives.

10. An adhesive resin composition according to claim **1**, wherein if aliphatic metal salts exist within said adhesive resin composition, a concentration thereof is less than 100 weight ppm.

11. An adhesive resin composition according to claim **1**, wherein said unsaturated carboxylic acid is an acid anhydride.

12. An adhesive resin composition according to claim **11**, wherein a ring opening ratio of acid anhydride groups of said adhesive resin composition following graft modification is maintained at no more than 10%.

13. An adhesive resin composition according to claim **11**, wherein said acid anhydride is maleic anhydride.

14. A multi-layer laminated structure comprising an adhesive layer formed from an adhesive resin composition according to claim **1**, and at least a principal material layer formed on an outside of said adhesive layer, and a barrier layer formed on an inside of said adhesive layer.

15. A multi-layer laminated structure according to claim **14**, wherein said principal material layer is a high density polyethylene layer and/or a regrind layer using recycled material.

16. A multi-layer laminated structure according to claim **14**, formed from a 3 type 5 layer structure comprising a principal material layer formed from a high density polyethylene layer and/or a regrind layer/an adhesive resin composition layer/a barrier layer/an adhesive resin composition layer/and a principal material layer formed from a high density polyethylene layer and/or a regrind layer.

17. A multi-layer laminated structure according to claim **14**, wherein a high density polyethylene of said principal material layer has a density of 0.93 to 0.97 g/cm^3 and a melt flow rate of 0.01 to 50 g/10minutes.

18. A multi-layer laminated structure according to claim **14**, wherein said barrier layer is at least one material selected from a group consisting of saponified products of ethylene-vinyl acetate copolymers, polyamide resins, polyester resins and vinylidene chloride resins.

19. A multi-layer laminated structure according to claim **14**, wherein an adhesion interface between said adhesive resin composition layer and/or a regrind layer, and said barrier layer is formed as an irregular surface.

20. A multi-layer laminated structure according to claim **19**, wherein viewing an interface structure of said multi-layer laminated structure with a transmission electron microscope at a magnification within a range from 20,000× to 50,000× reveals irregularities with an elevation difference of at least 100 nm.

21. A multi-layer laminated structure according to claim **19**, wherein said barrier layer is formed from a saponified product of an ethylene-vinyl acetate copolymer.

22. A vessel formed from a multi-layer laminated structure according to claim **14**.

23. A vessel according to claim **22**, which is a blow vessel selected from a group consisting of a fuel tank, a food vessel, and an industrial chemical vessel.

24. An adhesive resin composition according to claim **1**, wherein said adhesive resin composition (III) comprises:

(a) 85 to 15% by mass of a modified high density polyethylene with a melt flow rate of 0.1 to 2.0 g/10 minutes, and a density of 0.93 to 0.96 g/cm^3, and

(b') 15 to 85% by mass of an unmodified high density polyethylene with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.93 to 0.96 g/cm^3,

wherein said adhesive resin composition (III) further comprises (C") 5 to 60% by mass of a modified and/or unmodified linear low density polyethylene with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.91 or greater and less than 0.93 g/cm^3, and/or

(d") 5 to 40% by mass of a modified and/or unmodified ultra low density polyethylene with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.86 to 0.91 g/cm^3, and (a)+(b ')+(c")+(d") totals 100% by mass, and

said linear low density polyethylene (c") and/or said ultra low density polyethylene (d") are ethylene/ct-olefin copolymer which is produced using a single site catalyst.

25. An adhesive resin composition according to claim **1**, wherein said linear low density polyethylene (c) and/or (c') and/or said ultra low density polyethylene (d') have a plurality of peaks in an elution temperature vs. elution quantity curve obtained by a temperature rising elution

fractionation (TREF) method, and the highest temperature peak among the plurality of peaks is within a range from 85° C. to 100° C.

26. An adhesive resin composition according to claim **1**, wherein said linear low density polyethylene (c) and/or (c') and/or said ultra low density polyethylene (d') are ethylene/ci-olefin copolymer which is polymerized with a catalyst obtained by mixing the compounds alto a4 described below:

(a1): a compound represented by a general formula $Me^1R^1_pR^2_q(OR^3)_rX^1_{4-p-q-r}$ wherein, Me^1 represents zirconium, titanium or hafnium; R^1 and R^3 each represent a hydrocarbon group of 1 to 24 carbon atoms; R represents a 2,4-pentanedionato ligand or a derivative thereof, a benzoylmethanato ligand, or a benzoylacetonato ligand or a derivative thereof; X^1 represents a halogen atom; and p, q and r each represent integers which satisfy the ranges $0 \leqq p \leqq 4$, $0 \leqq q \leqq 4$, $0 \leqq r \leqq 4$, and $0 \leqq p+q+r \leqq 4$;

(a2): a compound represented by a general formula $Me^2R^4_{m(OR^5)_n}X^2_{z-m-n}$ wherein, Me^2 represents an element from group 1 to group 3 of the periodic table; R^4 and R^5 each represent a hydrocarbon group of 1 to 24 carbon atoms; X^2 represents a halogen atom or a hydrogen atom (although if X^2 is a hydrogen atom, then Me^2 can only be an element from group 3 of the periodic table); z represents the valency of Me^2, and m and n each represent integers which satisfy the ranges $0 \leqq m \leqq z$, $0 \leqq n \leqq z$, and moreover $0 \leqq m+n \leqq z$;

(a3): an organic cyclic compound with a conjugated double bond; and

(a4): a modified organic aluminum oxy compound incorporating a Al—O—Al linkage and/or a boron compound.

27. An adhesive resin composition according to claim **24**, wherein said linear low density polyethylene (c) andlor (c') and/or said ultra low density polyethylene (d') have a plurality of peaks in an elution temperature vs. elution quantity curve obtained by a temperature rising elution fractionation (TREF) method, and the highest temperature peak among the plurality of peaks is within a range from 85° C. to 100° C.

28. An adhesive resin composition according to claim **24**, wherein said linear low density polyethylene (c) and/or (c') and/or said ultra low density polyethylene (d') are ethylene/α-olefin copolymer which is polymerized with a catalyst obtained by mixing the compounds alto a4 described below:

(a 1): a compound represented by a general formula $Me^1R^1_pR^2_q(OR^3)_rX^1_{4-p-q-r}$ wherein, Me^1 represents zirconium, titanium or hafnium; R^1 and R^3 each represent a hydrocarbon group of 1 to 24 carbon atoms; R^2 represents a 2,4-pentanedionato ligand or a derivative thereof, a benzoylmethanato ligand, or a benzoylacetonato ligand or a derivative thereof; X^1 represents a halogen atom; and p, q and r each represent integers which satisfy the ranges $0 \leqq p \leqq 4$, $0 \leqq q \leqq 4$, $0 \leqq r \leqq 4$, and $0 \leqq p+q+r \leqq 4$;

(a2): a compound represented by a general formula $Me^2R^4_m(OR^5)_nX^2_{z-m-n}$ wherein, Me^2 represents an element from group 1 to group 3 of the periodic table; R^4 and R^5 each represent a hydrocarbon group of 1 to 24 carbon atoms; X^2 represents a halogen atom or a hydrogen atom (although if X^2 is a hydrogen atom, then Me^2 can only be an element from group 3 of the periodic table); z represents the valency of Me^2, and m and n each represent integers which satisfy the ranges $0 \leqq m \leqq z$, $0 \leqq n \leqq z$, and moreover $0 \leqq m+n \leqq z$;

(a3): an organic cyclic compound with a conjugated double bond; and

(a4): a modified organic aluminum oxy compound incorporating a Al—O—Al linkage and/or a boron compound.

29. An adhesive resin composition according to claim **1**, wherein said unmodified linear low density polyethylene (c') and/or said unmodified ultra low density polyethylene (d') are ethylene/α-olefin copolymer which is produced using a single site catalyst.

30. An adhesive resin composition (III) according to claim **1**,

wherein the modified polyethylene (I) is the modified high density polyethylene (a) with a melt flow rate of 0.1 to 2.0 g/10 minutes, and a density of 0.93 to 0.96 g/cm^3, and

wherein the unmodified polyethylene (II) is a mixture of the unmodified high density polyethylene (b') with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.93 to 0.96 g/cm^3, the unmodified linear low density polyethylene (c') with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.91 or greater and less than 0.93 g/cm^3, and the unmodified ultra low density polyethylene (d') with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.86 to 0.91 g/cm^3, and (a)+(b')+(c')+(d') totals 100% by mass.

31. An adhesive resin composition (III) according to claim **1**,

wherein the modified polyethylene (I) is the modified linear low density polyethylene (c) with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.91 or greater and less than 0.93 g/cm^3, and

wherein the unmodified polyethylene (II) is a mixture of the unmodified high density polyethylene (b') with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.93 to 0.96 g/cm^3, the unmodified linear low density polyethylene (c') with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.91 or greater and less than 0.93 g/cm^3, and the unmodified ultra low density polyethylene (d') with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.86 to 0.91 g/cm^3, and (c)+(b')+(c')+(d') totals 100% by mass.

32. An adhesive resin composition (III) according to claim **1**,

wherein the modified polyethylene (I) is a mixture of the modified high density polyethylene (a) with a melt flow rate of 0.1 to 2.0 g/10 minutes, and a density of 0.93 to 0.96 g/cm^3, and the modified linear low density polyethylene (c) with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.91 or greater and less than 0.93 g/cm^3, and

wherein the unmodified polyethylene (II) is a mixture of the unmodified high density polyethylene (b') with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.93 to 0.96 g/cm^3, the unmodified linear low density polyethylene (c') with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.91 or greater and less than 0.93 g/cm^3, and the unmodified ultra low density polyethylene (d') with a melt flow rate of 0.1 to 20 g/10 minutes, and a density of 0.86 to 0.91 g/cm^3, and (a)+(c)+(b')+(c')+(d') totals 100% by mass.

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(12) **United States Patent**
Maruyama et al.

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(54) **POLYESTER RESIN COMPOSITION, METHOD FOR PRODUCING SAME AND MOLDED BODY**

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(57) **ABSTRACT**

Provided are a resin composition which is colored little and has excellent gas barrier properties, transparency and mechanical properties, a method for producing it, and a shaped article. The composition is a polyester resin composition comprising from 2 to 30% by weight of a specific polyamide resin (A), from 69.5 to 97.99% by weight of a specific polyester resin (B) and from 0.01 to 0.5% by weight of a di- and/or tri-polycarboxylic acid compound (c), which satisfies $a \leq b$, $60 \leq a+b \leq 150$, $1 \leq c \times Cc \leq 20$, $1 \leq c \times Cc/(a \times Ca) \leq 12$ (wherein a is a concentration of the terminal amino group of the polyamide resin (A), b is a concentration of the terminal carboxyl group of the polyamide resin (A), c is a concentration of the carboxyl group in the polycarboxylic acid compound (C), Cc is a concentration of the polycarboxylic acid compound (C) in the polyester resin composition, and Ca is a concentration of the polyamide resin (A) in the polyester resin composition (g/g). The method is for producing the resin composition; and the shaped article is obtained by shaping the resin composition.

17 Claims, No Drawings

POLYESTER RESIN COMPOSITION, METHOD FOR PRODUCING SAME AND MOLDED BODY

TECHNICAL FIELD

The present invention relates to a polyester resin composition comprising a polyamide resin, a polyester resin and a polycarboxylic acid each having specific properties, in a specific ratio, and to a method for producing it; and also to a shaped article such as film, sheet and thin-wall hollow container.

BACKGROUND ART

A polyester resin that comprises an aromatic dicarboxylic acid as a principal dicarboxylic acid ingredient and an aliphatic diol as a principal diol ingredient (hereinafter this may be referred to as "aromatic polyester resin"), such as polyethylene terephthalate (PET) is characterized by having excellent mechanical properties, melt stability, solvent resistance, aroma preservability and recyclability. Accordingly, the aromatic polyester resin is widely utilized for packaging materials such as films, sheets and hollow containers. However, since the gas barrier properties thereof to oxygen, carbon dioxide and the like are not always good, the utilization thereof is limited in applications that require high gas barrier properties. For imparting gas barrier properties to an aromatic polyester resin, there are known a method of laminating it with metal foil such as aluminum, a method of coating or laminating it with any other resin having high gas barrier properties, a method of coating it with aluminum or silicon by vapor deposition. However, these methods are all problematic in that they may detract from transparency, they may require some complicated production step and they may detract from mechanical properties.

For imparting high gas barrier properties to the resin without requiring any complicated production step, there is known a method of mixing the resin with some other resin having high gas barrier properties. The resin having high gas barrier properties may be a polyamide resin such as typically nylon 6 and nylon 66; and in particular, a polyamide resin obtained through polymerization of metaxylylenediamine and adipic acid (hereinafter this may be referred to as "polyamide MXD6") has excellent gas barrier properties. On the other hand, there is known an ethylene/polyvinyl alcohol copolymer resin as another gas-barrier resin than polyamide resin. The ethylene/polyvinyl alcohol copolymer resin is poorly compatible with aromatic polyester resin, and therefore, a composition comprising the two may be cloudy, and in addition, the copolymer resin has other problems in that its crystallinity is high and therefore it detracts from the stretchability of aromatic polyester resin, and its thermal stability is poor.

On the other hand, polyamide MXD6 has high gas barrier properties, and its glass transition temperature, melting point and crystallinity are similar to those of aromatic polyester resin, especially polyethylene terephthalate, and further, the polyamide has excellent thermal stability in melting. Accordingly, its advantages are that it may be readily melt-mixed with aromatic polyester resin, it does not detract from the mechanical properties and the stretchability of aromatic polyester resin, and it may express high gas barrier properties.

However, a composition of an aromatic polyester resin and a polyamide resin such as polyamide MXD6 may give a pearly gloss depending on the dispersion condition and the concentration of the resin composition; and in particular, its glossiness may be more remarkable in thermal forming such as stretching, and its transparency may thereby lower. To that effect, the transparency of the composition of an aromatic polyester resin and a polyamide resin such as polyamide MXD6 is insufficient, and therefore the use of the resin composition in applications requiring high transparency is limited.

Patent Reference 1 proposes a composition prepared by adding a tetracarboxylic acid dianhydride to a mixture comprising a polyamide resin and a polyester resin. Patent Reference 1 has a description relating to the improvement of the mechanical properties of shaped articles used as engineering plastics, but has no description at all relating to a resin composition for films, sheets and thin-wall hollow containers having improved transparency. Patent Reference 2 proposes a compound having an epoxy group and an acid anhydride group as one type of a solubilizing agent for a composition of a thermoplastic polyester resin and a polyamide resin having a metaxylylene group in the main chain thereof. However, the compound obviously differs from the compound in the present invention.

Patent Reference 3 proposes a composition prepared by adding a tetracarboxylic acid dianhydride to a mixture comprising a polyamide resin and a polyester resin. However, the tetracarboxylic acid dianhydride reacts with the polyester resin and the polyamide resin mixed with it. Accordingly, the viscosity of the resin composition may excessively increase during mixing and shaping procedures, and the resin composition may be difficult to shape and work into films, sheets and thin-wall hollow containers. In addition, the dianhydride added may color the composition in yellow to light brown, and has another problem in that it may detract from the appearance of the shaped articles.

Patent Reference 4 proposes a composition prepared by adding a polycarboxylic acid having at least three carboxyl groups in one molecule and its anhydride to a mixture comprising a polyamide resin and a polyester resin. However, for the same reasons as in the above, the polycarboxylic acid anhydride reacts with the polyester resin and the polyamide resin mixed with it; and therefore, the viscosity of the resin composition may excessively increase during mixing and shaping procedures, and the resin composition may be difficult to shape and work into films, sheets and thin-wall hollow containers. In addition, the acid anhydride added may color the composition in yellow to light brown, and has another problem in that it may detract from the appearance of the shaped articles. Accordingly, it is desired to develop a polyester resin composition having high gas barrier properties not requiring the complicated production steps as in the above, and having excellent transparency.

[Patent Reference 1] JP-A 1-272660
[Patent Reference 2] JP-A 62-201963
[Patent Reference 3] JP-A 2000-34357
[Patent Reference 4] JP-A 2000-302952

DISCLOSURE OF THE INVENTION

Problems that the Invention is to Solve

The present invention is to provide a resin composition containing an aromatic polyester resin and a polyamide resin, which has excellent gas barrier properties, transparency and mechanical properties and is hardly colored, and to a method for producing it; and also to provide a shaped article such as a biaxially-stretched hollow container obtained by shaping the resin composition.

Means for Solving the Problems

The present inventors have assiduously studied and, as a result, have found that a resin composition comprising a polyamide resin, a polyester resin and a polycarboxylic acid each having specific properties, in a specific ratio can solve the above-mentioned problems. In addition, the inventors have further found that, when the resin composition is produced according to a specific melt-kneading method, then its coloration may be prevented and its gas barrier properties and transparency may be further improved. Further, the inventors have found that a hollow container obtained by molding the resin composition according to a specific injection-molding process into a precursor (hereinafter this may be referred to as "parison") followed by further shaping it is prevented from coloring and has further improved gas barrier properties and transparency. The invention is based on these findings.

Specifically, the invention is a polyester resin composition comprising:

from 2 to 30% by weight of a polyamide resin (A) in which at least 70 mol % of the diamine constitutive unit is derived from metaxylylenediamine and at least 70 mol % of the dicarboxylic acid constitutive unit is derived from adipic acid,

from 69.5 to 97.99% by weight of a polyester resin (B) in which at least 70 mol % of the dicarboxylic acid constitutive unit is derived from an aromatic dicarboxylic acid and at least 70 mol % of the diol constitutive unit is derived from an aliphatic diol, and

from 0.01 to 0.5% by weight of a polycarboxylic acid compound (C) comprising at least one tricarboxylic acid compound selected from a group consisting of aromatic tricarboxylic acids, alicyclic tricarboxylic acids and acid anhydrides of those tricarboxylic acids, and/or at least one dicarboxylic acid compound selected from a group consisting of aromatic dicarboxylic acids, alicyclic dicarboxylic acids and acid anhydrides of those dicarboxylic acids (provided that the total of the contents of the ingredients (A), (B) and (C) is 100% by weight).

and satisfying the following formulae (1) to (4):

$$a \leq b \quad (1)$$

$$60 \leq a+b \leq 150 \quad (2)$$

$$1 \leq c \times Cc \leq 20 \quad (3)$$

$$1 \leq c \times Cc/(a \times Ca) \leq 12 \quad (4)$$

wherein a, b, c, Cc and Ca are as follows:

a represents a concentration of the terminal amino group of the polyamide resin (A) (μequivalent/g),

b represents a concentration of the terminal carboxyl group of the polyamide resin (A) (μequivalent/g),

c represents a concentration of the carboxyl group in the polycarboxylic acid compound (C) (μequivalent/g), provided that one equivalent of acid anhydride group is calculated as 2 equivalents of carboxyl group,

Cc represents a concentration of the polycarboxylic acid compound (C) in the polyester resin composition (g/g), and Ca represents a concentration of the polyamide resin (A) in the polyester resin composition (g/g).

The invention also provides a method for producing the above-mentioned polyester resin composition comprising melt-kneading the polyamide resin (A), the polyester resin (B) and the polycarboxylic acid compound (C), or comprising a step of preparing a preliminary composition by melt-kneading the polyamide resin (A) and the polycarboxylic acid compound (C) followed by a step of melt-kneading the preliminary composition and the polyester resin (B).

The invention further relates to a shaped article obtained by shaping the polyester resin composition.

BEST MODE FOR CARRYING OUT THE INVENTION

(1) Polyester Resin Composition:

The polyester resin composition of the invention comprises at least one polyamide resin (A), at least one polyester resin (B) and at least one polycarboxylic acid compound (C) in a predetermined ratio, and satisfies specific conditions. The ingredients are described in detail hereinunder.

Polyamide Resin (A):

The polyamide resin (A) is obtained through polycondensation of a diamine and a dicarboxylic acid. In this, at least 70 mol % of the diamine constitutive unit is derived from metaxylylenediamine, and at least 70 mol % of the dicarboxylic acid constitutive unit is derived from adipic acid. The metaxylylenediamine-derived constitutive unit must account for at least 70 mol %, but preferably at least 80 mol %, more preferably at least 90 mol % (including 100 mol %). When the metaxylylenediamine-derived constitutive unit is less than 70 mol %, then the gas barrier properties may be insufficient. The adipic acid-derived constitutive unit must account for at least 70 mol %, but preferably at least 80 mol %, more preferably at least 90 mol % (including 100 mol %). When the adipic acid-derived constitutive unit is less than 70 mol %, the gas barrier properties may worsen and the crystallinity may excessively lower. As the polyamide resin (A), preferred is polymetaxylylenadipamide. The polyamide resin having the monomer composition and the constitutive unit profile mentioned above is similar to a polyester resin such as polyethylene terephthalate resin in point of the shaping processability, and is therefore advantageous as not detracting from the processability of the polyester resin composition.

Other diamines than metaxylylenediamine usable herein include paraxylylenediamine, 1,3-bis(aminomethyl)cyclohexane, 1,4-bis(aminomethyl)cyclohexane, tetramethylenediamine, hexamethylenediamine, nonamethylenediamine and 2-methyl-1,5-pentanediamine, to which, however, the invention should not be limited.

Other dicarboxylic acids than adipic acid usable herein include suberic acid, azelaic acid, sebasic acid, 1,10-decanedicarboxylic acid, terephthalic acid, isophthalic acid and 2,6-naphthalenedicarboxylic acid, to which, however, the invention should not be limited.

A small amount of a monoamine or a monocarboxylic acid may be added as a molecular weight-controlling agent in polycondensation to produce the polyamide resin (A).

Preferably, the polyamide resin (A) is produced through polycondensation in melt (hereinafter this may be referred to as "melt polycondensation"). For example, this is preferably produced according to a method that comprises heating a nylon salt of metaxylylenediamine and adipic acid according to a pressure process in the presence of water, and polymerizing it in melt with removing the added water and the condensed water. It may also be produced according to a method that comprises directly adding metaxylylenediamine to a melt of adipic acid followed by polycondensing it under normal pressure. In this case, in order that the reaction system could be kept in a uniform liquid state, metaxylylenediamine is continuously added to adipic acid to attain the polycondensation, and during this, the reaction system is preferably heated so that the reaction temperature could not be lower than the melting point of the formed oligoamide and polya-

mide. The polyamide obtained through the melt polycondensation may be further subjected to solid-phase polymerization to increase the molecular weight thereof. The thus-obtained, solid-phase polymerization polyamide may be used as the polyamide resin (A).

The polyamide resin (A) satisfies the following relational formulae (1) and (2) in point of the terminal amino acid concentration a (μequivalent/g) and the terminal carboxyl group concentration b (μequivalent/g):

$$a \leq b \quad (1)$$

$$60 \leq a+b \leq 150 \quad (2).$$

When the resin does not satisfy the formula (1), then it may be difficult to prevent the coloration of the polyester resin composition.

When the resin does not satisfy the formula (2), its reactivity with the polycarboxylic acid compound (C) and the polyester resin (B) to be mentioned below may be insufficient. In addition, a polyester resin composition in which the polyamide resin (A) is dispersed finely and which has excellent transparency and mechanical properties may be difficult to obtain. When (a+b) in formula (2) is less than 60, then sufficient reactivity could not be obtained. When (a+b) is more than 150, the reactivity with the polycarboxylic acid compound (C) may increase; however, the affinity to the polyester resin (B) may lower and, in addition, the viscosity may excessively lower and the dispersibility of the polyamide resin (A) may lower.

The concentration of the polyamide resin (A) in the polyester resin composition may be from 2 to 30% by weight relative to the total weight of the polyamide resin (A), the polyester resin (B) and the polycarboxylic acid compound (C), preferably from 2 to 20% by weight, more preferably from 2 to 15% by weight, even more preferably from 2 to 10% by weight, still more preferably from 2 to 5% by weight. When the concentration is less than 2% by weight, good gas barrier properties could not be obtained. When it is more than 30% by weight, then gas barrier properties may be good, but the transparency of the shaped packaging article may lower and the mechanical properties thereof may also worsen, and the commercial value thereof may be low.

The relative viscosity of the polyamide resin (A) (1 g of the polyamide resin is dissolved in 100 ml of 96% sulfuric acid, and its viscosity is measured at 25° C.) is preferably from 1.83 to 4.20, more preferably from 2.02 to 4.20, even more preferably from 2.30 to 4.20. When the relative viscosity falls within the above range, then the flowability of the resin melt in shaping the polyester resin composition of the invention into films, sheets, hollow containers or the like is good, therefore reducing die swelling and melt unevenness and bettering the shapability of the resin composition. In addition, the transparency of the shaped article may be improved, and the transparency reduction owing to whitening in high-humidity atmosphere may be inhibited.

The polyamide resin (A) having a relative viscosity of at least 2.30 may be readily obtained by continuing the reaction until the relative viscosity could reach a predetermined value in melt polymerization. However, when the reaction of melt polymerization is continued until the level of a predetermined relative viscosity, the time (reaction time) of keeping the melt condition may be long and the polyamide molecules may be thereby damaged or abnormal reaction (three-dimensional polymerization) such as non-linear molecular growth may occur, thereby forming gel or fish eyes. A shaped article of a polyester resin composition comprising the polyamide resin with much gel and fish eyes may have fish eyes and its producibility may be thereby lowered.

The polyamide resin (A) having a relative viscosity of at least 2.30 may be favorably produced according to a method that comprises preparing a polyamide resin having a relative viscosity of at most 2.28 through melt polymerization with inhibiting the generation of fish eyes owing to the increase in the thermal history in melt polymerization, then subjecting the melt polymerization polyamide resin to solid-phase polymerization thereby to make the resin have a relative viscosity of at least 2.30. The solid-phase polymerization may be attained by heating the pellets or powder of the melt polymerization polyamide resin having a relative viscosity of from 1.83 to 2.28 under reduced pressure or in an inert gas atmosphere at a temperature falling within a range of from 120° C. to lower than the melting point of the polyamide resin. After the solid-phase polymerization, the relative viscosity of the solid-phase polymerization polyamide resin is preferably from 2.30 to 4.20.

The polyester resin composition comprising the polyamide resin (A) having an increased relative viscosity of at least 2.30 through solid-phase polymerization may have extremely good shapability into shaped articles such as films, sheets, hollow containers. In addition, since the solid-phase polymerization polyamide resin has few fish eyes, the fish eyes to be caused by the polyamide rein in the shaped articles could be reduced and the producibility may be noticeably improved.

The moisture content of the polyamide resin (A) is preferably at most 0.15% by weight, more preferably at most 0.1% by weight, even more preferably from 0.01 to 0.09% by weight. In this case, the polyamide resin may be dried so as to have the moisture content falling within the above range. When the moisture content is at most 0.15% by weight, the hydrolysis of the polyester resin (B), which may be caused by water from the polyamide resin (A) in melt mixing with the polyester resin (B), may be inhibited. The polyamide resin may be dried in any conventional known method. For example, herein employable is a method of keeping the vent hole under reduced pressure in melt extrusion of the polyamide resin through a vented extruder, to thereby remove water from the polyamide resin; or a method of feeding the polyamide resin into a tumbler (rotary vacuum tank) and heating and drying it under reduced pressure at a temperature lower than the melting point of the polyamide resin. However, the invention should not be limited to these.

Preferably, the polyamide resin (A) has a melt viscosity of from 100 to 2000 Pa·s at 270° C. and at a shear rate of 100/sec. The polyamide (A) having a suitable viscosity within the above range has good dispersibility in polyester resin and therefore may more improve the transparency and the mechanical properties of the shaped article.

The polyamide resin (A) may contain a phosphorus compound for increasing the process stability in melt shaping or for preventing the coloration of the polyamide resin. As the phosphorus compound, favorably used is a phosphorus compound containing an alkali metal or an alkaline earth metal. For example, it includes sodium, magnesium or calcium phosphates, hypophosphites and phosphites; and those containing an alkali metal or alkaline earth metal hypophosphite are favorably used as especially excellent in the effect of preventing polyamide coloration. The concentration of the phosphorus compound in the polyamide resin (A) is preferably at most 200 ppm as the phosphorus atom, more preferably at most 160 ppm, even more preferably at most 100 ppm. When the phosphorus atom concentration in the polyamide resin (A) is at most 200 ppm and when the resin is mixed in melt with a polyester resin produced by the use of an anti-

mony catalyst, the mixture may be prevented from being blackened owing to the reduction of the antimony catalyst slightly remaining in the polyester resin. In addition to the above-mentioned phosphorus compound, the polyamide resin (A) may further contain lubricant, mat agent, heat-resistant stabilizer, UV absorbent, nucleating agent, plasticizer, flame retardant, antistatic agent, coloration inhibitor, gellation inhibitor and other additives within the range thereof not detracting from the effect of the invention.

Polyester Resin (B):

The polyester resin (B) may be obtained through polymerization of a dicarboxylic acid and a diol. In this, at least 70 mol % of the dicarboxylic acid constitutive unit is derived from an aromatic dicarboxylic acid, and at least 70 mol % of the diol constitutive unit is derived from an aliphatic diol. The proportion of the constitutive unit derived from an aromatic dicarboxylic acid is at least 70 mol %, preferably at least 80 mol %, more preferably at least 90 mol % (including 100 mol %). The proportion of the constitutive unit derived from an aliphatic diol is at least 70 mol %, preferably at least 80 mol %, more preferably at least 90 mol % (including 100 mol %). When the constitutive unit derived from an aromatic dicarboxylic acid is less than 70 mol %, then the heat resistance of the shaped article may lower. When the constitutive unit derived from an aliphatic diol is less than 70 mol %, the shapability may worsen.

The aromatic dicarboxylic acid includes terephthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid; naphthalenedicarboxylic acids such as 1,5-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid; 4,4'-biphenyldicarboxylic acid, 3,4'-biphenyldicarboxylic acid, and their ester-forming derivatives. Within a range not detracting the object of the invention, an aliphatic dicarboxylic acid such as adipic acid or sebasic acid, or a monocarboxylic acid such as benzoic acid, propionic acid or butyric acid may be used.

The aliphatic diol includes ethylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,4-cyclohexanedimethanol, 1,6-hexanediol, and their ester-forming derivatives. Within a range not detracting from the object of the invention, monoalcohols such as butyl alcohol, hexyl alcohol, octyl alcohol; and polyalcohols such as trimethylolpropane, glycerin, pentaerythritol may also be used.

For producing the polyester resin (B), employable is any known method of direct esterification or interesterification. The polycondensation catalyst to be used in producing the polyester resin (B) includes known antimony compounds such as antimony trioxide, antimony pentoxide; germanium compounds such as germanium oxide; titanium compounds such as titanium acetate; aluminium compounds such as aluminium chloride, to which, however, the invention should not be limited.

Preferred examples of the polyester resin (B) are polyethylene terephthalate resin, polyethylene terephthalate/isophthalate copolymer resin, polyethylene/1,4-cyclohexanedimethylene terephthalate copolymer resin, polyethylene 2,6-naphthalenedicarboxylate resin, polyethylene 2,6-naphthalenedicarboxylate/terephthalate copolymer resin, polyethylene terephthalate/4,4'-biphenyldicarboxylate resin, poly-1,3-propylene terephthalate resin, polybutylene terephthalate resin, polybutylene 2,6-naphthalenedicarboxylate resin. More preferred examples of the polyester resin (B) are polyethylene terephthalate resin, polyethylene terephthalate/isophthalate copolymer resin, polyethylene/1,4-cyclohexanedimethylene terephthalate copolymer resin, polybutylene terephthalate resin, and polyethylene 2,6-naphthalenedicarboxylate resin.

The moisture content of the polyester resin (B) (before melt kneading) is preferably at most 200 ppm, more preferably from 80 to 200 ppm, even more preferably from 80 to 100 ppm. A polyester resin may be dried to have the above-mentioned moisture content. Having a moisture content falling within the range, the polyester resin does not hydrolyze in the melt-kneading process, and its molecular weight may be prevented from being extremely lowered and the resin may be prevented from yellowing.

Not specifically defined, the intrinsic viscosity of the polyester resin (B) (measured in a mixed solvent of phenol/1,1,2,2-tetrachloroethane=60/40 by weight at 25° C.) is preferably from 0.5 to 1.5 dl/g, more preferably from 0.6 to 1.3 dl/g. Having the intrinsic viscosity falling within the range, the polyester resin may have a sufficiently high molecular weight, and may form a shaped articles having mechanical properties needed in various applications.

The concentration of the polyester resin (B) in the polyester resin composition is from 69.5 to 97.99% by weight relative to the total weight of the polyamide resin (A), the polyester resin (B) and the polycarboxylic acid compound (C), preferably from 79.6 to 97.99% by weight, more preferably from 84.8 to 97.99% by weight, even more preferably from 90 to 97.99% by weight, still more preferably from 95 to 97.99% by weight. When the concentration oversteps the range of from 69.5 to 97.99% by weight, then excellent gas barrier properties, transparency and mechanical properties could not be obtained.

Polycarboxylic Acid Compound (C):

The polycarboxylic acid compound (C) comprises at least one tricarboxylic acid compound selected from aromatic tricarboxylic acids alicyclic tricarboxylic acids and their acid anhydrides, and/or at least one dicarboxylic acid compound selected from aromatic dicarboxylic acids, alicyclic dicarboxylic acids and their acid anhydrides. The acid anhydrides are intramolecular acid anhydrides.

The tricarboxylic acid compound includes trimellitic acid, trimellitic acid anhydride, hemimellitic acid and its anhydride, trimesic acid, 1,2,4-cyclohexanetricarboxylic acid and its anhydride, 1,2,3-cyclohexanetricarboxylic acid and its anhydride, 1,3,5-cyclohexanetricarboxylic acid, naphthalenetricarboxylic acid (including position isomers) and its anhydride, anthracenetricarboxylic acid (including position isomers) and its anhydride, biphenyltricarboxylic acid (including position isomers) and its anhydride, benzophenonetricarboxylic acid (including position isomers) and its anhydride. Preferred are trimellitic acid anhydride, trimellitic acid, 1,2,4-cyclohexanetricarboxylic acid and its anhydride; and more preferred are trimellitic acid anhydride and trimellitic acid; and even more preferred is trimellitic acid anhydride.

The dicarboxylic acid compound includes, for example, phthalic acid, phthalic acid anhydride, isophthalic acid, terephthalic acid, naphthalenedicarboxylic acid (including position isomers) and its anhydride, anthracenedicarboxylic acid (including position isomers) and its anhydride, biphenyldicarboxylic acid (including position isomers) and its anhydride, benzophenonedicarboxylic acid (including position isomers) and its anhydride, cyclohexanedicarboxylic acid (including position isomers) and its anhydride. Preferred are phthalic acid and phthalic acid anhydride; and more preferred is phthalic acid anhydride.

The polycarboxylic acid compound (C) satisfies the following relational formulae (3) and (4):

$$1 \le c \times Cc \le 20 \quad (3)$$

$$1 \le c \times Cc/(a \times Ca) \le 12 \quad (4)$$

wherein a, c, Cc and Ca are as follows:

a represents the terminal amino group concentration of the polyamide resin (A) (μequivalent/g),

c represents the concentration of the carboxyl group in the polycarboxylic acid compound (C) (μequivalent/g), provided that one equivalent of acid anhydride group is calculated as 2 equivalents of carboxyl group,

Cc represents the concentration of the polycarboxylic acid (C) in the polyester resin composition (g/g), and

Ca represents the concentration of the polyamide resin (A) in the polyester resin composition (g/g).

c×Cc in formula (3) is preferably from 1 to 15, more preferably from 1 to 10. Falling within the range, the reactivity of the acid with the polyamide resin (A) and with the polyester resin (B) is good, and in addition, since the acid does not cause any excess viscosity increase, the transparency of the obtained shaped article may increase.

c×Cc/(a×Ca) in formula (4) is preferably from 1 to 10, more preferably from 1 to 8. Falling within the range, the reactivity of the acid with the polyamide resin (A) is good, and since the acid does not cause any excess viscosity increase, the transparency of the obtained shaped article may increase.

The concentration of the polycarboxylic acid compound (C) in the polyester resin composition may be from 0.01 to 0.5% by weight relative to the total weight of the polyamide resin (A), the polyester resin (B) and the polycarboxylic acid compound (C), preferably from 0.01 to 0.3% by weight, more preferably from 0.01 to 0.2% by weight, even more preferably from 0.01 to 0.1% by weight, still more preferably from 0.01 to 0.07% by weight. When the concentration falls outside the range of from 0.01 to 0.5% by weight, excellent gas barrier properties, transparency and mechanical properties could not be obtained.

The polycarboxylic acid compound (C) may be a mixture of a dicarboxylic acid compound and a tricarboxylic acid compound, but the individual carboxylic acid compounds may be used singly. In case where the two carboxylic acid compounds are combined and used, their blend ratio may be determined in any desired manner.

Preferably, (melt viscosity of polyamide resin (A))/(melt viscosity of polyester resin (B)) is from 0.3 to 1.2. The melt viscosity is measured at an apparent shear rate of 100/sec and at 270° C. When the ratio falls within the range, then shaped articles having more excellent transparency can be obtained.

In a preferred embodiment of the invention, the polyester resin composition comprises from 2 to 15% by weight of the polyamide resin (A), from 84.8 to 97.99% by weight of the polyester resin (B) and from 0.01 to 0.2% by weight of a tricarboxylic acid compound (the total of % by weight is 100% by weight). The content of the polyamide resin (A) is preferably from 2 to 10% by weight, more preferably from 2 to 5% by weight. The content of the polyester resin (B) is preferably from 90 to 97.99% by weight, more preferably from to 97.99% by weight. The content of the tricarboxylic acid compound is preferably from 0.01 to 0.1% by weight, more preferably from 0.01) 0.07% by weight.

In another preferred embodiment of the invention, the polyester resin composition comprises from 2 to 30% by weight of the polyamide resin (A), from 69.5 to 97.99% by weight of the polyester resin (B), from 0.01 to 0.5% by weight of a dicarboxylic acid compound and from 0 to 0.3% by weight of a tricarboxylic acid compound (in which the total of the dicarboxylic acid compound and the tricarboxylic acid compound is from 0.01 to 0.5% by weight). The total of % by weight of those ingredients is 100% by weight. The content of the polyamide resin (A) is preferably from 2 to 20% by weight, more preferably from 2 to 15% by weight. The content of the polyester resin (B) is preferably from 79.6 to 97.99% by weight, more preferably from 84.7 to 97.99% by weight. The content of the dicarboxylic acid compound is preferably from 0.01 to 0.3% by weight, more preferably from 0.01 to 0.2% by weight. The content of the tricarboxylic acid compound is preferably from 0 to 0.2% by weight, more preferably from 0 to 0.1% by weight. The total amount of the dicarboxylic acid compound and the tricarboxylic acid compound (the total amount of the polycarboxylic acid compound (C)) is preferably from 0.01 to 0.3% by weight, more preferably from 0.01 to 0.2% by weight. The polycarboxylic acid compound (C) is most preferably trimellitic acid anhydride, and apart from it, the compound is preferably phthalic acid anhydride, trimellitic acid, phthalic acid and other polycarboxylic acid compounds in that order.

(2) Production of Polyester Resin Composition:

The polyester resin composition of the invention may be produced according to the following production methods.

The order of melt-mixing the polyamide resin (A), the polyester resin (B) and the polycarboxylic acid compound (C) is not specifically defined. For melt-kneading them, for example, employable are the following methods.

(i) A polyamide resin (A), a polyester resin (B) and a polycarboxylic acid compound (C) are melt-kneaded all at a time.

(ii) A polyamide resin (A), a polyester resin (B) and a polycarboxylic acid compound (C) are melt-kneaded all at a time to prepare a preliminary composition (master batch), and then the preliminary composition is further melt-kneaded with a polyester resin (B) (polyester resin (B) for dilution) to give a polyester resin composition (master batch method).

(iii) A polyester resin (B) and a polycarboxylic acid compound (C) are previously melt-kneaded, and then this is melt-kneaded with a polyamide resin (A).

(iv) A polyamide resin (A) and a polycarboxylic acid compound (C) are melt-kneaded to prepare a preliminary composition, and then the preliminary composition is further melt-kneaded with a polyester resin (B).

The methods (ii) and (iv) are preferred, and the method (ii) is more preferred. In the master batch method (ii), it is desirable that a preliminary composition comprising from 10 to 40% by weight of a polyamide resin (A), from 59.00 to 89.95% by weight of a polyester resin (B) and from 0.05 to 1% by weight of a polycarboxylic acid compound (C) (the total % by weight of the ingredients (A), (B) and (C) is 100% by weight) is prepared, and then a mixture comprising, for example, from 5 to 50% by weight of the preliminary composition and from 50 to 95% by weight of a polyester resin (B) for dilution is melt-kneaded thereby to produce the polyester resin composition of the invention having the defined composition ratio.

The polyester resin (B) for dilution may be the same as or different from the polyester resin (B) in the preliminary composition. In case where the two differ, it is desirable that the preliminary composition (master batch) and the polyester resin for dilution satisfy the following formulae (5) and (6):

$$100 \leq x \leq 250 \quad (5)$$

$$0.1 \leq x/y \leq 0.5 \quad (6)$$

(wherein x represents the melt viscosity of the preliminary composition measured at 270° C. and at a shear rate of 100/sec (Pa·s); and y represents the melt viscosity of the polyester resin (B) for dilution measured under the same condition (Pa·s)).

The preliminary composition (master batch) satisfying the formula (5) has a suitable viscosity, and therefore, when it is melt-kneaded with a polyester resin (B) for dilution, the polyamide resin (A) could disperse more finely and the transparency and the mechanical properties of the obtained shaped articles may be bettered. Using the polyester resin (B) for dilution that satisfies the formula (6) betters the fine dispersion in melt kneading and, in addition, it reduces resin deterioration or coloration owing to overheating.

For melt-kneading the ingredients, for example, herein employable is a method of dry-blending the polyamide resin (A), the polyester resin (B) and the polycarboxylic acid (C) in a tumbler, a V-shaped blender or a Henschel mixer; a method of further melt-kneading the dry-blended mixture once or more in a single-screw extruder, a twin-screw extruder or a kneader; or a method of optionally processing the melted mixture for solid-phase polymerization in high vacuum or in an inert gas atmosphere. Of those, preferred is the method of melt-kneading the ingredients by the use of a twin-screw extruder.

In case where the polyamide resin (A), the polyester resin (B) and the polycarboxylic acid compound (C) are melt-kneaded in a twin-screw extruder, the melt-kneading temperature is preferably from 200 to 300° C., more preferably from 220 to 290° C. When a combination of counter-screw elements and kneading discs is used in the screw zone in the extruder, then the ingredients may be efficiently dispersed.

Preferably, the polyamide resin (A) is finely dispersed in the polyester resin composition of the invention since shaped articles having good transparency can be obtained. For example, in shaped articles before secondary processing for stretching and thermoforming, such as parisons, unstretched sheets or unstretched films, the mean dispersed particle size of the polyamide resin (A) is preferably from 0.05 to 0.35 μm, more preferably from 0.05 to 0.20.

The polyester resin composition of the invention may contain any other resin, as well as additives such as pigment, dye, carbon black, lubricant, mat agent, heat-resistant stabilizer, weather-resistant stabilizer, UV absorbent, fluorescent whitener, nucleating agent, plasticizer, flame retardant, antistatic agent, alkali compound for preventing gellation of polyamide resin, etc., within a range not detracting from the effect of the invention. Preferably, the amount of the other resin is at most 20% by weight relative to the total amount of the polyester resin composition; and the total of the additives is preferably at most 5% by weight. The other resin includes, for example, polyester resins such as polyethylene naphthalate resin, polybutylene terephthalate resin; polyamide resins such as nylon-6, nylon-6IT, nylon-66; and polyolefins such as polyethylene, polypropylene.

To the polyester resin composition of the invention, it is possible to add a recycled polyester and/or a recycled polyamide resin selected from recycled matter of polyethylene terephthalate products, recycled matter of modified polyethylene terephthalate products containing a small amount of isophthalic acid units, recycled matter of polyamide products, wastes and substandard products in shaped article production, within a range not intrinsically changing the properties of the composition.

(3) Shaped Article:

The shaped article of the invention is obtained by shaping the above-mentioned polyester resin composition. As so described hereinabove, the polyester resin composition of the invention can be used as a material for shaped articles that require high transparency. The shaped articles include, for example, unstretched or low-ratio stretched single-layered sheets and multilayered sheets obtained in a T-die process or a coextrusion process; films obtained by stretching the sheets; low-ratio deep-drawn containers obtained from the sheets; and unstretched or stretched thin-wall hollow containers having a body wall thickness of from 0.1 to 2 mm obtained according to direct blow molding or stretch blow molding. These shaped articles can be used as packaging materials for foods, drinks, chemicals, electronic parts, etc.

For the shaped article of the polyester resin composition of the invention, the dispersed particle size of the polyamide resin in the parison prepared by injection-molding under a specific condition may be reduced. A biaxially-stretched hollow container obtained by processing the parison in a mode of biaxial-stretch blow molding may have good transparency.

The biaxially-stretched hollow container may be obtained by injecting the above-mentioned polyester resin composition into the mold cavity of an injection-molding machine via the mold hot runner from the injection cylinder, thereby preparing a parison, and further processing the parison in a mode of biaxial-stretch blow molding.

The injection-molding condition for obtaining the parison, which is a precursor of a biaxially-stretched hollow container, preferably satisfies the following (a) to (e):

(a) resin temperature: 260 to 290° C.,

(b) screw back pressure: 2.5 to 5.0 MPa,

(c) screw speed: 80 to 250 rpm,

(d) injection speed: 80 to 180 cc/sec,

(e) mold temperature: 10 to 25° C.

The above-mentioned injection condition includes the data indicated by the instruments of the injection-molding device. In case where instruments are not installed in the injection-molding device, the data may be derived from those set in a process of injection molding with an injection-molding machine of the same type.

In the parison formed under the above condition, the dispersed particle size of the polyamide resin (A) in the polyester resin composition is small, and the dispersed particle size thereof fluctuates little, and accordingly, the transparency of the biaxially-stretched hollow container from it may be good. The mean diameter of the dispersed particles of the polyamide resin (A) in the polyester resin composition in an area of the body part of the parison is preferably from 0.05 to 0.20 μm. Also preferably, at least 60% of the dispersed particles have a particle size falling within a range of ±0.05 μm of the mean particle size.

The dispersed particle size of the polyamide resin (A) in the polyester resin composition is principally influenced by the condition in metering and injection. Specifically, when the screw back pressure is high and the screw speed is rapid in metering, then the kneading of the melted resin is promoted and the dispersed particle size is reduced. When the injection speed is high, then shear force is given to the melted resin and the dispersed particle size is reduced. However, when only the injection speed is increased, then only the mean value of the dispersed particle size may be reduced, and the polyamide resin may contain particles having a relatively large dispersed particle size. On the other hand, in metering, when only the back pressure is increased and the screw speed is elevated, then a uniform dispersed particle size may be obtained, but as compared with that in a case where the injection speed is increased, the mean dispersed particle size in this case may be large. Accordingly, by suitably combining the screw speed, the back pressure and the injection speed, the dispersed particle size of the polyamide resin (A) may be uniformly reduced.

The injection-molding condition (a) to (e) may be suitably selected in accordance with the melt viscosity of the resin to be shaped.

When the resin temperature is from 260 to 290° C., it is possible to prevent a non-melted matter from precipitating in the parison and to prevent the transparency of the parison from lowering. In addition, it is also possible to prevent the parison from yellowing and to prevent the appearance of the biaxially-stretched hollow container from worsening. When the mold temperature is from 10° C. to 25° C., then it is possible to prevent the appearance of the container from worsening owing to the crystallization thereof. In addition, the transparency of the biaxially-stretched hollow container may be bettered.

For forming a biaxially-stretched hollow container from the obtained parison, usable is an ordinary blow molding machine.

For example, using a biaxial-stretch blow molding machine, a parison is heated with an IR heater for 15 seconds to 4 minutes so as to make it have a surface temperature of from 90 to 120° C., then this is blow-molded with a stretch rod and under a pressure of from 0.5 to 3.5 MPa, thereby giving the intended container.

The shaped article of the invention has excellent gas barrier properties, transparency and mechanical properties. For example, a 500-ml bottle may have an oxygen transmission rate at 23° C. and 60% RH of at most 0.035 cc/bottle·day·0.21 atm, a haze value of at most 8% (thickness, 300 μm), and an yellow index (YI) of at most 12.

The shaped articles such as film, sheet and biaxially-stretched hollow container of the invention have excellent gas barrier properties and have excellent color tone and transparency. For example, they may be used for storing various substances such as liquid drinks; seasonings; pasty foods; liquid foods; processed rice products, high-water content foods; low-water content foods; solid or liquid chemicals; liquid and pasty medicines; cosmetics, skin care products, etc.

EXAMPLES

The invention is described concretely with reference to the following Examples and Comparative Examples; however, the invention should not be limited to the following Examples. The evaluation methods employed in Examples and Comparative Examples are as Follows:

(1) Concentration of Terminal Amino Group of Polyamide [NH_2] (μequivalent/g):

From 0.3 to 0.5 g of polyamide is accurately measured, and dissolved in 30 cc of a solution of phenol/ethanol=4/1 (by volume) by stirring at 20 to 30° C. After completely dissolved, this is titrated for neutralization with N/100 aqueous hydrochloric acid solution with stirring, thereby determining the intended concentration.

(2) Concentration of Terminal Carboxyl Group of Polyamide [COOH] (μequivalent/g):

From 0.3 to 0.5 g of polyamide is accurately measured, and dissolved in 30 cc of benzyl alcohol by stirring in a nitrogen flow at 160 to 180° C. After completely dissolved, this is cooled in a nitrogen flow to 80° C. or lower, and with stirring, 10 cc of methanol is added thereto, and this is titrated for neutralization with N/100 aqueous sodium hydroxide solution, thereby determining the intended concentration.

(3) Relative Viscosity:

One g of polyamide is accurately measured, and dissolved in 100 ml of 96% sulfuric acid with stirring at 20 to 30° C. After completely dissolved, 5 cc of the solution is immediately taken in a Canon-Fenske viscometer, and left in a thermostat at 25° C. for 10 minutes, and then its dropping speed (t) is measured. On the other hand, the dropping speed of 96% sulfuric acid itself (t_0) is also measured. From t and t_0, the relative viscosity is derived through calculation according to the following formula:

$$\text{Relative Viscosity} = t/t_0.$$

(4) Moisture Content (% by Weight):

Using Mitsubishi Chemical's Karl Fischer micromoisture meter (CA-05 Model) and vaporizer (VA-05 model), the amount of water in a sample is measured under a vaporization condition at the melting temperature for 30 minutes, and the moisture content of the sample is determined.

(5) Yellow Index YI:

Determined according to JIS K-7105. For the measurement, Nippon Denshoku Kogyo's haze meter (Model COH-300A) is used.

(6) Haze (Thickness: 300 μm (Bottle), 20 μm (Film):

Determined according to JIS K-7105. For the measurement, Nippon Denshoku Kogyo's haze meter (Model COH-300A) is used.

(7) Oxygen Transmission Rate and Oxygen Transmission Coefficient

Determined according to ASTM D3985. Using Modern Controls' device (Model OX-TRAN2/21), a bottle is analyzed at a temperature of 23° C. under the condition that the relative humidity inside the bottle is 100% and the relative humidity in the ambient atmosphere is 50%. The oxygen transmission coefficient of a film (cc·mm/m^2·day·atm) is measured at a temperature of 23° C. and a relative humidity of 60%.

(8) Melt Viscosity:

Using Toyo Seiki's Capillograph D-1, a sample is analyzed under the condition that the die is 1 mmϕ×10 mm length, the apparent shear speed is 100/sec, the test temperature is 270° C., and the water content of the sample is at most 300 ppm.

(9) Determination of Dispersed Particle Size (Transmittance Electronic Microscopy):

Using an ultramicrotome (Boeckeler Instruments' CR-X Power Tome XL), an ultra-thin test sample having a thickness of about 0.1 μm is cut out of the body of a bottle (parison) vertically in the machine direction (MD) thereof. The polyamide is stained with ruthenium chloride vapor, and then the sample is observed on a copper mesh with an electronic microscope.

Condition in Observation:

Electronic microscope: Hitachi's surface-observing electronic microscope S4800
Accelerating voltage: 30 kV
Current: 10 mA
Power of microscope: 25,000
Observation mode: TEM

From the shadowed density of the stained polyamide, the dispersed condition of polyamide is analyzed and the mean dispersed particle size thereof is determined.

(10) Intrinsic Viscosity of Polyester Resin:

0.5 g of polyester resin is accurately measured, and dissolved in 100 ml of a mixed solvent of phenol/1,1,2,2-tetrachloroethane (=6/4 by weight) with stirring at 120° C. to prepare a solution having a concentration of 0.5 g/dl. After cooled, the thick solution is diluted with the same solvent to prepare a ½ diluted solution (concentration, 0.25 g/dl) and a ⅕ diluted solution (concentration, 0.1 g/dl). Next, using an automatic viscometer (Shibayama Scientific Instruments' SS-600-L1), the dropping time of each solution at 25° C., tc, and the dropping time of the solvent, to, are measured. The ratio of the specific viscosity ηsp to the concentration C, ηsp/C is extrapolated relative to the concentration 0 (zero), thereby determining the intrinsic viscosity of the resin.

Specific viscosity ηsp=(tc/to)−1,
Intrinsic viscosity $[\eta]=\lim_{c\to 0}(\eta sp/C)$.

Synthesis Example 1

15.00 kg of adipic acid, as accurately measured, was put into a jacketed polymerization tank equipped with a stirrer, a partial condenser, a condenser, a thermometer, a dropping funnel and a nitrogen gas-introducing duct, then fully purged with nitrogen, and heated in a small amount of a nitrogen flow, and at 170° C., adipic acid was dissolved to be a uniform flow state. With stirring, 13.91 kg of metaxylylenediamine was dropwise added to it, taking 160 minutes. During this, the inner temperature was continuously elevated up to 245° C., and water evaporating out simultaneously with the dropwise addition of metaxylylenediamine was removed out of the system via the partial condenser and the condenser. After the dropwise addition of metaxylylenediamine, the inner temperature was continuously elevated up to 255° C., and the reaction was continued for 15 minutes. Next, the inner pressure of the reaction system was continuously reduced to 600 mmHg, taking 10 minutes, and then the reaction was continued for 40 minutes. During this, the reaction temperature was continuously elevated up to 260° C. After the reaction, a pressure of 0.2 MPa was given to the polymerization tank with nitrogen gas, and the polymer (polymetaxylylenadipamide) was taken out through the nozzle at the bottom of the polymerization tank as strands, these were cooled with water and cut to give 25 kg of pellets. The relative viscosity of the obtained pellets was 2.13, and the moisture content thereof was 0.62%. This was fed into a tumbler (rotary vacuum tank) with a jacket heated with a heat carrier, at room temperature. The heat carrier was kept at 170° C. until polymetaxylylenadipamide crystallization at a pellet temperature rising over 120° C. Next, the heat carrier temperature was lowered to 225° C., and the temperature of the pellets in the tank was elevated up to 200° C. During this, when the pellet temperature rose over 140° C., the pressure inside the tank was reduced to be a reduced pressure state (0.5 to 10 Torr), and in that condition, this was kept heated at 200° C. for 20 minutes to attain solid-phase polymerization. Next, nitrogen was again introduced to keep normal pressure, and cooling the tank was started. When the pellet temperature reached 90° C. or lower, the pellets were taken out of the tank, thereby obtaining a polyamide 1 (hereinafter referred to as PA1). PA1 was analyzed, and as a result, the terminal amino group concentration was 21 μeq/g; the terminal carboxyl group concentration was 62 μeq/g; the relative viscosity was 2.64; and the moisture content was 0.03%.

Synthesis Examples 2 to 7

PA2 to PA7 having the properties shown in Table 1 were produced in the same manner as in Synthesis Example 1, for which, however, the amount of metaxylylenediamine used in the reaction, the reaction time and the temperature were changed. In Synthesis Example 2 (PA2) and Synthesis Example 7 (PA7), the melt polymerization polyamide was dried in a tumbler at 140° C. in place of processing it for solid-phase polymerization. Table 1 shows the relative viscosity of dried products.

[Table 1]

TABLE 1

Polyamide	Melt Polymerization, Solid-Phase Polymerization	Relative Viscosity of Melt Polymerization Polymer	$[NH_2]$ (μequivalent/g)	[COOH] (μequivalent/g)	Relative Viscosity of Dried Polymer or Solid-Phase Polymerization Polymer	Moisture content (wt. %)
PA1	solid-phase polymerization	2.13	21	62	2.64	0.03
PA2	melt polymerization	2.08	39	84	2.12	0.04
PA3	solid-phase polymerization	2.16	34	47	2.66	0.03
PA4	solid-phase polymerization	2.07	64	17	2.65	0.03
PA5	solid-phase polymerization	2.12	10	75	2.62	0.03
PA6	solid-phase polymerization	2.20	24	28	3.82	0.02
PA7	melt polymerization	1.80	37	132	1.83	0.04

Example 1

The following polyester resin, polyamide resin and polycarboxylic acid compound were mixed in a tumbler, and melt-kneaded in a twin-screw extruder (screw diameter: 20 mmϕ, L/D: 25), at an extrusion temperature of 280° C. and an extrusion speed of 15 kg/hr, while the pressure in the extruder cylinder was reduced with a vacuum pump, and the extruded strands were pelletized into pellets.

Polyester resin: 79.8 parts by weight of dry pellets of polyethylene terephthalate resin (Invista's grade 1101E, intrinsic viscosity 0.80 dl/g),

Polyamide resin: 20 parts by weight of PA1,

Polycarboxylic acid compound: 0.2 parts by weight of trimellitic acid anhydride (hereinafter referred to as TMAn).

The obtained pellets were dried in vacuum at 150° C. for 6 hours, thereby giving a resin composition (preliminary master batch). 10 parts by weight of the preliminary master batch pellets and 90 parts by weight of polyethylene terephthalate resin (Invista's grade: 1101E) were dry-blended in a tumbler, and the mixture was injection-molded in an injection-molding device (Meiki Seisakusho's M200PDM-MJ) to give a parison having a length of 96 mm, a wall thickness of 4.0 mm, an outer diameter of 22.5 mm and a weight of 27 g. The injection molding condition was as follows: The resin temperature was 280° C., the mold temperature was 15° C., and the screw speed was 150 rpm.

The obtained parison was processed for biaxial-stretch blow molding, using a blow-molding device (Frontier's EFB1000ET), to give a biaxially-stretched blow bottle having a height of 223 mm, a body diameter of 65 mm, a capacity of 500 mL and a mean thickness of about 300 μm. The obtained bottle was colored little, and had good transparency and gas barrier properties. The results are shown in Table 2.

Example 2

A parison and a stretch blow bottle were produced under the same condition as in Example 1, for which, however, the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 25/75 parts by weight. The obtained bottle was colored little, and had good transparency and gas barrier properties. The results are shown in Table 2.

Example 3

A parison and a stretch blow bottle were produced under the same condition as in Example 1, for which, however, the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 35/65 parts by weight. The obtained bottle was colored little, and had good transparency and gas barrier properties. The results are shown in Table 2.

Comparative Example 1

A parison and a stretch blow bottle were produced under the same condition as in Example 1, for which, however, the polycarboxylic acid compound was not used. The results are shown in Table 4.

Example 4

A parison and a stretch blow bottle were produced under the same condition as in Example 1, for which, however, PA2 (dried product) was used as the polyamide resin, a preliminary master batch comprising polyamide resin(PA2)/polyethylene terephthalate/polycarboxylic acid compound=20/79.74/0.24 (by weight) was prepared, and the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 25/75 parts by weight. The results are shown in Table 2.

Example 5

A parison and a stretch blow bottle were produced under the same condition as in Example 2, for which, however, a preliminary master batch comprising polyamide resin/polyethylene terephthalate/polycarboxylic acid compound=20/79.88/0.12 (by weight) was used. The results are shown in Table 3.

Example 6

A parison and a stretch blow bottle were produced under the same condition as in Example 2, for which, however, PA3 was used as the polyamide resin and a preliminary master batch comprising polyamide resin(PA3)/polyethylene terephthalate/polycarboxylic acid compound=20/79.6/0.4 (by weight) was used. The results are shown in Table 3.

Comparative Example 2

A parison and a stretch blow bottle were produced under the same condition as in Example 2, for which, however, PA4 was used as the polyamide resin. The results are shown in Table 4.

Comparative Example 3

A parison and a stretch blow bottle were produced under the same condition as in Example 6, for which, however, PA3 was used as the polyamide resin and a preliminary master batch comprising polyamide resin (PA3)/polyethylene terephthalate/polycarboxylic acid compound=20/78.8/1.2 (by weight) was used. The obtained bottle was colored and looked dark yellow, and its transparency was low. The results are shown in Table 4.

Comparative Example 4

A parison and a stretch blow bottle were produced under the same condition as in Example 2, for which, however, PA5 was used as the polyamide resin and a preliminary master batch comprising polyamide resin (PA5)/polyethylene terephthalate/polycarboxylic acid compound=20/79.72/0.28 (by weight) was used. The transparency of the obtained bottle was low. The results are shown in Table 4.

Comparative Example 5

A parison and a stretch blow bottle were produced under the same condition as in Example 2, for which, however, PA6 was used as the polyamide resin. The results are shown in Table 4.

Comparative Example 6

A parison and a stretch blow bottle were produced under the same condition as in Example 2, for which, however, PA7 (dried product) was used as the polyamide resin. The obtained bottle was colored and looked dark yellow, and its transparency was low. The results are shown in Table 5.

Comparative Example 7

A parison and a stretch blow bottle were produced under the same condition as in Example 1, for which, however, the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 5/95 (by weight). The obtained bottle had poor gas barrier properties. The results are shown in Table 5.

Comparative Example 8

A parison and a stretch blow bottle were produced under the same condition as in Example 1, for which, however, a preliminary master batch comprising polyamide resin (PA1)/polyethylene terephthalate/polycarboxylic acid compound=20/79.82/0.18 (by weight) was prepared and the preliminary master batch was directly molded as it was. The obtained bottle was colored and looked dark yellow, and its transparency was low. The results are shown in Table 5.

Example 7

A parison and a stretch blow bottle were produced under the same condition as in Example 2, for which, however, trimellitic acid (hereinafter referred to as TMA) was used as the polycarboxylic acid compound. The results are shown in Table 3.

Example 8

A parison and a stretch blow bottle were produced under the same condition as in Example 2, for which, however, 1,2,4-cyclohexanetricarboxylic acid anhydride (hereinafter referred to as CHTAn) was used as the polycarboxylic acid compound. The results are shown in Table 3.

Comparative Example 9

A parison and a stretch blow bottle were produced under the same condition as in Example 2, for which, however, pyromellitic acid anhydride (hereinafter referred to as PMDA) was used as the polycarboxylic acid compound. The obtained bottle was colored and looked dark yellow. The results are shown in Table 5.

[Table 2]

TABLE 2

	Example			
	1	2	3	4
Polyester resin composition (wt. %)				
polyamide resin	2.00	5.00	7.00	5.00
polyester resin	97.98	94.95	92.93	94.94
polycarboxylic acid compound				
TMAn	0.02	0.05	0.07	0.06
TMA	—	—	—	—
CHTAn	—	—	—	—
PMDA	—	—	—	—
Polyamide resin	PA1	PA1	PA1	PA2
terminal amino group concentration a (μeq/g)	21	21	21	39
terminal carboxyl group concentration b (μeq/g)	62	62	62	84
formula (2) a + b (μeq/g)	83	83	83	123
Polycarboxylic acid compound				
carboxyl group concentration c (μeq/g)	10400	10400	10400	10400
formula (3) c × Cc (μeq/g)	2.0	5.2	7.2	6.2
formula (4) (c × Cc)/(a × Ca) (μeq/g)	4.9	4.9	4.9	3.2
Relative viscosity of polyamide resin	2.64	2.64	2.64	2.12
Melt viscosity ratio (polyamide resin/polyester resin)	1.0	1.0	1.0	0.7
Test results				
polyamide mean dispersed particle size in parison body (μm)	0.19	0.18	0.20	0.20
haze of bottle body (%)	3.2	5.5	6.2	5.7
YI of bottle body	6.2	8.7	10.8	8.9
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.030	0.020	0.017	0.020

[Table 3]

TABLE 3

	Example			
	5	6	7	8
Polyester resin composition (wt. %)				
polyamide resin	5.00	5.00	5.00	5.00
polyester resin	94.97	94.90	94.95	94.95
polycarboxylic acid compound				
TMAn	0.03	0.10	—	—
TMA	—	—	0.05	—
CHTAn	—	—	—	0.05
PMDA	—	—	—	—
Polyamide resin	PA1	PA3	PA1	PA1
terminal amino group concentration a (μeq/g)	21	34	21	21
terminal carboxyl group concentration b (μeq/g)	62	47	62	62
formula (2) a + b (μeq/g)	83	81	83	83
Polycarboxylic acid compound				
carboxyl group concentration c (μeq/g)	10400	10400	14300	10100
formula (3) c × Cc (μeq/g)	3.2	10.4	7.1	5.1
formula (4) (c × Cc)/(a × Ca) (μeq/g)	3.1	6.0	6.8	4.8
Relative viscosity of polyamide resin	2.64	2.66	2.64	2.64
Melt viscosity ratio (polyamide resin/polyester resin)	1.0	1.0	1.0	1.0
Test results				
polyamide mean dispersed particle size in parison body (μm)	0.21	0.22	0.21	0.34
haze of bottle body (%)	5.7	7.2	5.8	7.5
YI of bottle body	9.3	9.8	9.0	9.8
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.021	0.020	0.020	0.020

[Table 4]

TABLE 4

	Comparative Example				
	1	2	3	4	5
Polyester resin composition (wt. %)					
polyamide resin	5.00	5.00	5.00	5.00	5.00
polyester resin	95.00	94.95	94.70	94.93	94.95
polycarboxylic acid compound					
TMAn	—	0.05	0.30	0.07	0.05
TMA	—	—	—	—	—
CHTAn	—	—	—	—	—
PMDA	—	—	—	—	—
Polyamide resin	PA1	PA4	PA3	PA5	PA6
terminal amino group concentration a (μeq/g)	21	64	34	10	24
terminal carboxyl group concentration b (μeq/g)	62	17	47	75	28
formula (2) a + b (μeq/g)	83	81	81	85	52
Polycarboxylic acid compound					
carboxyl group concentration c (μeq/g)	—	10400	10400	10400	10400
formula (3) c × Cc (μeq/g)	—	5.2	31.2	7.3	5.2
formula (4) (c × Cc)/(a × Ca) (μeq/g)	—	1.6	9.8	14.6	4.3
Relative viscosity of polyamide resin	2.64	2.65	2.66	2.62	3.82
Melt viscosity ratio (polyamide resin/polyester resin)	1.0	1.0	1.0	0.9	3.3
Test results					
polyamide mean dispersed particle size in parison body (μm)	0.44	0.24	0.44	0.39	0.36
haze of bottle body (%)	16.3	7.7	14.0	14.2	16.5
YI of bottle body	13.2	16.9	13.3	11.4	12.9
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.020	0.021	0.020	0.021	0.022

30

[Table 5]

TABLE 5

	Comparative Example			
	6	7	8	9
Polyester resin composition (wt. %)				
polyamide resin	5.00	1.00	20.00	5.00
polyester resin	94.95	98.99	79.82	94.95
polycarboxylic acid compound				
TMAn	0.05	0.01	0.18	—
TMA	—	—	—	—
CHTAn	—	—	—	—
PMDA	—	—	—	0.05
Polyamide resin	PA7	PA1	PA1	PA1
terminal amino group concentration a (μeq/g)	37	21	21	21
terminal carboxyl group concentration b (μeq/g)	132	62	62	62
formula (2) a + b (μeq/g)	169	83	83	83
Polycarboxylic acid compound				
carboxyl group concentration c (μeq/g)	10400	10400	10400	9200
formula (3) c × Cc (μeq/g)	5.2	1.0	18.8	4.6
formula (4) (c × Cc)/(a × Ca) (μeq/g)	2.8	4.9	4.5	4.4
Relative viscosity of polyamide resin	1.83	2.64	2.64	2.64
Melt viscosity ratio (polyamide resin/polyester resin)	0.1	1.0	1.0	1.0
Test results				
polyamide mean dispersed particle size in parison body (μm)	0.42	0.19	0.25	0.22
haze of bottle body (%)	15.3	2.5	19.4	8.2
YI of bottle body	14.2	4.8	22.7	14.7
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.023	0.038	0.008	0.022

Example 9

The following polyester resin, polyamide resin and polycarboxylic acid compound were mixed in a tumbler, and melt-kneaded in a twin-screw extruder (screw diameter: 20 mmϕ, L/D: 25), at an extrusion temperature of 280° C. and an extrusion speed of 15 kg/hr, while the pressure in the extruder cylinder was reduced with a vacuum pump, and the extruded strands were pelletized into pellets.

Polyester resin: 79.8 parts by weight of dry pellets of polyethylene terephthalate resin (Invista's grade 1101E, intrinsic viscosity 0.80 dl/g),

Polyamide resin: 20 parts by weight of PA1,

Polycarboxylic acid compound: 0.2 parts by weight of phthalic anhydride (hereinafter referred to as PAn).

The obtained pellets were dried in vacuum at 150° C. for 6 hours, thereby giving a resin composition (preliminary master batch). 10 parts by weight of the preliminary master batch pellets and 90 parts by weight of polyethylene terephthalate resin (Invista's grade: 1101E) were dry-blended in a tumbler, and the mixture was injection-molded in an injection-molding device (Meiki Seisakusho's M200PDM-MJ) to give a parison having a length of 96 mm, a wall thickness of 4.0 mm, an outer diameter of 22.5 mm and a weight of 27 g. The injection molding condition was as follows: The resin temperature was 280° C., the mold temperature was 15° C., and the screw speed was 150 rpm.

The obtained parison was processed for biaxial-stretch blow molding, using a blow-molding device (Frontier's EFB1000ET), to give a biaxially-stretched blow bottle having a height of 223 mm, a body diameter of 65 mm, a capacity of 500 mL and a mean thickness of about 300 μm. The obtained bottle was colored little, and had good transparency and gas barrier properties. The results are shown in Table 6.

Example 10

A parison and a stretch blow bottle were produced under the same condition as in Example 9, for which, however, the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 25/75 parts by weight. The obtained bottle was colored little, and had good transparency and gas barrier properties. The results are shown in Table 6.

Example 11

A parison and a stretch blow bottle were produced under the same condition as in Example 9, for which, however, the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 35/65 parts by weight. The obtained bottle was colored little, and had good transparency and gas barrier properties. The results are shown in Table 6.

Comparative Example 10

A parison and a stretch blow bottle were produced under the same condition as in Example 9, for which, however, the polycarboxylic acid compound was not used. The results are shown in Table 8.

Example 12

A parison and a stretch blow bottle were produced under the same condition as in Example 9, for which, however, PA2 (dried product) was used as the polyamide resin, a preliminary master batch comprising polyamide resin(PA2)/polyethylene terephthalate/polycarboxylic acid compound (PAn)=20/79.74/0.24 (by weight) was prepared, and the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 25/75 parts by weight. The results are shown in Table 6.

Example 13

A parison and a stretch blow bottle were produced under the same condition as in Example 10, for which, however, PA3 was used as the polyamide resin and a preliminary master batch comprising polyamide resin(PA3)/polyethylene terephthalate/polycarboxylic acid compound (PAn)=20/79.6/0.4 (by weight) was used. The results are shown in Table 7.

Comparative Example 11

A parison and a stretch blow bottle were produced under the same condition as in Example 10, for which, however, PA4 was used as the polyamide resin (A). The obtained bottle was colored and looked dark yellow. The results are shown in Table 8.

Comparative Example 12

A parison and a stretch blow bottle were produced under the same condition as in Example 10, for which, however, PA3 was used as the polyamide resin and a preliminary master batch comprising polyamide resin (PA3)/polyethylene terephthalate/polycarboxylic acid compound (PAn)=20/78.6/1.4 (by weight) was used. The obtained bottle was colored and looked dark yellow, and its transparency was low. The results are shown in Table 8.

Comparative Example 13

A parison and a stretch blow bottle were produced under the same condition as in Example 10, for which, however, PA5 was used as the polyamide resin and a preliminary master batch comprising polyamide resin (PA5)/polyethylene terephthalate/polycarboxylic acid compound (PAn)=20/79.6/0.4 (by weight) was used. The transparency of the obtained bottle was low. The results are shown in Table 8.

Comparative Example 14

A parison and a stretch blow bottle were produced under the same condition as in Example 10, for which, however, PA6 was used as the polyamide resin. The transparency of the obtained bottle was low. The results are shown in Table 8.

Comparative Example 15

A parison and a stretch blow bottle were produced under the same condition as in Example 10, for which, however, PA7 (dried product) was used as the polyamide resin (A). The obtained bottle was colored and looked dark yellow, and its transparency was low. The results are shown in Table 9.

Comparative Example 16

A parison and a stretch blow bottle were produced under the same condition as in Example 9, for which, however, the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 5/95 (by weight). The obtained bottle had poor gas barrier properties. The results are shown in Table 9.

Comparative Example 17

A parison and a stretch blow bottle were produced under the same condition as in Example 9, for which, however, a preliminary master batch comprising polyamide resin (PA1)/polyethylene terephthalate/polycarboxylic acid compound (PAn)=35/64.65/0.35 (by weight) was prepared and the preliminary master batch was directly molded as it was. The obtained bottle was colored and looked dark yellow, and its transparency was low. The results are shown in Table 9.

Example 14

A parison and a stretch blow bottle were produced under the same condition as in Example 10, for which, however, PAn and trimellitic acid anhydride (hereinafter referred to as TMAn) were used as the polycarboxylic acid compound, and a preliminary master batch comprising polyamide resin (PA1)/polyethylene terephthalate/PAn/TMAn=20/79.76/0.12/0.12 (by weight) was used. The results are shown in Table 7.

Example 15

A parison and a stretch blow bottle were produced under the same condition as in Example 10, for which, however, the composition of the preliminary master batch was changed to polyamide resin (PA1)/polyethylene terephthalate/PAn/TMAn=20/79.80/0.16/0.04 (by weight) The results are shown in Table 7.

Comparative Example 18

A parison and a stretch blow bottle were produced under the same condition as in Example 10, for which, however, pyromellitic acid anhydride (hereinafter referred to as PMDA) was used as the polycarboxylic acid compound. The obtained bottle was colored and looked dark yellow. The results are shown in Table 9.

[Table 6]

TABLE 6

	Example			
	9	10	11	12
Polyester resin composition (wt. %)				
polyamide resin	2.00	5.00	7.00	5.00
polyester resin	97.98	94.95	92.93	94.94
polycarboxylic acid compound				
PAn	0.02	0.05	0.07	0.06
TMAn	—	—	—	—
PMDA	—	—	—	—
Polyamide resin	PA1	PA1	PA1	PA2
terminal amino group concentration a (μeq/g)	21	21	21	39
terminal carboxyl group concentration b (μeq/g)	62	62	62	84
formula (2) a + b (μeq/g)	83	83	83	123
Polycarboxylic acid compound				
carboxyl group concentration c (μeq/g)	6760	6760	6760	6760
formula (3) c × Cc (μeq/g)	1.4	3.4	4.7	4.1
formula (4) (c × Cc)/(a × Ca) (μeq/g)	3.2	3.2	3.2	2.1
Relative viscosity of polyamide resin	2.64	2.64	2.64	2.12
Melt viscosity ratio (polyamide resin/polyester resin)	1.0	1.0	1.0	0.7
Test results				
polyamide mean dispersed particle size in parison body (μm)	0.21	0.20	0.21	0.19
haze of bottle body (%)	3.6	6.0	6.6	6.2
YI of bottle body	5.1	7.4	9.8	8.1
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.031	0.022	0.017	0.020

[Table 7]

TABLE 7

	Example		
	13	14	15
Polyester resin composition (wt. %)			
polyamide resin	5.00	5.00	5.00
polyester resin	94.90	94.94	94.95
Polycarboxylic acid compound			
Pan	0.10	0.03	0.04
TMAn	—	0.03	0.01
PMDA	—	—	—
Polyamide resin	PA3	PA1	PA1
terminal amino group concentration a (μeq/g)	34	21	21
terminal carboxyl group concentration b (μeq/g)	47	62	62
formula (2) a + b (μeq/g)	81	83	83
Polycarboxylic acid compound			
carboxyl group concentration c (μeq/g)	6760	8580	7490
formula (3) c × Cc (μeq/g)	6.8	5.2	3.7
formula (4) (c × Cc)/(a × Ca) (μeq/g)	4.0	4.9	3.6
Relative viscosity of polyamide resin	2.66	2.64	2.64
Melt viscosity ratio (polyamide resin/polyester resin)	1.0	1.0	1.0
Test results			
polyamide mean dispersed particle size in parison body (μm)	0.21	0.19	0.21
haze of bottle body (%)	7.7	5.7	5.8
YI of bottle body	9.0	8.1	7.7
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.020	0.020	0.020

[Table 8]

TABLE 8

	Comparative Example				
	10	11	12	13	14
Polyester resin composition (wt. %)					
polyamide resin	5.00	5.00	5.00	5.00	5.00
polyester resin	95.00	94.95	94.65	94.90	94.95
polycarboxylic acid compound					
PAn	—	0.05	0.35	0.10	0.05
TMAn	—	—	—	—	—
PMDA	—	—	—	—	—
Polyamide resin	PA1	PA4	PA3	PA5	PA6
terminal amino group concentration a (μeq/g)	21	64	34	10	24
terminal carboxyl group concentration b (μeq/g)	62	17	47	75	28
formula (2) a + b (μeq/g)	83	81	81	85	52
Polycarboxylic acid compound					
carboxyl group concentration c (μeq/g)	—	6760	6760	6760	6760
formula (3) c × Cc (μeq/g)	—	3.4	23.6	6.8	3.4
formula (4) (c × Cc)/(a × Ca) (μeq/g)	—	1.1	13.9	13.5	2.8
Relative viscosity of polyamide resin	2.64	2.65	2.66	2.62	3.82
Melt viscosity ratio (polyamide resin/polyester resin)	1.0	1.0	1.0	0.9	3.3
Test results					
polyamide mean dispersed particle size in parison body (μm)	0.44	0.26	0.42	0.36	0.39
haze of bottle body (%)	16.3	8.4	14.2	13.3	16.2
YI of bottle body	13.2	14.7	12.3	10.5	11.9
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.020	0.020	0.021	0.020	0.021

[Table 9]

TABLE 9

	Comparative Example			
	15	16	17	18
Polyester resin composition (wt. %)				
polyamide resin	5.00	1.00	35.00	5.00
polyester resin	94.95	98.99	64.65	94.95
polycarboxylic acid compound				
PAn	0.05	0.01	0.35	—
TMAn	—	—	—	—
PMDA	—	—	—	0.05
Polyamide resin	PA7	PA1	PA1	PA1
terminal amino group concentration a (μeq/g)	37	21	21	21
terminal carboxyl group concentration b (μeq/g)	132	62	62	62
formula (2) a + b (μeq/g)	169	83	83	83
Polycarboxylic acid compound				
carboxyl group concentration c (μeq/g)	6760	6760	6760	9200
formula (3) c × Cc (μeq/g)	3.4	0.7	23.6	4.6
formula (4) (c × Cc)/(a × Ca) (μeq/g)	1.8	3.2	3.2	4.4
Relative viscosity of polyamide resin	1.83	2.64	2.64	2.64
Melt viscosity ratio (polyamide resin/polyester resin)	0.1	1.0	1.0	1.0
Test results				
polyamide mean dispersed particle size in parison body (μm)	0.40	0.22	0.26	0.22
haze of bottle body (%)	14.7	3.0	22.4	8.2
YI of bottle body	13.3	4.5	18.9	14.7
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.021	0.040	0.007	0.022

Example 16

The preliminary master batch obtained in Example 9 was melt-kneaded and formed into a film according to a T-die method, in which the cylinder temperature was from 270 to 290° C., the T-die temperature was 280° C., the screw speed was 100 rpm, the cooling roll temperature was 70° C., thereby producing an unstretched sheet having a width of 120 mm and a thickness of about 0.3 mm. Next, using a tenter-type biaxial stretcher by Toyo Seiki, the unstretched sheet was preheated at 90 to 110° C. for 30 seconds and then biaxially-stretched in the machine direction and in the cross direction both at a draw ratio of 3.5 times, at a linear stretching speed of 60%/sec, thereby giving a stretched film having a thickness of 20 μm.

Thus obtained, the unstretched sheet had a haze of 3.5% and YI of 2.2, and the stretched film had a haze of 3.8% and YI of 2.8 and its oxygen transmission coefficient was 0.26 cc·mm/m^2·day/atm (23° C., 60% RH).

Comparative Example 19

The preliminary master batch (PA1/polyethylene terephthalate=20/80, by weight) obtained in Comparative Example 10 was melt-kneaded and formed into a film according to a T-die method, in which the cylinder temperature was from 270 to 290° C., the T-die temperature was 280° C., the screw speed was 100 rpm, the cooling roll temperature was 70° C., thereby producing an unstretched sheet having a width of 120 mm and a thickness of about 0.3 mm. Next, using a tenter-type biaxial stretcher by Toyo Seiki, the unstretched sheet was preheated at 90 to 110° C. for 30 seconds and then biaxially-stretched in the machine direction and in the cross direction both at a draw ratio of 3.5 times, at a linear stretching speed of 60%/sec, thereby giving a stretched film having a thickness of 20 μm. Thus obtained, the unstretched sheet had a haze of 12.5% and YI of 5.6, and the stretched film had a haze of 13.9% and YI of 5.9 and its oxygen transmission coefficient was 0.28 cc·mm/m^2·day/atm (23° C., 60% RH).

Example 17

The process of Example 1 was repeated to produce a biaxially-stretched blow bottle. The results are shown in Table 10.

Example 18

A parison and a stretch blow bottle were produced under the same condition as in Example 1, for which, however, the ratio of the preliminary master batch prepared in Example 17 to polyethylene terephthalate resin was changed to 25/75 parts by weight. The obtained bottle was colored little, and had good transparency and gas barrier properties. The results are shown in Table 10.

Example 19

A parison and a stretch blow bottle were produced under the same condition as in Example 1, for which, however, the ratio of the preliminary master batch prepared in Example 17 to polyethylene terephthalate resin was changed to 35/65 parts by weight. The obtained bottle was colored little, and had good transparency and gas barrier properties. The results are shown in Table 10.

Example 20

A parison and a stretch blow bottle were produced under the same condition as in Example 17, for which, however, a preliminary master batch comprising 99% by weight of PA1 and 1.0% by weight of a polycarboxylic acid compound (C), TMAn was prepared and the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 5/95% by weight. The obtained bottle was colored little, and had good transparency and gas barrier properties. The results are shown in Table 10.

Example 21

A parison and a stretch blow bottle were produced under the same condition as in Example 17, for which, however, a preliminary master batch comprising polyamide resin(PA1)/polyethylene terephthalate/polycarboxylic acid compound=35/64.65/0.35% by weight was prepared, and the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 14.29/85.71% by weight. The obtained bottle was colored little, and had good transparency and gas barrier properties. The results are shown in Table 10.

Comparative Example 20

A parison and a stretch blow bottle were produced under the same condition as in Example 17, for which, however, a polycarboxylic acid compound was not used. The results are shown in Table 12.

Reference Example 1

A parison and a stretch blow bottle were produced under the same condition as in Example 17, for which, however, a preliminary master batch comprising polyamide resin (PA1)/polyethylene terephthalate=20/80% by weight was prepared and the ratio of preliminary master batch/polyethylene terephthalate resin/polycarboxylic acid (TMAn) was 25/74.95/0.05% by weight. The results are shown in Table 12.

Reference Example 2

A parison and a stretch blow bottle were produced under the same condition as in Example 17, for which, however, a master batch process was not used, and a resin composition prepared by dry-blending the ingredients in a composition ratio of polyamide resin (PA1)/polyethylene terephthalate/polycarboxylic acid (TMAn)=5/94.95/0.05% by weight and melting them all at a time was used. The results are shown in Table 12.

Reference Example 3

A parison and a stretch blow bottle were produced under the same condition as in Example 17, for which, however, a preliminary master batch comprising polyethylene terephthalate/polycarboxylic acid compound (TMAn)=99.75/0.25% by weight was prepared and the ratio of preliminary master batch/polyamide resin (PA1)/polyethylene terephthalate was 20/5/75% by weight. The results are shown in Table 12.

Example 22

A parison and a stretch blow bottle were produced under the same condition as in Example 17, for which, however, PA2 (dried product) was used as the polyamide resin (A), a preliminary master batch comprising polyamide resin (PA2)/polyethylene terephthalate/polycarboxylic acid compound=20/79.74/0.24% by weight was prepared, and the ratio of preliminary master batch to the polyethylene terephthalate resin was 25/75% by weight. The results are shown in Table 11.

Example 23

A parison and a stretch blow bottle were produced under the same condition as in Example 18, for which, however, a preliminary master batch comprising polyamide resin/polyethylene terephthalate/polycarboxylic acid compound=20/79.88/0.12% by weight was used. The results are shown in Table 11.

Example 24

A parison and a stretch blow bottle were produced under the same condition as in Example 18, for which, however, PA3 was used as the polyamide resin, and a preliminary master batch comprising polyamide resin (PA3)/polyethylene terephthalate/polycarboxylic acid compound=20/79.6/0.4 (by weight) was used. The results are shown in Table 11.

Comparative Example 21

A parison and a stretch blow bottle were produced under the same condition as in Example 18, for which, however, PA4 was used as the polyamide resin. The obtained bottle was colored and looked dark yellow. The results are shown in Table 12.

Comparative Example 22

A parison and a stretch blow bottle were produced under the same condition as in Example 18, for which, however, PA6 was used as the polyamide resin. The results are shown in Table 12.

Comparative Example 23

A parison and a stretch blow bottle were produced under the same condition as in Example 18, for which, however, PA7 (dried product) was used as the polyamide resin. The obtained bottle was colored and looked dark yellow, and its transparency was low. The results are shown in Table 13.

Reference Example 4

A parison and a stretch blow bottle were produced under the same condition as in Example 17, for which, however, the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 5/95 (by weight). The obtained bottle had poor gas barrier properties. The results are shown in Table 13.

Comparative Example 24

A parison and a stretch blow bottle were produced under the same condition as in Example 17, for which, however, a preliminary master batch comprising polyamide resin (PA1)/polyethylene terephthalate/polycarboxylic acid compound=35/64.65/0.35% by weight was prepared and the preliminary master batch was directly molded as it was. The obtained bottle was colored and looked dark yellow, and its transparency was low. The results are shown in Table 13.

Example 25

A parison and a stretch blow bottle were produced under the same condition as in Example 18, for which, however, trimellitic acid (hereinafter referred to as TMA) was used as the polycarboxylic acid compound. The results are shown in Table 11.

Example 26

A parison and a stretch blow bottle were produced under the same condition as in Example 18, for which, however, phthalic anhydride (hereinafter referred to as PAn) was used as the polycarboxylic acid compound (C). The results are shown in Table 11.

Reference Example 5

A parison and a stretch blow bottle were produced under the same condition as in Example 18, for which, however, pyromellitic acid anhydride (hereinafter referred to as PMDA) was used as the polycarboxylic acid compound. The obtained bottle was colored and looked dark yellow. The results are shown in Table 13.

Reference Example 6

A parison and a stretch blow bottle were produced under the same condition as in Example 17, for which, however, a preliminary master batch comprising polyamide resin (PA1)/polyethylene terephthalate/polycarboxylic acid compound=50/49.5/0.5% by weight was prepared, and the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 10/90% by weight. The obtained bottle has poor transparency. The results are shown in Table 13.

Reference Example 7

A parison and a stretch blow bottle were produced under the same condition as in Example 17, for which, however, a preliminary master batch comprising polyamide resin (PA1)/polyethylene terephthalate/polycarboxylic acid compound=80/19.2/0.8% by weight was prepared, and the ratio of the preliminary master batch to the polyethylene terephthalate resin was changed to 6.25/93.75% by weight. The obtained bottle has poor transparency. The results are shown in Table 13.

TABLE 10

	Example				
	17	18	19	20	21
Polyester resin composition (wt. %)					
polyamide resin	2.00	5.00	7.00	4.95	5.00
polyester resin	97.98	94.95	92.93	95.00	94.95
polycarboxylic acid compound					
TMAn	0.02	0.05	0.07	0.05	0.05
TMA	—	—	—	—	—
PAn	—	—	—	—	—
PMDA	—	—	—	—	—
Production method for polyester resin composition	MB*	MB	MB	MB	MB

TABLE 10-continued

	Example				
	17	18	19	20	21
Master batch composition (wt. %)					
polyamide resin	20.00	20.00	20.00	99.00	35.00
polyester resin	79.80	79.80	79.80	—	64.65
polycarboxylic acid compound	0.20	0.20	0.20	1.00	0.35
Polyamide resin	PA1	PA1	PA1	PA1	PA1
terminal amino group concentration a (μeq/g)	21	21	21	21	21
terminal carboxyl group concentration b (μeq/g)	62	62	62	62	62
formula (2) a + b (μeq/g)	83	83	83	83	83
Relative viscosity of polyamide resin	2.64	2.64	2.64	2.64	2.64
Intrinsic viscosity of polyester resin	0.80	0.80	0.80	0.80	0.80
Melt viscosity ratio (polyamide resin/polyester resin)	1.0	1.0	1.0	1.0	1.0
Test results					
polyamide mean dispersed particle size in parison body (μm)	0.19	0.18	0.20	0.20	0.21
haze of bottle body (%)	3.2	5.5	6.2	6.3	6.5
YI of bottle body	6.2	8.7	10.8	9.2	9.5
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.030	0.020	0.017	0.021	0.020

MB*: master batch system.

TABLE 11

	Example				
	22	23	24	25	26
Polyester resin composition (wt. %)					
polyamide resin	5.00	5.00	5.00	5.00	5.00
polyester resin	94.94	94.97	94.90	94.95	94.95
polycarboxylic acid compound					
TMAn	0.06	0.03	0.10	—	—
TMA	—	—	—	0.05	—
PAn	—	—	—	—	0.05
PMDA	—	—	—	—	—
Production method for polyester resin composition	MB*	MB	MB	MB	MB
Master batch composition (wt. %)					
polyamide resin	20.00	20.00	20.00	20.00	20.00
polyester resin	79.76	79.88	79.60	79.80	79.80
polycarboxylic acid compound	0.24	0.12	0.40	0.20	0.20
Polyamide resin	PA2	PA1	PA3	PA1	PA1
terminal amino group concentration a (μeq/g)	39	21	34	21	21
terminal carboxyl group concentration b (μeq/g)	84	62	47	62	62
formula (2) a + b (μeq/g)	123	83	81	83	83
Relative viscosity of polyamide resin	2.12	2.64	2.66	2.64	2.64
Intrinsic viscosity of polyester resin	0.80	0.80	0.80	0.80	0.80
Melt viscosity ratio (polyamide resin/polyester resin)	0.7	1.0	1.0	1.0	1.0
Test results					
polyamide mean dispersed particle size in parison body (μm)	0.20	0.21	0.22	0.21	0.20
haze of bottle body (%)	5.7	5.7	7.2	5.8	6.0
YI of bottle body	8.9	9.3	9.8	9.0	7.4
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.020	0.021	0.020	0.020	0.022

MB*: master batch system.

TABLE 12

	Comparative Example 20	Reference Example 1	Reference Example 2
Polyester resin composition (wt. %)			
polyamide resin	5.00	5.00	5.00
polyester resin	95.00	94.95	94.95
polycarboxylic acid compound			
TMAn	—	0.05	0.05
TMA	—	—	—

TABLE 12-continued

PAn	—	—	—
PMDA	—	—	—
Production method for polyester resin composition	MB*	MB	DB*
Master batch composition (wt. %)			
polyamide resin	20.00	20.00	—
polyester resin	80.00	80.00	—
polycarboxylic acid compound	—	—	—
Polyamide resin	PA1	PA1	PA1
terminal amino group concentration a (μeq/g)	21	21	21
terminal carboxyl group concentration b (μeq/g)	62	62	62
formula (2) a + b (μeq/g)	83	83	83
Relative viscosity of polyamide resin	2.64	2.64	2.64
Intrinsic viscosity of polyester resin	0.80	0.80	0.80
Melt viscosity ratio (polyamide resin/polyester resin)	1.0	1.0	1.0
Test results			
polyamide mean dispersed particle size in parison body (μm)	0.44	0.41	0.40
haze of bottle body (%)	16.3	13.5	13.4
YI of bottle body	13.2	14.2	13.9
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.020	0.020	0.020

	Reference	Comparative Example	
	Example 3	21	22
Polyester resin composition (wt. %)			
polyamide resin	5.00	5.00	5.00
polyester resin	94.95	94.95	94.95
polycarboxylic acid compound			
TMAn	0.05	0.05	0.05
TMA	—	—	—
PAn	—	—	—
PMDA	—	—	—
Production method for polyester resin composition	MB	MB	MB
Master batch composition (wt. %)			
polyamide resin	—	20.00	20.00
polyester resin	99.75	79.80	79.80
polycarboxylic acid compound	0.25	0.20	0.20
Polyamide resin	PA1	PA4	PA6
terminal amino group concentration a (μeq/g)	21	64	24
terminal carboxyl group concentration b (μeq/g)	62	17	28
formula (2) a + b (μeq/g)	83	81	52
Relative viscosity of polyamide resin	2.64	2.65	3.82
Intrinsic viscosity of polyester resin	0.80	0.80	0.80
Melt viscosity ratio (polyamide resin/polyester resin)	1.0	1.0	3.3
Test results			
polyamide mean dispersed particle size in parison body (μm)	0.49	0.24	0.36
haze of bottle body (%)	14.5	7.7	16.5
YI of bottle body	13.5	16.9	12.9
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.020	0.021	0.022

MB*: master batch system.

DB*: direct batch system.

TABLE 13

	Comparative Example 23	Reference Example 4	Comparative Example 24
Polyester resin composition (wt. %)			
polyamide resin	5.00	1.00	35.00
polyester resin	94.95	98.99	64.65
polycarboxylic acid compound			
TMAn	0.05	0.01	0.35
TMA	—	—	—
PAn	—	—	—
PMDA	—	—	—
Production method for polyester resin composition	MB*	MB	MB

TABLE 13-continued

Master batch composition (wt. %)			
polyamide resin	20.00	20.00	35.00
polyester resin	79.80	79.80	64.65
polycarboxylic acid compound	0.20	0.20	0.35
Polyamide resin	PA7	PA1	PA1
terminal amino group concentration a (μeq/g)	37	21	21
terminal carboxyl group concentration b (μeq/g)	132	62	62
formula (2) a + b (μeq/g)	169	83	83
Relative viscosity of polyamide resin	1.83	2.64	2.64
Intrinsic viscosity of polyester resin	0.80	0.80	0.80
Melt viscosity ratio (polyamide resin/polyester resin)	0.1	1.0	1.0
Test results			
polyamide mean dispersed particle size in parison body (μm)	0.42	0.19	0.37
haze of bottle body (%)	15.3	2.5	21.0
YI of bottle body	14.2	4.8	25.6
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.023	0.038	0.007

	Reference Example		
	5	6	7
Polyester resin composition (wt. %)			
polyamide resin	5.00	5.00	5.00
polyester resin	94.95	94.95	94.95
polycarboxylic acid compound			
TMAn	—	0.05	0.05
TMA	—	—	—
PAn	—	—	—
PMDA	0.05	—	—
Production method for polyester resin composition	MB	MB	MB
Master batch composition (wt. %)			
polyamide resin	20.00	50.00	80.00
polyester resin	79.80	49.50	19.20
polycarboxylic acid compound	0.20	0.50	0.80
Polyamide resin	PA1	PA1	PA1
terminal amino group concentration a (μeq/g)	21	21	21
terminal carboxyl group concentration b (μeq/g)	62	62	62
formula (2) a + b (μeq/g)	83	83	83
Relative viscosity of polyamide resin	2.64	2.64	2.64
Intrinsic viscosity of polyester resin	0.80	0.80	0.80
Melt viscosity ratio (polyamide resin/polyester resin)	1.0	1.0	1.0
Test results			
polyamide mean dispersed particle size in parison body (μm)	0.22	0.36	0.39
haze of bottle body (%)	8.2	11.5	12.5
YI of bottle body	14.7	10.2	9.6
oxygen transmission rate of bottle (cc/bottle · day · 0.21 atm)	0.022	0.022	0.021

MB*: master batch system.

Example 27

The preliminary master batch obtained in Example 17 and polyethylene terephthalate resin were dry-blended in a ratio of 25/75% by weight, and melt-kneaded into a film according to a T-die method, in which the cylinder temperature was from 270 to 290° C., the T-die temperature was 280° C., the screw speed was 100 rpm and the cooling roll temperature was 70° C., thereby producing an unstretched sheet having a width of 120 mm and a thickness of about 0.3 mm. Next, using a tenter-type biaxial stretcher by Toyo Seiki, the unstretched sheet was preheated at 90 to 110° C. for 30 seconds and then biaxially-stretched in the machine direction and in the cross direction both at a draw ratio of 3.5 times, at a linear stretching speed of 60%/sec, thereby giving a stretched film having a thickness of 20 μm. Thus obtained, the unstretched sheet had a haze of 0.5% and YI of 1.4, and the stretched film had a haze of 0.6% and YI of 1.9 and its oxygen transmission coefficient was 0.95 cc·mm/m^2·day·atm (23° C., 60% RH).

Reference Example 8

An unstretched sheet and a stretched film were produced under the same condition as in Example 27 but dry-blending the ingredient in a ratio of polyamide resin (PA1)/polyethylene terephthalate/polycarboxylic acid compound (TMAn)= 5/94.95/0.05% by weight. Thus obtained, the unstretched sheet had a haze of 6.5% and YI of 3.2, and the stretched film had a haze of 5.8% and YI of 4.5 and its oxygen transmission coefficient was 0.96 cc·mm/m^2·day·atm (23° C., 60% RH).

Example 28

Master batch pellets (moisture content, 130 ppm) were prepared in the same manner as in Example 17.

Polyamide resin	
relative viscosity	2.65
melt viscosity (Pa · s)	500
Polyester resin	
intrinsic viscosity (dl/g)	0.84
Composition (% by weight)	
polyamide resin	20.0
polyester resin	79.8
polycarboxylic acid compound	0.2
Melt viscosity ratio (polyamide resin/polyester resin)	1.0
Melt viscosity x (Pa · s)	130

25% by weight of the master batch pellets were dry-blended with 75% by weight of a polyester resin for dilution, polyethylene terephthalate resin (Nippon Unipet's trade name, UNIPET, grade RT553C, moisture content 90 ppm) in a tumbler to prepare a polyester resin composition.

Polyester resin for dilution	
intrinsic viscosity (dl/g)	0.84
melt viscosity y (Pa · s)	500
x/y	0.26
Composition (% by weight)	
polyamide resin	5.00
polyester resin	94.95
polycarboxylic acid compound	0.05

The polyester resin composition was injection-molded in an injection-molding device (Meiki Seisakusho's M200PDM-MJ) to give a parison having a length of 96 mm, a wall thickness of 4.0 mm, an outer diameter of 22.5 mm and a weight of 27 g. The injection molding condition was as follows: The resin temperature was 280° C., the mold temperature was 15° C., and the screw speed was 150 rpm. The body of the obtained parison was observed with an electronic microscope. The mean dispersed particle size of the polyamide resin in a cross section of about 19 μm^2 of the sample was 0.18 μm.

The obtained parison was processed for biaxial-stretch blow molding, using a blow-molding device (Frontier's EFB1000ET), to give a biaxially-stretched blow bottle having a height of 223 mm, a body diameter of 65 mm, a capacity of 500 mL and a mean thickness of about 300 μm. The obtained bottle was colored little, and had good transparency and gas barrier properties.

Test Results:

haze of bottle body (%)	5.5
YI of bottle body	8.7
oxygen transmission rate of bottle	0.020 cc/bottle · day · 0.21 atm

Example 29

A parison and a stretch blow bottle were produced under the same condition as in Example 28, for which, however, polyethylene terephthalate resin (Nippon Unipet's trade name UNIPET, grade RT580CA (moisture content 150 ppm)) was used as the polyester resin for dilution. The obtained bottle was colored little and had good transparency and gas barrier properties.

Master batch	
Polyamide resin	
relative viscosity	2.65
melt viscosity (Pa · s)	500
Polyester resin	
intrinsic viscosity (dl/g)	0.84
Composition (% by weight)	
polyamide resin	20.0
polyester resin	79.8
polycarboxylic acid compound	0.2
Melt viscosity ratio (polyamide resin/polyester resin)	1.0
Melt viscosity x (Pa · s)	130
Polyester resin composition	
polyester resin for dilution	
intrinsic viscosity (dl/g)	1.17
melt viscosity y (Pa · s)	650
x/y	0.20
composition (% by weight)	
polyamide resin	5.00
polyester resin	94.95
polycarboxylic acid compound	0.05

Test Results:

polyamide mean dispersed particle size in parison body (μm)	0.15
haze of bottle body (%)	5.2
YI of bottle body	8.4
oxygen transmission rate of bottle	0.019 cc/bottle · day · 0.21 atm

Example 30

A parison and a stretch blow bottle were produced under the same condition as in Example 28, for which, however, polyethylene terephthalate resin (Nippon Unipet's trade name UNIPET, grade RT580CA (moisture content 150 ppm)) was used in preparing the master batch. The obtained bottle was colored little and had good transparency and gas barrier properties.

Master batch	
Polyamide resin	
relative viscosity	2.65
melt viscosity (Pa · s)	500
Polyester resin	
intrinsic viscosity (dl/g)	1.17
Composition (% by weight)	
polyamide resin	20.0
polyester resin	79.8
polycarboxylic acid compound	0.2
Melt viscosity ratio (polyamide resin/polyester resin)	0.8
Melt viscosity x (Pa · s)	150
Polyester resin composition	
polyester resin for dilution	
intrinsic viscosity (dl/g)	0.84
melt viscosity y (Pa · s)	500
x/y	0.30

-continued

composition (% by weight)	
polyamide resin	5.00
polyester resin	94.95
polycarboxylic acid compound	0.05

Test Results:

polyamide mean dispersed particle size in parison body (μm)	0.19
haze of bottle body (%)	5.3
YI of bottle body	9.5
oxygen transmission rate of bottle	0.020 cc/bottle · day · 0.21 atm

Example 31

The following polyester resin, polyamide resin and polycarboxylic acid compound were mixed in a tumbler, and melt-kneaded in a twin-screw extruder at an extrusion temperature of 280° C. and an extrusion speed of 15 kg/hr, while the pressure in the extruder cylinder was reduced with a vacuum pump, and the extruded strands were pelletized into pellets.

Polyester resin: 80 parts by weight of dry pellets of polyethylene terephthalate resin (Invista's grade 1101E, intrinsic viscosity 0.80 dl/g),

Polyamide resin: 20 parts by weight of MX nylon (Mitsubishi Gas Chemical's grade S6007, relative viscosity 2.65), 0.2 parts by weight of trimellitic acid dianhydride (TMAn).

The obtained pellets were dried in vacuum at 150° C. for 6 hours, thereby giving a resin composition (preliminary master batch). 25 parts by weight of the preliminary master batch pellets and 75 parts by weight of dry pellets of polyethylene terephthalate resin (grade: 1101E) were dry-blended, and the mixture was injection-molded in an injection-molding device (Meiki Seisakusho's M200PDM-MJ) to give a parison having a length of 96 mm, a wall thickness of 4.0 mm, an outer diameter of 22.5 mm and a weight of 27 g. The dispersed particle size of the polyamide resin in a test sample having a length of about 5.0 μm and a width of about 3.8 μm (area of about 19 μm^2), as cut out from the body of the parison, was measured. The parison was processed for biaxial-stretch blow molding, using a blow-molding device (Frontier's EFB1000ET), to give a biaxially-stretched blow bottle having a height of 223 mm, a body diameter of 65 mm, a capacity of 500 mL and a mean thickness of about 300 μm. The results are shown in Table 14.

Example 32

A parison and a biaxially-stretched hollow container were produced under the same condition as in Example 31, for which, however, the injection speed was 100 m/sec. The results are shown in Table 14.

Example 33

A parison and a biaxially-stretched hollow container were produced under the same condition as in Example 31, for which, however, the back pressure was 2.8 MPa. The results are shown in Table 14.

Example 34

A parison and a biaxially-stretched hollow container were produced under the same condition as in Example 31, for which, however, the back pressure was 3.5 MPa, the screw speed was 100 rpm and the injection speed was 125 cc/sec. The results are shown in Table 14.

Reference Example 9

A parison and a biaxially-stretched hollow container were produced under the same condition as in Example 31, for which, however, the back pressure was 1.0 MPa and the injection speed was 30 cc/sec. The results are shown in Table 14.

[Table 16]

TABLE 14

	Example				Reference
	31	32	33	34	Example 9
Resin					
PET (wt. pt.)	95	95	95	95	95
MX nylon (wt. pt.)	5	5	5	5	5
TMAn (wt. pt.)	0.05	0.05	0.05	0.05	0.05
Mixing method	MB*	MB*	MB*	MB*	MB*
Injection condition					
back pressure (MPa)	4.0	4.0	2.8	3.5	1.0
screw speed (rpm)	150	150	150	100	150
injection speed (cc/sec)	155	100	155	125	30
resin temperature (° C.)	280	280	280	280	280
mold temperature (° C.)	15	15	15	15	15
Dispersed particle size					
mean diameter (μm)	0.088	0.11	0.12	0.13	0.22
proportion of ±0.05 μm particles (%)	95.7	86.3	66.0	70.9	44.3
Bottle Haze (%)	5.1	6.4	5.7	5.6	8.0

MB*: master batch system.

[Industrial Applicability]

The polyester resin composition of the invention has good shapability, and the shaped article obtained from it has practically sufficient gas barrier properties and mechanical properties, and it is colored little and its transparency is improved. The shaped article is extremely useful as packing materials for foods, drinks, chemicals, electronic parts, etc., and the industrial value of the invention is high.

The invention claimed is:

1. A polyester resin composition comprising:

from 2 to 30% by weight of a polyamide resin (A) containing diamine constitutive units and dicarboxylic acid constitutive units, in which at least 70 mol % of the diamine constitutive units is derived from metaxylylenediamine and at least 70 mol % of the dicarboxylic acid constitutive units is derived from adipic acid; from 69.5 to 97.99% by weight of the sum of the amount of a polyester resin (B) and of a polyester resin (B'), each of the polyester resin (B) and the polyester resin (B') containing diol constitutive units and dicarboxylic acid constitutive units, in which at least 70 mol % of the dicarboxylic acid constitutive units of the polyester resin (B) and of the polyester resin (B') is derived from an aromatic dicarboxylic acid and at least 70 mol% of the diol constitutive units is derived from an aliphatic diol; and from 0.01 to 0.5% by weight of a polycarboxylic acid compound (C) comprising at least one tricarboxylic acid compound selected from the group consisting of aromatic tricarboxylic acids, alicyclic tricarboxylic acids

and acid anhydrides of those tricarboxylic acids, and/or at least one dicarboxylic acid compound selected from the group consisting of aromatic dicarboxylic acids, alicyclic dicarboxylic acids and acid anhydrides of those dicarboxylic acids (provided that the total of the contents of the ingredients (A), (B), (B'), and (C) in the polyester resin composition is 100% by weight),

and satisfying the following formulae (1) to (4):

$$a \leq b \quad (1)$$

$$60 \leq a+b \leq 150 \quad (2)$$

$$1 \leq c \times Cc \leq 20 \quad (3)$$

$$1 \leq c \times Cc/(a \times Ca) \leq 12 \quad (4)$$

(wherein "a" represents the concentration of the terminal amino group of the polyamide resin (A) (μequivalent/g); "b" represents the concentration of the terminal carboxyl group of the polyamide resin (A) (μequivalent/g); "c" represents the concentration of the carboxyl group in the polycarboxylic acid compound (C) (μequivalent/g), provided that one equivalent of acid anhydride group is calculated as 2 equivalents of carboxyl group; "Cc" represents the concentration of the polycarboxylic acid compound (C) in the polyester resin composition (g/g); and "Ca" represents the concentration of the polyamide resin (A) in the polyester resin composition (g/g)),

the polyester resin composition having been prepared by mixing (I) a preliminary resin composition comprising from 10 to 40% by weight of the polyamide resin (A), from 89.95 to 59.00% by weight of the polyester resin (B) and from 0.05 to 1% by weight of the polycarboxylic acid compound (C), the total % by weight of the ingredients (A), (B) and (C) in the preliminary resin composition being 100% by weight, with (II) the polyester resin (B'), so as to provide the polyester resin composition having from 2 to 30% by weight of the polyamide resin (A), from 69.5 to 97.99% by weight of the sum of the amount of (1) the polyester resin (B) and (2) the polyester resin (B'), and from 0.01 to 0.5% by weight of the polycarboxylic acid compound (C),

the polyamide resin (A) being finely dispersed in the polyester resin composition.

2. The polyester resin composition as claimed in claim **1**, wherein the polyamide resin (A) is a solid-phase polymerization polyamide resin having a relative viscosity of from 2.30 to 4.20 that is obtained through additional solid-phase polymerization of a melt polymerization polyamide resin obtained from a diamine providing the diamine constitutive units and a dicarboxylic acid providing the dicarboxylic acid constitutive units of the polyamide resin (A) and having a relative viscosity of from 1.83 to 2.28.

3. The polyester resin composition as claimed in claim **1**, which is prepared by melt-kneading a mixture comprising from 5 to 50% by weight of the preliminary resin composition and from 50 to 95% by weight of the polyester resin (B'), the total weight of the preliminary resin composition and the polyester resin (B') being 100% by weight.

4. The polyester resin composition as claimed in claim **1**, wherein the polyamide resin (A) is polymetaxylylenadipamide.

5. The polyester resin composition as claimed in claim **1**, wherein each of the polyester resin (B) and the polyester resin (B') is at least one resin selected from polyethylene terephthalate resin, polyethylene terephthalate/isophthalate copolymer resin, polyethylene/1,4-cyclohexanedimethylene terephthalate copolymer resin, polybutylene terephthalate resin, and polyethylene 2,6-naphthalenedicarboxylate resin.

6. The polyester resin composition as claimed in claim **1**, wherein the tricarboxylic acid compound is at least one compound selected from the group consisting of trimellitic acid and trimellitic acid anhydride.

7. The polyester resin composition as claimed in claim **1**, wherein the dicarboxylic acid compound is at least one compound selected from the group consisting of phthalic acid and phthalic anhydride.

8. The polyester resin composition as claimed in claim **1**, wherein melt viscosity of polyamide resin (A)/melt viscosity of polyester resin (B) is from 0.3 to 1.2.

9. A shaped article obtained by shaping the polyester resin composition of claim **1**.

10. The shaped article as claimed in claim **9**, which is a biaxially-stretched hollow container obtained by preparing a parison through injection molding of the polyester resin composition under the following condition (a) to (e):

(a) resin temperature of from 260 to 290° C.,

(b) screw back pressure of from 2.5 to 5.0 MPa,

(c) screw speed of from 80 to 250 rpm,

(d) injection speed of from 80 to 180 cc/sec, and

(e) mold temperature of from 10 to 25° C., and processing the parison in a mode of biaxial-stretch blow molding.

11. The polyester resin composition as claimed in claim **1**, wherein said polyester resin (B') is a different polyester resin than the polyester resin (B).

12. The polyester resin composition as claimed in claim **11**, wherein the polyester resin (B') and the preliminary resin composition satisfy the following formulae (5) and (6):

$$100 \leq x \leq 250 \quad (5)$$

$$0.1 \leq x/y \leq 0.5 \quad (6)$$

(wherein x represents the melt viscosity of the preliminary resin composition measured at 270° C. and at a shear rate of 100/sec (Pa·s); and y represents the melt viscosity of the polyester resin (B') measured at 270° C. and at a shear rate of 100/sec (Pa·s)).

13. The polyester resin composition as claimed in claim **1**, wherein said polyester resin (B') is the same polyester resin as the polyester resin (B).

14. The polyester resin composition as claimed in claim **1**, which includes the polycarboxylic acid compound (C) in an amount of 0.01 to 0.07% by weight.

15. A method for producing a polyester resin composition comprising (I) a step of preparing a preliminary composition (i) by melt-kneading from 10 to 40% by weight of a polyamide resin (A) containing diamine constitutive units and dicarboxylic acid constitutive units, in which at least 70 mol % of the diamine constitutive units is derived from metaxylylenediamine and at least 70 mol % of the dicarboxylic acid constitutive units is derived from adipic acid, from 59.00 to 89.95% by weight of a polyester resin (B), containing dicarboxylic acid constitutive units and diol constitutive units, in which at least 70 mol % of the dicarboxylic acid constitutive units of the polyester resin (B) is derived from an aromatic dicarboxylic acid and at least 70 mol % of the diol constitutive units is derived from an aliphatic diol, and from 0.05 to 1% by weight of a polycarboxylic acid compound (C) comprising at least one tricarboxylic acid compound selected from the group consisting of aromatic tricarboxylic acids, alicyclic tricarboxylic acids and acid anhydrides of those tricarboxylic acids, and/or at least one dicarboxylic acid compound selected from the group consisting of aromatic dicarboxylic acids, alicyclic dicarboxylic acids and acid anhydrides of

those dicarboxylic acids (provided that the total of the contents of the ingredients (A), (B) and (C) of the preliminary composition is 100% by weight), or (ii) by melt-kneading a polyamide resin (A) containing diamine constitutive units and dicarboxylic acid constitutive units, in which at least 70 mol % of the diamine constitutive units is derived from metaxylylenediamine and at least 70 mol % of the dicarboxylic acid constitutive units is derived from adipic acid, and a polycarboxylic acid compound (C) comprising at least one tricarboxylic acid compound selected from the group consisting of aromatic tricarboxylic acids, alicyclic tricarboxylic acids and acid anhydrides of those tricarboxylic acids, and/or at least one dicarboxylic acid compound selected from the group consisting of aromatic dicarboxylic acids, alicyclic dicarboxylic acids and acid anhydrides of those dicarboxylic acids (provided that the total of the contents of the ingredients (A) and (C) of the preliminary composition is 100% by weight); and (II) a step of melt-kneading the preliminary composition and a polyester resin (B'), wherein the polyester resin (B') contains dicarboxylic acid constitutive units and diol constitutive units, in which at least 70 mol % of the dicarboxylic acid constitutive units of the polyester resin (B') is derived from an aromatic dicarboxylic acid and at least 70 mol % of the diol constitutive units is derived from an aliphatic diol;

wherein the polyester resin composition comprises from 2 to 30% by weight of the polyamide resin (A); from 69.5 to 97.99% by weight of the sum of the amount of (1) the polyester resin (B) and (2) the polyester resin (B'); and from 0.01 to 0.5% by weight of the polycarboxylic acid compound (C) (provided that the total of the contents of the ingredients (A), (B), (B'), and (C) of the polyester resin composition is 100% by weight), and satisfies the following formulae (1) to (4):

$$a \leq b \quad (1)$$

$$60 \leq a+b \leq 150 \quad (2)$$

$$1 \leq c \times Cc \leq 20 \quad (3)$$

$$1 \leq c \times Cc/(a \times Ca) \leq 12 \quad (4)$$

(wherein "a" represents the concentration of the terminal amino group of the polyamide resin (A) (μequivalent/g);

"b" represents the concentration of the terminal carboxyl group of the polyamide resin (A) (μequivalent/g);

"c" represents the concentration of the carboxyl group in the polycarboxylic acid compound (C) (μequivalent/g), provided that one equivalent of acid anhydride group is calculated as 2 equivalents of carboxyl group;

"Cc" represents the concentration of the polycarboxylic acid compound (C) in the polyester resin composition (g/g); and

"Ca" represents the concentration of the polyamide resin (A) in the polyester resin composition (g/g)); and

wherein the polyamide resin (A) is finely dispersed in the polyester resin composition.

16. The method for producing the polyester resin composition as claimed in claim **15**, wherein the preliminary composition is prepared (i) by melt-kneading from 10 to 40% by weight of said polyamide resin (A), from 59.00 to 89.95% by weight of said polyester resin (B), and from 0.05 to 1% by weight of said polycarboxylic acid compound (C) (provided that the total of the contents of the ingredients (A), (B) and (C) of the preliminary composition is 100% by weight).

17. The method for producing the polyester resin composition as claimed in claim **15**, wherein the polyester resin composition produced includes the polycarboxylic acid compound (C) in an amount of 0.01 to 0.07% by weight.

* * * * *