CASTELLANOS & CO.
A B O G A D O S
Calle 94 A No. 7 A - 09
Bogotá, D.C., COLOMBIA

Señora
Jefe de la División de Nuevas Creaciones
Superintendencia de Industria y Comercio
Ministerio de Desarrollo Económico
E. S. D.

Ref.: Expediente No. **05 048.988**
Solicitud de Patente de Invención para: **PELICULA LAMINADA DE BARRERA DE GAS**
Solicitante: **TOPPAN PRINTING CO. LTD.**

RESPUESTA AL EXAMEN DE FONDO

MARGARITA CASTELLANOS ABONDANO, mayor de edad, identificada y domiciliada como aparece al pié de mi firma, atentamente me permito presentar respuesta al oficio No. 1646 notificado por fijación en lista el 8 de febrero de 2008 correspondiente al examen de fondo, estando dentro del término legal en los siguientes términos:

Me permito presentar a su Despacho un nuevo capítulo reivindicatorio en el cual la reivindicación 6 se ha incluido dentro de la reivindicación 1.

Nivel Inventivo

Argumenta su Despacho que la diferencia entre la solicitud en estudio y D1 corresponde al compuesto de silicio de la capa de recubrimiento. Sin embargo, D2 sugiere una capa de recubrimiento que contiene dicho compuesto de silicio y los demás componentes de la solicitud.

En primer lugar, pongo de presente a su Despacho que ninguno de los documentos D1 o D2 contiene el compuesto representado por la fórmula (2) indicada a continuación:

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Formula General $(R^2Si(OR^3)_3)n$.....(2)

En dicha fórmula, R^2 comprende al menos uno de los siguientes compuestos, vinilo, epoxi, metacriloxi, ureido e isocianato.

Adicionalmente, y contrario a la afirmación del señor examinador, el compuesto glicidoxilalquilalcoxisilano revelado en D2 **no corresponde** al compuesto representado por la fórmula (2) de la presente invención.

Por otra parte, dado que la capa recubridora de barrera de gas de la presente invención está compuesta de tres clases de componentes, la misma puede ser suficientemente insolubilizada. Ahora bien, dado que el compuesto $(R^2Si(OR^3)_3$ de la fórmula general (2) es capaz , a través de hidrólisis de la misma de formar un enlace de hidrógeno con el compuesto $Si(OR^1)_4$ de la fórmula general (1) y también con el polímero soluble en agua, es posible **inhibir la generación de poros en la capa de barrera**. Adicionalmente, dado que el grupo funcional orgánico es capaz de crear una red, es posible **prevenir el hinchamiento del polímero soluble en agua** que puede ser generado debido a la adición de agua al enlace de hidrógeno, de tal modo que hace posible **aumentar en gran manera la resistencia de la película al agua**. Es más, dado que la capa recubridora de barrera de gas es formada sobre un sustrato en combinación con la capa de deposición de vapor de barrera de gas, es posible obtener excelentes propiedades de barrera de gas. Más aún, incluso si no se interpone una capa recubridora adhesiva o también llamada primera capa o una capa tratada especialmente entre el sustrato y la capa de deposición de vapor inorgánico, es posible prevenir el deterioro en términos de permeabilidad del oxígeno y la fuerza de laminado incluso después del tratamiento de esterilización de ebullición. Adicionalmente, es posible proporcionar una película laminada la cual es capaz de prevenir sustancialmente la exfoliación de la capa de deposición de vapor a partir del sustrato que puede ser fabricada a bajo costo y excelente en viabilidad.

Así las cosas, la presente invención no es obvia para una persona versada en la materia en vista de las enseñanzas de los documentos D1 y D2 ya que las mismas no contienen el compuesto de silicio reivindicado en la presente solicitud y non presentan las ventajas en cuanto a las propiedades de barrera anteriormente descritas.

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Cumplido así con lo dispuesto, respetuosamente solicito a su Despacho conceder el privilegio de patente a la presente invención toda vez que las objeciones planteadas por su Despacho han sido superadas.

Anexos

- Nuevo capítulo reivindicatorio
- Formulario de Modificaciones
- Recibo de Pago

De la Señora Jefe,

Margarita Castellanos Abondano
C.C. No. **39.779.654** de Usaquén
T.P.A. No.**70819** del C. Sup. de la Judicatura
Calle 94 A No. 7 A - 09
Teléfonos: 610 74 20

Bogotá, D.C.,

PATENTES/11/P1196/MEMORIAL FONDO 1646

Industria y Comercio
SUPERINTENDENCIA

Espacio reservado para el adhesivo de radicación

FORMULARIO ÚNICO DE CORRECCIONES Y MODIFICACIONES

① **SOLICITUD DE:**

☐ **Corrección de Errror Material** ☒ **Modificación a una solicitud**

② **SOLICITANTE**

Nombre: **TOPPAN PRINTING CO., LTD.**

Dirección: **5-1, Taito 1-chome, Taito-ku, Tokyo 110-0016 JAPON**

Domicilio: **Tokyo 110-0016 JAPON**

Lugar de Constitución: **Japón**

Teléfono: Fax:
E-mail:

IDENTIFICACIÓN

C.C. ☐ NIT ☐
C.E. ☐ Otro ☐
Cual
Número

③ **REPRESENTANTE O APODERADO**

Nombre: **MARGARITA CASTELLANOS A.**

Dirección: **CALLE 94A No. 7A-09**

Teléfono: **610 74 20** Fax: **610 07 06**

E-mail: info@castellanosyco.com

IDENTIFICACIÓN

C.C. ☒ NIT ☐
C.E. ☐ Otro ☐
Cual
Número **39'779.654** TPA **70.819**

④ **Número de Expediente:** **05.048.988**

⑤ **Descripción de la corrección o modificación solicitada:**

Presento nuevo capítulo reivindicatorio sobre el cual solicito que se realice el examen de patentabilidad.

⑥ **Comprobante de pago No.** **8-34,782** **Fecha** **30 de abril de 2008**

⑦ **Anexos:**

☒ Comprobante de pago de la tasa.
☐ Poderes si fuere el caso, junto con la sustitución de los mismos a mi favor.
☐ Documento que acredita la existencia y representación legal de las partes, cuando sean personas jurídicas
☒ Nuevo capítulo reivindicatorio

⑧ **NOMBRE** **MARGARITA CASTELLANOS A.** **FIRMA**
CC 39'779.654 Usaquén - TPA 70.819 CSJ

Instrucciones para el diligenciamiento del presente formulario, ver reverso de esta página - MCA/1196

1196
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NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 8 - 34,782
FECHA : ABRIL 30 DE 2008

Ri

***** C O N S I G N A C I O N *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
ALVARO CASTELLANOS	RECIBO DE CAJA			34776	30/04/2008	2,020,000.00

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

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-03 CAMBIO DE MODALIDAD Y MODIFICA	12 MARCAS Y LEMAS COMERCIALES	103,000.00
		TOTAL :	$ 103,000.00

SON: CIENTO TRES MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL ASUNTO No.

REIVINDICACIONES

1. Una película laminada de barrera de gas caracterizada porque comprende:

un sustrato de resina;

una capa de deposición de vapor de barrera de gas formada sobre el sustrato de resina y que principalmente contiene un compuesto inorgánico; y

una capa recubridora de barrera de gas formada sobre la capa de deposición de vapor de barrera de gas;

en donde la capa recubridora de barrera de gas es formada a través de recubrimiento y secado de un líquido de recubrimiento que comprende:

uno de los materiales seleccionados de un compuesto de silicio representada por la fórmula general de $Si(OR^1)_4$ ... (1) y los hidrolizados del mismo;

uno de los materiales seleccionados de un compuesto de silicio representado por la fórmula general de $(R^2Si(OR^3)_3)n$ --- (2) y los hidrolizados del mismo (en donde R' y R^3 son individualmente CH_3, C_2H_5 ó $C_2H_4OCH_3$; y R^2 es un grupo funcional orgánico); donde el grupo funcional orgánico (R^2) de la fórmula general $(R^2Si(OR^3)_3)n$ --- (2) es seleccionado del grupo que consiste de vinilo, epoxilo, metacriloxilo, ureido e isocianato y

un polímero soluble en agua que tiene grupo hidroxilo.

2. La película laminada de barrera de gas de acuerdo con la reivindicación 1, caracterizada porque el compuesto inorgánico es transparente.

3. La película laminada de barrera de gas de acuerdo con la reivindicación 2, caracterizada porque el compuesto inorgánico es óxido de aluminio.

4. La película laminada de barrera de gas de acuerdo con la reivindicación 3, caracterizada porque el óxido de aluminio es seleccionado de aquellos donde la abundancia entre aluminio y oxigeno es limitada dentro del intervalo de: Al:O = 1: 1.5-1: 2.0.

5. La película laminada de barrera de gas de acuerdo con cualquiera de las reivindicaciones 1 a 4, caracterizada porque el grupo hidrolizable (R1) de la fórmula general Si $(OR^1)4$ ... (1) es C_2H_5

6. La película laminada de barrera de gas de acuerdo con cualquiera de las reivindicaciones 1 a 5, caracterizada porque cuando el $Si(OR^1)_4$ es calculado como SiO_2 y cuando el $R^2Si(OR^3)_3$ es calculado como $R^2Si(OH)_3$, la materia sólida de $R^2Si(OH)_3$ es limitada dentro del intervalo de 1 a 50% en peso basada en e l peso total de las materias sólidas.

7. La película laminada de barrera de gas de acuerdo con la reivindicación 1, caracterizada porque la fórmula general $(R^2Si(OR^3)_3)n$ --- (2) es un trímero 1,3,5-tris(3-trialcoxisililalquil) isocianurato que es representado por la fórmula (NCO-$R^4Si(OR^3)_3)_3$ en donde R4 es $(CH_2)_n$, n es 1 o más.

8. La película laminada de barrera de gas de acuerdo con la reivindicación 1, caracterizada porque el grupo funcional orgánico (R^2) es el grupo 3-glicidoxipropil 6 grupo 2-(3,4-epoxiciclo hexil).

9. La película laminada de barrera de gas de acuerdo con cualquiera de las reivindicaciones 1 a 8, caracterizada porque cuando el $Si(OR^1)_4$ es calculado como SiO_2 y el $R^2Si(OR^3)_3$ es calculado como $R^2Si(OH)_3$, la proporción de mezcla, basada en peso, de las materias sólidas, esto es, SiO_2/ ($R^2Si(OH)_3$/polímero soluble en agua), es limitada dentro del intervalo de 100/100 a 100/30.

10. La película laminada de barrera de gas de acuerdo con cualquiera de las reivindicaciones 1 a 9, caracterizada porque una primera capa que comprende poliol acrílico, isocianato y un agente acopiador de silano es interpuesta entre el sustrato y la capa de deposición de vapor inorgánica.

11. La película laminada de barrera de gas de acuerdo con cualquiera de las reivindicaciones 1 a 10, caracterizada porque una capa de sellado al calor es dispuesta adicionalmente sobre la capa recubridora de barrera de gas.

US005942320A

United States Patent [19]

Miyake et al.

[11] Patent Number: 5,942,320

[45] Date of Patent: *Aug. 24, 1999

[54] **BARRIER COMPOSITE FILMS AND A METHOD FOR PRODUCING THE SAME**

[75] Inventors: **Ryuta Miyake**, Takatsuki; **Takaaki Murai**, Otake, both of Japan

[73] Assignee: **Daicel Chemical Industries, Ltd.**, Osaka, Japan

[*] Notice: This patent is subject to a terminal disclaimer.

[21] Appl. No.: **08/917,345**

[22] Filed: **Aug. 26, 1997**

[30] **Foreign Application Priority Data**

Sep. 3, 1996 [JP] Japan 8-232898

[51] **Int. Cl.**[6] **B32B 27/32**; B32B 27/34; B32B 27/36

[52] **U.S. Cl.** **428/216**; 427/387; 428/213; 428/215; 428/336; 428/423.5; 428/423.7; 428/424.2; 428/425.5; 428/448; 428/451

[58] **Field of Search** 428/213, 215, 428/336, 423.5, 423.7, 424.2, 425.5, 448, 451, 216; 427/387

[56] **References Cited**

U.S. PATENT DOCUMENTS

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3239537	10/1991	Japan .
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5131590	5/1993	Japan .
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Primary Examiner—D. S. Nakarani
Attorney, Agent, or Firm—Birch, Stewart, Kolasch & Birch, LLP

[57] **ABSTRACT**

A barrier composite film comprises a base film, an anchor coat layer, an inorganic layer such as a silicon oxide layer, and a coating layer containing a silane coupling agent and a barrier resin (e.g. a vinylidene chloride-series copolymer, an ethylene-vinyl alcohol copolymer), the layers being formed on at least one side of the base film in the order of reference. The anchor coat layer can be made of (A) a chlorine-containing resin such as a vinyl chloride-vinyl acetate copolymer, (B) a polyisocyanate compound, and (C) a saturated polyester resin having a glass transition temperature of −10° C. to 20° C. and being substantially unreactive to the component (B). A heat-sealing layer may be formed on the surface of the coating layer or the other side of the base film. This composite film provided with the inorganic layer can avoid a loss of its adhesive properties and barrier properties even under severe conditions such as retort treatment.

29 Claims, No Drawings

BARRIER COMPOSITE FILMS AND A METHOD FOR PRODUCING THE SAME

FIELD OF THE INVENTION

The present invention relates to a barrier composite film which has prominent gas barrier properties against water vapour, oxygen and aromatic components and which is suitable for a film for dried food preservation, a film for retort treatment or microwave heating of food, a packaging film for pharmaceutical products and precision electronic parts, a film for production of a balloon or a hot-air balloon and a film for other applications, and a method for producing the barrier composite film.

BACKGROUND OF THE INVENTION

Conventional technologies have suggested that a barrier property of a base film can be improved to a great extent by coating the base film with an inorganic oxide thin layer. Further, a resin layer provided on the inorganic oxide thin layer imparts heat-sealing properties to the barrier film and protects the inorganic oxide thin layer.

For instance, Japanese Patent Application Laid-open No. 237940/1988 (JP-A-63-237940) discloses a composite film which comprises a metal oxide thin layer of indium oxide or tin oxide formed by sputtering, and a heat-sealing layer of an ethylene-propylene copolymer or the like formed thereon. Japanese Patent Application Laid-open No. 202435/1989 (JP-A-1-202435) and Japanese Patent Application Laid-open No. 202436/1989 (JP-A-1-202436) disclose packaging materials for microwave heating or for retort-processing in which the surface of a base film is covered with a vapour-deposited layer of silicon oxide, and either of a heat-sealing layer or a protective layer, the heat-sealing layer being formed by lamination of a polypropylene film or other heat-sealing resin films, while the protective layer being formed by lamination of a film or coating of a thermosetting resin.

However, where a polymer layer is formed by extrusion-lamination process, the barrier property of a film is terribly deteriorated because the heat and the external mechanical force generated during the process cause a crack or defect on the inorganic thin layer. A dry-lamination process for film-lamination is also affected by external mechanical force during the lamination of films or the coating of an adhesive agent, and thus is likely to damage the inorganic thin layer formed on the base film. In the case of a coating process utilised in the formation of a protective layer on an inorganic thin layer, external mechanical force instantly destroys an inorganic thin layer only to give critically decreased barrier properties, not to mention that the coating hinders the development of barrier properties. All of the above-mentioned films, including a film as produced by laminating or coating a vinylidene chloride-series resin or the like onto an inorganic oxide thin layer provided on a base film, have limited adhesive properties of the inorganic oxide thin layer to the base film. Besides, when these films are utilised as a packaging material to be subjected to external mechanical strength or as a packaging material to be exposed to a high temperature/high humidity environment, it is impossible to expect high adhesive properties and high barrier properties which can last for a long period. In particular, the adhesive properties and the barrier properties of these films decline crucially when exposed to severe conditions such as a boiling process or retort treatment process (retorting process).

Japanese Patent Application Laid-open No. 86539/1991 (JP-A-3-86539) discloses a retortable packaging film which

is produced by coating the surface of a base film with a reactive two-component curable resin composition composed of a polyisocyanate compound and a saturated polyester polyol and forming a silicon oxide thin layer on the coated surface. Disclosed in Japanese Patent Application Laid-open No. 278946/1991 (JP-A-3-278946) is a packaging material for retort treatment applications which comprises an anchor coat layer, a metal oxide thin layer and a heat-sealing layer provided in this order on the surface of a base layer. Japanese Patent Application Laid-open No. 173137/1992 (JP-A-4-173137) discloses a laminate for a balloon having a good barrier property against helium and hydrogen gas, which is produced by forming an undercoat layer of a two-component curable polyurethane or the like on a film, providing an inorganic oxide thin layer on the undercoat layer, and coating the inorganic oxide thin layer with a vinyl chloride-vinyl acetate copolymer, a polyamide, a polyester or an acrylic resin, or with a hot-melt coating composition.

Japanese Patent Application Publication No. 18395/1996 (JP-H-8-18395) discloses a vapour-deposited film which comprises a base film, a mixture layer of a two-component curable polyurethane and 5 to 30% by weight of a vinyl chloride-vinyl acetate copolymer formed on the base film, and a vapour-deposited layer of a metal oxide such as magnesium oxide deposited on the mixture layer. This literature teaches the use of a reactive two-component curable polyurethane composed of a polyol component and a polyisocyanate compound for prevention of permeation of water, and the use of a vinyl chloride-vinyl acetate copolymer for enhanced adhesive properties of the vapour-deposited layer.

Japanese Patent Application Laid-open No. 131590/1993 (JP-A-5-131590) discloses a laminated film produced by depositing a silicon oxide thin layer on at least one side of a base film, thereon coating a thin layer of a silane coupling agent having an amino group in the terminal, and laminating a resin layer having an acid anhydride group on top of the layers. Japanese Patent Application Laid-open No. 239537/1991 (JP-A-3-239537) discloses a laminated film which comprises a base film, a first transparent layer of silicon oxide, a second transparent layer of a silane coupling agent, and another transparent layer of a pressure-sensitive or heat-sensitive adhesive layer laminated in this order on the base film.

These composite films can improve adhesive strength between the base film and the inorganic oxide thin layer. However, a composite film which shows high adhesive properties and barrier properties in an ordinary state (i.e. a film before subjected to retort treatment) still fails to retain good barrier properties as well as the adhesive properties between the base film and the inorganic oxide thin layer, when used as a film for retort treatment. It is impossible for these films to keep, after retort treatment as well as in an ordinary state (before retort treatment), the adhesive properties between the base film and the inorganic oxide thin layer and the barrier properties at high standards or levels. Moreover, the tackiness of the coated layer of a reactive two-component curable resin composition tends to cause blocking, making winding and rewinding of the film difficult. Thus, the productivity has to be sacrificed. Since the polyol component and the polyisocyanate compound are reactive to each other, the prepared or used two-component curable polyurethane cannot be used repeatedly and has to be discarded only to end in wasteful use of the undercoat resin composition.

To be more demanding, a packaging film for food, medical and pharmaceutical products, and precision electronic

The preferred inorganic substance includes, among others, Group 2A elements such as magnesium, calcium, barium, etc.; transition elements such as titanium, zirconium, tantalum, ruthenium, etc.; Group 2B elements such as zinc; Group 3B elements such as aluminum, indium, thallium, etc.; Group 4B elements such as silicon, tin, etc.; Group 6B elements such as selenium; and the oxides of these elements. The inorganic layer is most preferably formed of *one of Group 3B or Group 4B elements or its oxide.*

Among the inorganic substances mentioned above, the oxides of the elements (e.g. tin oxide, aluminium oxide, *indium oxide*, the corresponding composite oxide, silicon oxide, etc.) are very satisfactory in transparency and barrier properties. Particularly, silicon oxide has more advantages in addition to the above characteristics. It can form a dense layer and has a good affinity for the polymer constituting the silane coupling agent-containing barrier resin layer. Further, a layer of silicon oxide does not develop any crack or defect even when external mechanical force is imposed, and it shows sustained high barrier properties for a long time even at high temperatures. It should be understood that the above silicon oxide includes not only silicon monoxide and silicon dioxide but also silicon-containing oxides which are represented by the compositional formula SiO_x (wherein $0<x\leqq 2$, preferably $0.8\leqq x\leqq 1.5$).

As a packaging material for microwave heating, use can be made of inorganic compounds having low electric conductivity, such as the oxides, halides, carbides, nitrides, and other electrically nonconductive substances. The preferred electrically nonconductive inorganic substance includes oxides such as silicon oxide.

The thickness of the inorganic layer can be selected within the range of generally about 100 to 5,000 Å (0.01 to 0.5 μm), *preferably about* 200 to 3,000 Å (0.02 to 0.3 μm) and *more* preferably about 300 to 1,500 Å (0.03 to 0.15 μm). If the thickness is less than 100 Å, it is difficult to form a *homogeneous thin layer, giving only insufficient barrier* effects and mechanical strength. An inorganic layer with a thickness of over 5,000 Å does not contribute to appreciable improvement in barrier performance, but leads to loss of transparency or deterioration of the external appearance, being economically disadvantaged as well.

[Barrier Resin Layer]

As the barrier resins constituting the coating layer, there may be mentioned a resin having the above-mentioned high gas barrier properties, including vinylidene chloride-based copolymers, ethylene-vinyl alcohol copolymers, polyamide-series polymers, polyvinyl alcohol-series polymers, polyacrylonitrile-series polymers, urethane polymers and so on. Incidentally, some of the resins do not show the above-specified barrier properties depending on the composition of the barrier resin in the coating layer. An example of such resins is a thermoplastic polyurethane having a comparatively long segment (e.g. a polyalkyleneoxy segment). The barrier resins mentioned above can be used singly or in combination.

The preferred barrier resin includes vinylidene chloride-based copolymers and ethylene-vinyl alcohol copolymers. The vinylidene chloride-based polymers are copolymers of vinylidene chloride with other copolymerizable monomers. As the copolymerizable monomers, there may be exemplified vinyl chloride, vinyl acetate, crotonic acid, acrylic acid and acrylates (e.g. a C_{1-8} alkyl acrylate) such as methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, isobutyl acrylate, tert-butyl acrylate, pentyl acrylate, hexyl acrylate, etc., acrylonitrile, methacrylonitrile, and methacrylic acid and methacrylates corresponding to the acrylates mentioned above. Among these vinylidene chloride-based copolymers, the preferred copolymers are a vinylidene chloride-acrylonitrile copolymer, a vinylidene chloride-methacrylic acid copolymer, a vinylidene chloride-acrylate copolymer, a vinylidene chloride-methacrylate copolymer, a vinylidene chloride-vinyl acetate copolymer and so on. The vinylidene chloride contents in the vinylidene chloride-based copolymers are generally about 85 to 99 weight % and preferably about 90 to 97 weight %.

The ethylene-vinyl alcohol copolymer is preferably a solvent-soluble or solvent-dispersible ethylene-vinyl alcohol copolymer. The ethylene content of the ethylene-vinyl alcohol copolymer is generally about 5 to 50 mol %, preferably about 10 to 45 mol %, and more preferably about 25 to 35 mol %, and its molecular weight (weight average molecular weight) may be, for example, about 1×10^4 to 10×10^4, preferably about 2×10^4 to 7×10^4, and more preferably about 4×10^4 to 5×10^4. The degree of saponification is preferably not less than 99.5%. Such a solvent-soluble ethylene-vinyl alcohol copolymer is soluble or dispersible in water or in a mixed solvent of water and an alcohol, and gives a thin film by coating.

Depending on the desired barrier performance (barrier properties with respect to, for example, oxygen, water vapour, carbon dioxide, organic solvent gas and an aroma component such as limonene), the barrier resin layer may comprise *at least one species, or more than one species* of the above barrier resins (preferably, vinylidene chloride-based copolymers and ethylene-vinyl alcohol copolymers). The *barrier resin layer* may be formed with a plurality of layers each containing the barrier resin. For example, the barrier resin coating layer may have a multi-layered structure including a vinylidene chloride-based copolymer layer and an ethylene-vinyl alcohol copolymer layer. The barrier resin content of the barrier resin layer is not less than 50 weight %, preferably about 75 to 100 weight %, and more preferably about 90 to 100 weight %.

Furthermore, the barrier resin layer may contain other polymers such as an ethylene-vinyl acetate copolymer, an ethylene-ethyl acrylate copolymer and other olefinic polymers; acrylic polymers; styrenic polymers; polyesters; polyacetals; polyvinyl acetate; polyvinyl chloride; a vinyl chloride-vinyl acetate copolymer; polyamides; urethane-series polymers; acrylonitrile-series polymers; polycarbonates; chlorinated polyolefins; cellulosic polymers and so on.

Where necessary, the barrier resin layer may contain additives such as those mentioned above, an antiblocking agent, and an adhesion improver such as *polyethyleneimines, polyisocyanates and so on.*

[Silane Coupling Agent]

The silane coupling agent includes various compounds which can improve adhesive properties to the inorganic layer, base film layer or barrier coating layer, such as a silicon compound having at least one functional group selected *from the group consisting of a halogen atom, an* epoxy group, an amino group, a hydroxyl group, a mercapto group, a carboxyl group, a vinyl group, and a (meth)acryloyl group, as well as an alkoxy group.

The halogen atom includes fluorine, chlorine, bromine and iodine atoms, practically being a chlorine atom or a bromine atom. The epoxy group may be composed of an epoxy ring formed by oxidation of an unsaturated bond of a hydrocarbon group (e.g. an unsaturated double bond of a cyclopentenyl group, a cyclohexenyl group, a cyclooctenyl group or other cycloalkenyl groups), or an epoxy ring of a glycidyl group. The amino group may be substituted with 1 or 2 lower alkyl groups (e.g. a C_{1-4} alkyl group such as methyl, ethyl, propyl, isopropyl and butyl groups). The (meth)acryloyl group may be formed by a (meth) acryloyloxy group.

As the alkoxy groups, there may be mentioned, for instance, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, s-butoxy, t-butoxy and other C_{1-4} alkoxy groups. A preferable alkoxy group includes a hydrolysable alkoxy group (in particular, a methoxy group or an ethoxy group). The silicon compound has about 1 to 3 (specifically 1 or 2) reactive functional groups and about 1 to 3 (practically 2 or 3) alkoxy groups.

A desirable example of the silane coupling agent includes a silicon compound shown by the following formula,

$$Y-(R)_n-SiX_3$$

wherein Y represents one functional group selected from the group consisting of a halogen atom, an epoxy group, an amino group, a mercapto group, a carboxyl group, a vinyl group and a (meth)acryloyl group; R represents a hydrocarbon residue; X indicates the same or different alkoxy group; and n denotes 0 or 1.

The functional group represented by Y and the alkoxy group indicated by X are similar to *those exemplified above.*

As the hydrocarbon residues represented by R, there may be mentioned, for example, an alkylene group (e.g. *methylene, ethylene, trimethylene,* propylene, 2,2-dimethylmethylene, tetramethylene, pentamethylene, hexamethylene and other straight-chain or branched-chain C_{1-6} alkylene groups), a cycloalkene residue (e.g. cycloheptene, cyclohexene, cyclopentene, cyclooctene and other C_{4-10} cycloalkene residues), a cycloalkene-alkyl residue (e.g. cycloheptene-, cyclohexene-, cyclopentene- and other C_{4-10} cycloalkene-C_{1-6} alkyl groups) and so on. Incidentally, the cycloalkene residue and cycloalkene-alkyl residue may practically be a residue formed by epoxidation of a double bond as mentioned above. The preferred hydrocarbon residue R includes a C_{1-4} alkylene residue (particularly, a C_{2-4} alkylene residue) and a C_{5-8} cycloalkene-C_{1-4} alkyl residue (specifically, a cyclohexene-C_{2-4} alkyl residue).

Further in the formula, n denotes 0 or 1. When Y is a vinyl group, n may practically be 0, and when Y is another *functional group, n may practically be* 1.

Examples of the silane coupling agent include;

(i) halogen-containing silane coupling agents (e.g. 2-*chloroethyltrimethoxysilane*, 2-chloroethyltriethoxysilane, 3-chloropropyltrimethoxysilane, 3-chloropropyltriethoxysilane),

(ii) epoxy group-containing silane coupling agents [e.g. 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane, 3-(3,4-epoxycyclohexyl)propyltrimethoxysilane, 2-glycidyloxyethyltrimethoxysilane, 2-glycidyloxyethyltriethoxysilane, 3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxypropyltriethoxysilane, etc.],

(iii) amino group-containing silane coupling agents (e.g. 2-aminoethyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 2-[N-(2-aminoethyl)amino]ethyltrimethoxysilane, 3-[N-(2-aminoethyl)amino]propyltrimethoxysilane, 3-(2-aminoethyl)amino]propyltriethoxysilane, 3-[N-(2-aminoethyl)amino]propyl methyl dimethoxysilane),

(iv) mercapto group-containing silane coupling agents (e.g. 2-mercaptoethyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane),

(v) carboxyl group-containing silane coupling agents (e.g. carboxymethyltrimethoxysilane, carboxymethyltriethoxysilane, 2-carboxyethyltrimethoxysilane, 2-carboxyethyltriethoxysilane, 3-*carboxypropyltrimethoxysilane*, 3-carboxypropyltriethoxysilane),

(vi) vinyl group-containing silane coupling agents (e.g. *vinyltrimethoxysilane*, vinyltriethoxysilane), and

(vii) (meth)acryloyl group-containing silane coupling agents (e.g. 2-methacryloyloxyethyltrimethoxysilane, 2-methacryloyloxyethyltriethoxysilane, 2-acryloyloxyethyltrimethoxysilane, 3-methacryloyloxypropyltrimethoxysilane, 3-methacryloyloxypropyltriethoxysilane, 3-acryloyloxypropyltrimethoxysilane). These silane coupling agents may be used singly or in combination.

The amount of the silane coupling agent can be selected within the range for improving the adhesive properties of the inorganic layer, and is, for instance, about 0.05 to 10 parts by weight (e.g. about 0.1 to 10 parts by weight), preferably about 0.1 to 7 parts by weight (e.g. about 0.2 to 7 parts by weight) and more preferably about 0.5 to 5 parts by weight (e.g. about 0.5 to 3 parts by weight) relative to 100 parts by weight of the barrier resin.

The thickness of the barrier resin layer can be selected within the range not adversely affecting the film *characteristics*, and may be, for example, about 0.05 to 15 μm, preferably about 0.1 to 10 μm (e.g. 0.2 to 7 μm), and more preferably about 0.25 to 5 μm (e.g. 0.3 to 3 μm). If the coating layer is thinner than 0.05 μm, it is difficult to impart desirable barrier properties. A coating layer thicker than 15 μm would not be rewarded with a commensurate improvement of barrier performance, but would rather be uneconomical.

The thickness ratio of the barrier resin layer to the inorganic layer can be selected as desired, but it should be noted that this ratio has an influence on barrier properties. In order to provide high gas barrier properties and chemical or physical resistance, the ratio T/t, i.e. the ratio of the thickness T (μm) of the barrier resin layer relative to the thickness t (μm) of the inorganic layer, may be, for example, about 0.1 to 1,500, preferably about 0.5 to 500 (e.g. about 0.5 to 60, preferably about 1 to 200), and more preferably about 1 to 100. In many instances, the preferred ratio is about 2 to 50 (e.g. about 5 to 50). If the thickness ratio deviates from the above range, it is difficult to give high gas barrier properties to a film. If the above ratio is less than 0.1, the inorganic layer tends to be damaged by external force. On the other hand, a film with a ratio of over 1,500 would not be rewarded with a commensurate improvement in barrier performance and be uneconomical.

[Characteristics of the Barrier Composite Film]

One of the characteristics of the barrier composite film of this invention is that the film comprises a soft anchor coat layer. Namely, the barrier composite film of this invention further includes a barrier composite film comprising a soft anchor coat layer (an anchor coat layer with an elastic modulus of 0.1×10^1 to 1×10^5 N/mm^2), an inorganic oxide thin layer, and a barrier resin layer formed on at least one side of a base film layer in the order of reference. A preferable anchor coat layer has an elastic modulus of about 0.5×10^1 to 7×10^2 N/mm^2, above all, about 1×10^1 to 5×10^2

-continued

	Component (A)	Component (B)	Component (C)
Example 23:	100	75	11.3
Example 24:	100	150	22.5
Example 25:	100	300	45

Table 5 shows the characteristics of the composite films of Examples 20 to 25 as well as those of Examples 2 and 9.

TABLE 5

	Anchor coat composition			Elastic modulus of anchor coat layer
	Component (A)	Component (B)	Component (C)	
Example 9	100	45	9	4.8×10^8
Example 20	100	38	9	4.2×10^8
Example 21	100	60	6	5.4×10^8
Example 22	100	60	3	2.0×10^9
Example 23	100	75	23.3	7.3×10^7
Example 2	100	100	15	5.2×10^8
Example 24	100	150	22.5	4.8×10^8
Example 25	100	300	45	2.8×10^8

	Before retort treatment			After retort treatment		
	Adhesive strength (g/15 mm)	O_2-TR (cc/m^2 · 24 hrs)	WV-TR (g/m^2 · 24 hrs)	Adhesive strength (g/15 mm)	O_2-TR (cc/m^2 · 24 hrs)	WV-TR (g/m^2 · 24 hrs)
Example 9	405	0.1	0.8	235	3.2	8.2
Example 20	375	0.5	1.2	195	3.0	7.4
Example 21	375	0.1	0.3	260	0.8	1.8
Example 22	325	0.8	1.4	260	4.8	7.3
Example 23	370	0.2	0.4	255	4.4	8.2
Example 2	315	0.1	0.3	290	0.8	1.3
Example 24	315	0.2	0.5	230	0.5	0.7
Example 25	230	2.0	4.8	—	3.3	7.3

O_2-TR: Oxygen gas permeability
WV-TR: Water-vapour permeability

What is claimed is:

1. A barrier composite film which comprises a base film layer, an anchor coat layer formed on at least one side of said base film, an inorganic layer has a thickness of 100 to 5,000 Å formed on said anchor coat layer, and a barrier resin layer containing a silane coupling agent and formed on said inorganic layer.

2. A barrier composite film as claimed in claim 1, wherein said base film layer comprises any of a polypropylene, a polyalkylene terephthalate or a polyamide.

3. A barrier composite film as claimed in claim 1, wherein said anchor coat layer comprises (i) an anchor coat composition containing at least a chlorine-containing resin, or (ii) an anchor coat composition containing a polyisocyanate compound, and at least one resin selected from the group consisting of a chlorine-containing resin and a saturated polyester resin.

4. A barrier composite film as claimed in claim 1, wherein said anchor coat layer comprises (A) a chlorine-containing resin, (B) a polyisocyanate compound, and (C) a saturated polyester resin having a glass transition temperature of −10° C. to 20° C. and being substantially unreactive to the polyisocyanate compound.

5. A barrier composite film as claimed in claim 3, wherein said chlorine-containing resin is a vinyl chloride-vinyl acetate-series copolymer comprising at least vinyl chloride and vinyl acetate as monomer components.

6. A barrier composite film as claimed in claim 3, wherein said polyisocyanate compound (B) is a compound having at least two isocyanate groups per molecule with a molecular weight of 150 to 1,000.

7. A barrier composite film as claimed in claim 3, wherein said saturated polyester resin (C) is a noncrystalline saturated polyester with a hydroxy value of 0 to 15 mg KOH/g or an acid value of 0 to 10 mg KOH/g.

8. A barrier composite film as claimed in claim 3, wherein the number average molecular weight of the saturated polyester resin (C) is 1×10^4 to 5×10^4.

9. A barrier composite film as claimed in claim 3, wherein said anchor coat layer comprises 10 to 500 parts by weight of the polyisocyanate compound (B) and 1 to 50 parts by weight of the saturated polyester resin (C), relative to 100 parts by weight of the chlorine-containing resin (A).

10. A barrier composite film as claimed in claim 1, wherein said anchor coat layer comprises 25 to 400 parts by weight of a polyisocyanate compound (B) having three or more isocyanate groups per molecule with a molecular weight of 150 to 1,000, and 2 to 50 parts by weight of a noncrystalline saturated polyester resin (C) having a glass transition temperature of 0 to 20° C., a number average molecular weight of 1×10^4 to 3×10^4, and a hydroxyl value of 0 to 10 mg KOH/g or an acid value of 0 to 10 mg KOH/g, relative to 100 parts by weight of a noncrystalline thermoplastic chlorine-containing resin (A) having a glass transition temperature of 25 to 60° C. and an acid value of 0 to 30 mg KOH/g.

11. A barrier composite film as claimed in claim 1, wherein said inorganic layer is formed with at least one oxide of a metal selected from the group consisting of Group 2A elements, transition elements, Group 2B elements, Group 3B elements, Group 4B elements and Group 6B elements of the Periodic Table of the Elements.

12. A barrier composite film as claimed in claim 1, wherein said inorganic layer is formed with an oxide of a Group 3B element or a Group 4B element of the Periodic Table of the Elements.

13. A barrier composite film as claimed in claim 1, wherein said inorganic layer has a thickness of 100 to 5,000 Å.

14. A barrier composite film as claimed in claim 1, wherein said barrier resin layer comprises a vinylidene chloride-series copolymer or an ethylene-vinyl alcohol copolymer.

15. A barrier composite film as claimed in claim 1, wherein said silane coupling agent has at least one functional group selected from the group consisting of a halogen atom, an epoxy group, an amino group, a hydroxyl group, a mercapto group, a carboxyl group, a vinyl group and a (meth)acryloyl group, as well as an alkoxy group.

16. A barrier composite film as claimed in claim 1, wherein said silane coupling agent is a compound shown by the following formula,

$$Y-(R)_n-SiX_3$$

wherein Y is a functional group selected from the group consisting of a halogen atom, an epoxy group, an amino group, a mercapto group, a carboxyl group, a vinyl group and a (meth)acryloyl group; R represents a hydrocarbon residue; and X indicates the same or different alkoxy group, n denoting 0 or 1.

17. A barrier composite film as claimed in claim 16, wherein the hydrocarbon residue shown by R is a C_{1-4} alkylene group, or a C_{5-8} cycloalkene-C_{1-4} alkyl residue, the double bond of the said cycloalkene being epoxidated, and wherein X is the same or different methoxy group or ethoxy group.

18. A barrier composite film as claimed in claim 1, wherein the proportion of the silane coupling agent is 0.05 to 10 parts by weight relative to 100 parts by weight of the barrier resin.

19. A barrier composite film as claimed in claim 1, wherein the thickness of the barrier resin layer is 0.05 to 15 μm.

20. A barrier composite film as claimed in claim 1, wherein a ratio T/t of the thickness T (μm) of the barrier resin layer relative to the thickness t (μm) of the inorganic layer is 0.1 to 1,500.

21. A barrier composite film as claimed in claim 1, wherein said film comprises:

a base film layer made of a polypropylene, a polyalkylene terephthalate or a polyamide,

an anchor coat layer containing (i) at least a chlorine-containing resin, or (ii) a polyisocyanate compound, and either of a chlorine-containing resin or a saturated polyester resin or both of them,

an inorganic layer composed of a metal oxide and having transparency, and

a barrier resin layer comprising a silane coupling agent, and either of a vinylidene chloride-series copolymer or an ethylene-vinyl alcohol copolymer,

said layers being formed in that order on at least one side of said base film layer.

22. A barrier composite film comprising a base film layer, an anchor coat layer formed on at least one side of said base film layer, an inorganic oxide thin layer formed on the anchor coat layer, and a barrier resin layer formed on the inorganic oxide layer has a thickness of 100 to 5,000 Å, wherein the elastic modulus of said anchor coat layer is 0.1×10^4 to 1×10^3 N/mm^2.

23. A barrier composite film comprising a base film layer, an anchor coat layer formed on at least one side of said base film layer, an inorganic oxide thin layer formed on the anchor coat layer, and a barrier resin layer formed on the inorganic oxide layer has a thickness of 100 to 5,000 Å, wherein said barrier resin layer has a peeling strength of not lower than 100 g/15 mm for the base film layer as measured after 30 minutes of retort treatment at a temperature of 120° C.

24. A barrier composite film as claimed in claim 23, wherein said composite film has an oxygen gas permeability of not higher than 2 cc/m^2·24 hr. and a water vapour permeability of not higher than 3 g/m^2·24 hr. after 30 minutes of retort treatment at 120° C., provided that the base film layer has a thickness of 10 to 30 μm and that the coating layer comprising the anchor coat layer, the inorganic layer and the barrier resin layer has a thickness of 0.5 to 5 μm.

25. A barrier composite film as claimed in claim 23, wherein said composite film has an oxygen gas permeability of not higher than 1 cc/m^2·24 hr. at 25° C., and a water vapour permeability of not higher than 3 g/m^2·24 hr. at 40° C. and 90% R.H., provided that the base film layer has a thickness of 10 to 30 μm and that the covering or coating layer comprising the anchor coat layer, the inorganic layer and the barrier resin layer has a thickness of 0.5 to 5 μm.

26. A barrier composite film as claimed in claim 23, wherein said anchor coat layer comprises (A) a chlorine-containing resin, (B) a polyisocyanate compound, and (C) a substantially unreactive saturated polyester resin with a glass transition temperature of −10° C. to 20° C., and is formed with a resin composition having an elastic modulus of 1×10^1 to 5×10^2 N/mm^2.

27. A barrier composite film as claimed in claim 1, wherein the other side of the base film layer or the surface of the barrier resin layer is covered with a polymer layer.

28. A barrier composite film as claimed in claim 27, wherein said polymer layer is a heat-sealing layer.

29. A process for producing a barrier composite film which comprises forming an anchor coat layer, an inorganic layer has a thickness of 100 to 5,000 Å, and a barrier resin layer containing a silane coupling agent on at least one side of a base film in the order of reference.

* * * * *

Jp08-099390

CLAIMS

[Claim(s)]

[Claim 1]A constituent containing a base film,; alkoxysilane, a silane coupling agent, and ethylene vinyl alcohol copolymer which become with thermoplastics, A laminated film which is produced by carrying out a polycondensation by a sol-gel method, in which the main ingredients became by straight-chain-shape compound polymer which consists of a random copolymer of ethylene vinyl alcohol, and were laminated by at least one side of this base film and which has at least one-layer compound polymer layer and;.

[Claim 2]A base film,; alkoxysilane, a silane coupling agent which become with thermoplastics, Polyvinyl alcohol and a constituent containing ethylene vinyl alcohol copolymer, It becomes by straight-chain-shape compound polymer which is produced by carrying out a polycondensation by a sol-gel method and which the main ingredients become from a random copolymer of polyvinyl alcohol and ethylene vinyl alcohol, A laminated film which was laminated by at least one side of this base film and which has at least one-layer compound polymer layer and;.

[Claim 3]A constituent containing a base film,; alkoxysilane, a silane coupling agent, and polyvinyl alcohol which become with thermoplastics, It becomes by compound polymer which is produced by carrying out a polycondensation by a sol-gel method and which the main ingredients become from straight-chain-shape polymer, The 1st [of at least one layer] compound polymer layer and; alkoxysilane that were laminated by at least one side of this base film, A constituent containing a silane coupling agent and ethylene vinyl alcohol copolymer, becoming by straight-chain-shape compound polymer which is produced by carrying out a polycondensation by a sol-gel method and which the main ingredients become from a random copolymer of ethylene vinyl alcohol -- this -- a laminated film which was laminated on the 1st compound polymer layer and which has 2nd at least one-layer compound polymer layer and;.

[Claim 4]A laminated film given in claim 1, 2, or 3 in which a constituent containing said ethylene vinyl alcohol copolymer contains one or more sorts of metal alkoxides further.

[Claim 5]Alkoxysilane, a silane coupling agent, and a constituent containing ethylene vinyl alcohol copolymer, A process of preparing coating liquid containing straight-chain-shape compound polymer of this constituent in which a polycondensation is carried out under existence of a sol-gel method catalyst, acid, water, and an organic solvent, and the main ingredients consist of a random copolymer of ethylene vinyl alcohol; at least on one side of a base film which becomes with thermoplastics. A manufacturing method of a laminated film which are 80 ** - 150 **, and heat-treats process; and this layered product which apply this coating liquid at temperature below the melting point of this thermoplastics, and includes process; which forms a compound polymer layer in this base film surface.

[Claim 6]Alkoxysilane, a silane coupling agent, polyvinyl alcohol, And a constituent containing ethylene vinyl alcohol copolymer, A polycondensation is carried out under existence of a sol-gel method catalyst, acid, water, and an organic solvent, A process of preparing coating liquid containing straight-chain-shape compound polymer which the main ingredients become from a random copolymer of polyvinyl alcohol and ethylene vinyl alcohol; at least on one side of a base film which becomes with thermoplastics. A manufacturing method of a laminated film which are 80 ** - 150 **, and heat-treats process; and this layered product which apply this coating liquid at temperature below the melting point of this thermoplastics, and includes process; which forms a compound polymer layer in this base film surface.

[Claim 7]Polyvinyl alcohol content coating liquid is applied at least to one side of a base film which becomes with thermoplastics, Are the 1st compound polymer layer a process to form, and this polyvinyl alcohol content coating liquid, Alkoxysilane, a silane coupling agent, and a constituent containing polyvinyl alcohol, . Are obtained by carrying out a polycondensation under existence of a sol-gel method catalyst, acid, water, and an organic solvent. . The main ingredients are the coating liquid containing compound polymer which consists of straight-chain-shape polymer. process; -- this -- ethylene vinyl-alcohol-copolymer content coating liquid on the 1st compound polymer layer, [apply and] Are the 2nd compound polymer layer a process to form, and this ethylene vinyl-alcohol-copolymer content coating liquid, Alkoxysilane, a silane coupling agent, and a constituent containing ethylene vinyl alcohol copolymer, . Are obtained by carrying out a polycondensation under existence of a sol-gel method catalyst, acid, water, and an organic solvent. Are 80 ** - 150 **, and a layered product containing process; and this 1st and 2nd compound polymer which are the coating liquid containing straight-chain-shape compound polymer which the main ingredients become from a random copolymer of ethylene vinyl alcohol is heat-treated at temperature below the melting point of this thermoplastics, A manufacturing method of a laminated film which includes process; which forms a compound polymer layer of a double layer in this base film surface.

[Claim 8]A method given in claim 5, 6, or 7 in which a constituent containing said ethylene vinyl alcohol copolymer contains one or more sorts of metal alkoxides further.

[Claim 9]A method given in claim 5, 6, or 7 in which said sol-gel method catalyst is insoluble and tertiary amine meltable to an organic solvent substantially [water].

[Claim 10]A way according to claim 9 said tertiary amine is N,N-dimethylbenzylamine.

[Claim 11]A method given in claim 5, 6, or 7 for which said water is used at a rate of 0.8 to 2 mol to said 1 mol of alkoxysilane.

[Claim 12]A constituent containing a base,; alkoxysilane, a silane coupling agent, and ethylene vinyl alcohol copolymer which become with thermoplastics, At least one-layer compound polymer layer and a Plastic solid which has; which are acquired by carrying out a polycondensation by a sol-gel method and in which the main ingredients became by straight-chain-shape compound polymer which consists of a random copolymer of ethylene vinyl alcohol, and were laminated by at least one side of this base.

[Claim 13]A base,; alkoxysilane, a silane coupling agent which become with thermoplastics, Polyvinyl alcohol and a constituent containing ethylene vinyl alcohol copolymer, It becomes by straight-chain-shape compound polymer which is produced by carrying out a polycondensation by a sol-gel method and which the main ingredients become from straight-chain-shape polymer of polyvinyl alcohol, and a random copolymer of ethylene vinyl alcohol, At least one-layer compound polymer layer and a Plastic solid which has; which were laminated by at least one side of this base.

[Claim 14]A constituent containing a base,; alkoxysilane, a silane coupling agent, and polyvinyl alcohol which become with thermoplastics, It becomes by compound polymer which is produced by carrying out a polycondensation by a sol-gel method and which the main ingredients become from straight-chain-shape polymer, The 1st [of at least one layer] compound polymer layer and; alkoxysilane that were laminated by at least one side of this base, A constituent containing a silane

coupling agent and ethylene vinyl alcohol copolymer, becoming by straight-chain-shape compound polymer which is produced by carrying out a polycondensation by a sol-gel method and which the main ingredients become from a random copolymer of ethylene vinyl alcohol -- this -- 2nd at least one-layer compound polymer layer and a Plastic solid which has; which were laminated on the 1st compound polymer layer.
[Claim 15]A Plastic solid given in claim 12, 13, or 14 in which a constituent containing said ethylene vinyl alcohol copolymer contains one or more sorts of metal alkoxides further.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the gas-barrier laminated film excellent in hot water resistance which has the GASUBARIA nature outstanding also after boiling treatment and retorting in more detail about the laminated film which has the outstanding GASUBARIA nature. This invention relates to the Plastic solid which used the manufacturing method of this laminated film, and this laminated film further.
[0002]
[Description of the Prior Art]A thermoplastic resin film, especially a polyester system film are excellent in a mechanical strength, chemical resistance, and transparency, and are widely used from a price being still cheaper etc. For example, it is used for industrial use materials, such as films for electric appliances, such as a base film for photographs, a base film for magnetic tape, a drafting film, and a capacitor, a membrane switch, a touch panel, a keyboard, and a label.It is used also as a package agent for food packing.
[0003]However, when using a polyester system film for wrapping, such as food packing, generally GASUBARIA nature is insufficient. For example, the permeability of oxygen of the polyethylene terephthalate (PET) film currently most used widely as a polyester system film and the polyvinylidene chloride (PVDC) film which is films excellent in GASUBARIA nature, and a steam is shown in Table 1.
[0004]
[Table 1]

[0005]1) It is the quantity of the oxygen gas which penetrated the film by 1atm for 24 hours using the film of 20 micrometers.
[0006]2) It is the quantity of the water which penetrated the film at 40 ** and relative humidity (RH)90% for 24 hours using the film of 20 micrometers.
[0007]A PET film often penetrates oxygen gas and a steam, and its GASUBARIA nature is low so that clearly from Table 1.
[0008]Since the :1. polymer which is the characteristic which generally synthesized the adsorptivity, diffusibility, and release to gas-barrier ** of a substrate and the substrate of gas, and has the following tendencies about a polymer nature substrate is not a perfect crystalline which is looked at by metal, it does not have the GASUBARIA nature like metal. In the film or sheet which comprises crystalline polymer, compatibility with the gas of this polymer is small, the crevice between molecules is small, and barrier property is so good that it has a polar group with a large operation of adsorptivity and diffusibility, and release. [as opposed to gas in polymer]
[0009]2. GASUBARIA nature is as good as the polymer substrate of a high degree of crystallinity.
[0010]3. The GASUBARIA nature of polymer which generally has molecular structure with symmetry is good.
[0011]4. GASUBARIA nature is so good that the stacking tendency of the crystal of polymer is large.
[0012]5. GASUBARIA nature is so good that the rigidity of a polymer chain is high.
[0013]6. Gas-barrier ** of the associative strength between polymer chains is greatly good so that the cohesive energy density of polymer is high. The polymer which has a polar group corresponds to this.
[0014]The character of the above 2-6 shows that GASUBARIA nature is as high as the substrate which comprises precise polymer of molecular structure.
[0015]As mentioned above, the polymer which generally has a polar group has good GASUBARIA nature. However, it is easy to combine polar groups, such as a hydroxyl group and an amide group, with a water molecule, and it falls as the gas-barrier ****** becomes high. Therefore, GASUBARIA nature is laminated with the PVCD film which is not influenced by humidity, and the film which becomes by the resin which has such a polar group is used as a layered product film which has the outstanding GASUBARIA nature independent of humidity. As other types, there are a copolymer of ethylene vinyl alcohol copolymer (trade name: Eval), PVCD, and acrylonitrile, etc., and since it has the oxygen GASUBARIA nature which was not influenced by humidity and was excellent, these are broadly used as a film for food packing.
[0016]However, since most of these gas-barrier films use chlorine-based polymers except for ethylene vinyl alcohol copolymer, there are various problems, such as depletion etc. of the ozone layer by the carcinogenicity by the organic salt matter produced in the manufacturing process and abandonment course and gaseous chlorine. GASUBARIA nature falls [the film which consists only of ethylene vinyl alcohol copolymer] by boiling treatment. Although until is gradually recovered to some extent after gas-barrier ** boiling treatment, in addition, it is insufficient and unsuitable to a package of a pouch-packed food.
[0017]It is indicated by JP,4-35841,A by laminating the compound polymer layer produced by carrying out the polycondensation of the constituent containing polyvinyl alcohol to a base film with a sol-gel method that the laminated film excellent in GASUBARIA nature is obtained. However, since the thickness of this laminated film decreases and a mechanical strength etc. become weak when it is inferior to hot water resistance and processing (120 ** for 30 minutes) by manufacture of a pouch-packed food is performed, this laminated film is unsuitable to a package of a pouch-packed food.
[0018]
[Problem(s) to be Solved by the Invention]This invention solves the above-mentioned conventional fault. The purpose is to provide the laminated film excellent in hot water resistance and GASUBARIA nature.
The purpose of this invention is to provide the manufacturing method of the laminated film which has such the outstanding characteristic. Other purposes of this invention are to provide the Plastic solid

thermoplastics, polyolefin-system-resin; polyethylene terephthalate, such as polyethylene and polypropylene, Polyethylene isophthalate, the polyethylene 2, 6-naphthalate, polyester system resin [, such as polybutylene terephthalate,]; -- polyether system resin [, such as polyoxymethylene,]; -- polyamide system resin; polystyrene, such as nylon 6, nylon 6, 6, and polymeta xylene adipamide,. Vinyl system resin; polycarbonate system resin, such as poly(meta) acrylic ester, polyacrylonitrile, and polyvinyl acetate; Cellophane, cellulose type resin [, such as acetate,]; -- polyimide; -- polyether imide; -- polyphenylene sulfide; -- polyether sulphone; -- polysulfone; -- polyether ether ketone; -- there are polyether ketone ketone etc. These resin may be homopolymers or may be a copolymer. If a mechanical strength, a moldability, and economical efficiency are especially taken into consideration, polyester system resin, such as polyethylene terephthalate, polybutylene terephthalate, and polyethylenenaphthalate, is preferred. Preferably terephthalic acid as a dicarboxylic acid component More than 80 mol %. as a glycol component -- ethylene glycol -- more than 80 mol % -- a mixture of copolymerized polyester to contain or polyester which contains polyethylene terephthalate at 80% of the weight or more of a rate is used.

[0030]as other dicarboxylic acid components used for this copolymerized polyester and polyester other than polyethylene terephthalate -- both aromatic series aliphatic series and alicycle fellows dicarboxylic acid -- although -- it may be used. As aromatic dicarboxylic acid, isophthalic acid, alt.phthalic acid, 2, and 6-naphthalene dicarboxylic acid etc. are used. As aliphatic dicarboxylic acid, succinic acid, adipic acid, sebacic acid, oxalic acid, etc. are used. As alicycle fellows dicarboxylic acid, 1,3-cyclopentane dicarboxylic acid, 1, and 4-cyclohexanedicarboxylic acid etc. are used. As a glycol component, alicycle fellows glycol of 6-12 is preferred for aliphatic series glycol of 2-8, or a carbon number for a carbon number. As such glycol, a 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol, There are 1,2-cyclohexane dimethanol, 1,3-cyclohexane dimethanol, 1,4-cyclohexane dimethacrylate, p-xylene glycol, a diethylene glycol, triethylene glycol, etc. Polyether glycol may also be used as a glycol component, for example, a polyethylene glycol, a polypropylene glycol, polytetramethylene glycol, etc. may be used. Oxy acid, such as para-hydroxybenzoic acid, may also be used as a part of copolymer component.

[0031]These dicarboxylic acid components and glycol components polymerize by a usual method (or copolymerization), and polyester is prepared.

[0032]What a base film was a simple substance about such thermoplastics, or carried out melting mixing and fabricated one or more sorts of resin to film state is used. Such a base film may be an unstretched film, or may be one axis or a biaxial oriented film. A layered product which laminated such two or more films may also be used.

[0033]Thermoplastics which is a raw material of the above-mentioned base film also as a raw material of a base of a Plastic solid of this invention is used.

[0034]Alkoxysilane used for this invention is expressed with $Si(OR^1)_4$, and R^1 is a low-grade alkyl group. Specifically, $Si(O\text{-}CH_3)_4$, $Si(O\text{-}C_2H_5)_4$, etc. are used. These alkoxysilane may be mixed and used.

[0035]Metal alkoxides, such as zirconium alkoxide and a titanium alkoxide, may be used for this invention with the above-mentioned alkoxysilane if needed. Zirconium alkoxide is shown by $Zr(OR^2)_4$ and R^2 is a low-grade alkyl group. Specifically, $Zr(O\text{-}CH_3)_4$, $Zr(O\text{-}C_2H_5)_4$, $Zr(O\text{-iso-}C_3H_7)_4$, $Zr(O\text{-}C_4H_9)_4$, etc. may be used. Two or more sorts of these alkoxides may be mixed and used. By using zirconium alkoxide, the toughness of a laminated film obtained, heat resistance, etc. improve, and a fall of the retort-proof nature of a film at the time of extension, etc. is avoided. A range of the amount of zirconium alkoxide used is ten or less weight sections to the alkoxysilane 100 above-mentioned weight section, and it is about 5 weight sections preferably. If it exceeds ten weight sections, it becomes easy to gel compound polymer formed, and when the brittleness of compound polymer becomes large and covers a base film, a compound polymer layer will exfoliate easily. A titanium alkoxide is shown by $Ti(OR^3)_4$ and R^3 is a low-grade alkyl group. Specifically, $Ti(O\text{-}CH_3)_4$, $Ti(O\text{-}C_2H_5)_4$, $Ti(O\text{-}C_3H_7)_4$, $Ti(O\text{-}C_4H_9)_4$, etc. may be used. Two or more sorts of these alkoxides may be mixed and used. By using a titanium alkoxide, thermal conductivity of a coat obtained becomes low and the heat resistance of a substrate improves remarkably. A range of the amount of titanium alkoxide used is five or less weight sections to the alkoxysilane 100 above-mentioned weight section, and it is about 3 weight sections preferably. If it exceeds five weight sections, when the brittleness of compound polymer formed becomes large and covers a base film, compound polymer will exfoliate easily.

[0036]As a silane coupling agent used with the above-mentioned alkoxide, known organic reactivity group content organoalkoxysilane may be used. Organoalkoxysilane which has an epoxy group especially is preferred. There are gamma-glycidoxypropyltrimetoxysilane, gamma-glycidoxypropylmethyldietoxysilane, and beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane in it, for example. Such a silane coupling agent may mix and use two or more sorts. The amount of such silane coupling agent used is within the limits of one to 20 weight section to the alkoxysilane 100 above-mentioned weight section. Rigidity and brittleness of compound polymer which will be formed if 20 or more weight sections are used become large, and the insulation of a compound polymer layer and processability fall.

[0037]In this invention, combination of ethylene vinyl alcohol copolymer or polyvinyl alcohol, and ethylene vinyl alcohol copolymer is used for a constituent which constitutes a compound polymer layer. By adding ethylene vinyl alcohol copolymer, the gas-barrier ** water resisting property of compound polymer obtained, weatherability, etc. improve remarkably. In addition to the above-mentioned gas-barrier ** water resisting property and weatherability, a film which will be obtained if combination of polyvinyl alcohol and ethylene vinyl alcohol copolymer is adopted is excellent in hot water resistance and GASUBARIA nature after hot water processing.

[0038]As for each content weight ratio in a case of adopting combination of polyvinyl alcohol and ethylene vinyl alcohol copolymer, it is preferred that it is 10:0.5-10:6, and about 3:2 is still more preferred.

[0039]Content of the above-mentioned ethylene vinyl alcohol copolymer, Or content of the sum total of the above-mentioned polyvinyl alcohol and ethylene vinyl alcohol copolymer is the range of 50 to 200 weight section to total quantity 100 weight section of the above-mentioned alkoxysilane and a metal alkoxide, and is about 100 weight sections preferably. If it exceeds 200 weight sections, the brittleness of compound polymer will become large and the water resisting property of a laminated film and weatherability which are obtained will also fall. If less than 50 weight sections, GASUBARIA nature will fall. A sol-gel method catalyst used for a method of this invention and a tertiary amine meltable [mainly as a polycondensation catalyst] to an organic solvent substantially insoluble to water are used. There are for example, N,N-dimethylbenzylamine, tripropylamine, tributylamine, tripentylamine, etc. in it, and N,N-dimethylbenzylamine is especially preferred. The amount used is

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES

2020

Abogada
MARGARITA CASTELLANOS ABONDANDO
Apoderada

ASUNTO	Radicación	**05-48988**
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	6254
	Folios	013

Patente de Invención ☒ Patente de Modelo de Utilidad ☐

Vía Nacional ☐

Vía PCT (fase nacional) ☒ Cap.I ☐ Cap. II ☒

No. Sol. Internacional PCT/JP03/14935
Fecha de Presentación Internal. 21 de noviembre de 2003

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

1. Documentos estudiados

1.1. Descripción: Folios: 59 a 99

1.2. Reivindicaciones: Folios: 100 a 102
Folios: 136 a 138 (modificación)

1.3 Dibujos: Folios: 104

1.4 Rta. del Solicitante: Folios: 131 a 133

1.5 Prioridad: 11 de noviembre de 2002, Japón 2002-339115

2. Objeto de la invención

- La invención se titula: **"PELICULA LAMINADA DE BARRERA DE GAS"** (Folio 1).

- La presente invención se relaciona con una película laminada de barrera de gas que se utiliza en los campos de materiales para empaques alimenticios, electrónicos y médicos. La película laminada de barrera de gas es capaz de prevenir que oxígeno o vapor de agua entre al paquete, inhibiendo el deterioro o desnaturalización de los contenidos del paquete.

  En la **Reivindicación Independiente 1** se plantea una película laminada de barrera de gas **caracterizada porque** comprende:

  Un sustrato de resina;

  Una capa de deposición de vapor de barrera de gas formada sobre el sustrato de resina y que principalmente contiene un compuesto inorgánico; y

  Una capa recubridora de barrera de gas formada sobre la capa de deposición de vapor de barrera de gas;

  en donde la capa recubridora de barrera de gas es formada a través de recubrimiento y secado de un líquido de recubrimiento que comprende:

  - Uno de los materiales seleccionados de un compuesto de silicio representada por la fórmula general de $Si(OR_1)_4$ ... (1) y los hidrolizados del mismo;

  - Uno de los materiales seleccionados de un compuesto de silicio representado por la fórmula general de

    $$(R_2Si(OR_3)_3)_n \text{ --- } (2)$$

    Y los hidrolizados del mismo;

    (en donde R_1 y R_3 son individualmente CH_3, C_2H_5 o $C_2H_4OCH_3$; y R_2 es un grupo funcional orgánico); donde el grupo funcional orgánico (R_2) de la fórmula general $(R_2Si(OR_3)_3)_n$ --- (2) es seleccionado del grupo que consiste de vinilo, epoxilo, metacriloxilo, ureido e isocianato; y

  - Un polímero soluble en agua que tiene grupo hidroxilo.

- El problema planteado en esta solicitud consiste en desarrollar un material de empaque transparente con propiedades de barrera bajo condiciones de altas temperaturas y humedades que permita la aplicación de detectores de metales, pueda ser utilizado para ebullición y tratamientos de retorta y no comprenda sustancias perjudiciales para el ambiente.

- El objeto de la invención se clasificó como **B32B 9/00** según la Clasificación Internacional de Patentes (IPC).

3. De la solicitud de Patente

3.2 Reivindicaciones (artículo 30 D 486)

- En la reivindicación independiente 1 se incluye la definición de la composición de la capa recubridora de barrera de gas mencionando lo siguiente:

> *"...Uno de los materiales seleccionados de un compuesto de silicio representado por la fórmula general de*
>
> $(R^2Si(OR^3)_3)_n$--- (2)
>
> *Y los hidrolizados del mismo;*
>
> *(en donde R^1 y R^3 son individualmente CH_3, C_2H_5 o $C_2H_4OCH_3$; y R^2 es un grupo funcional orgánico); donde el grupo funcional orgánico (R^2) de la fórmula general $(R^2Si(OR^3)_3)_n$ --- (2) es seleccionado del grupo que consiste de vinilo, epoxilo, metacriloxilo, ureido e isocianato"*

En primer lugar, no se define cuál es el intervalo de valores que puede tomar el subíndice "**n**", por esto, tal como se encuentra la fórmula 2 se entendería que el componente puede ser un monómero, un dímero, un trímero, etc. Por lo tanto, se recomienda realizar la aclaración de conformidad con lo especificado en la descripción.

- En conclusión, la reivindicación 1 no cumple con el requisito de claridad del artículo 30 de la Decisión 486.

4. Determinación del Estado de la Técnica

- La fecha que se ha tenido en cuenta para determinar el Estado de la Técnica es:

  Fecha de presentación de la solicitud prioritaria: **22 de noviembre de 2002**

- Consultadas las bases de datos con que cuenta la oficina y las otras fuentes utilizadas para determinar el estado de la técnica se encontraron los siguientes documentos relevantes:

No.	Documento	Título	Fecha de publicación
D1	EP0646611	"GAS BARRIER LAMINATED MATERIAL"	5 de abril de 1995
D2	US20010031811	"DURABLE COATING COMPOSITION PROCESS FOR PRODUCING DURABLE, ANTIREFLECTIVE COATINGS AND COATED ARTICLES"	18 de octubre de 2001
D3	US5942320	"BARRIER COMPOSITE FILMS AND A METHOD FOR PRODUCING THE SAME"	24 de agosto de 1999
D4	JP08-099390	"BARRIER LAMINATED FILM AND PRODUCTION THEREOF"	16 de abril de 1996

5. Análisis de patentabilidad (artículo 14 D 486)

5.1 Nivel inventivo (artículo 18 D 486)

El Técnico

El técnico de nivel medio versado en la materia encargado de resolver el problema técnico puede ser un ingeniero químico que labore en la industria de polímeros y que atiende a planes de mejoramiento normalmente formulados por las empresas.

El Problema

El problema técnico que se espera solucionar y que se encuentra resumido en el numeral 2 del presente concepto técnico, ya se encuentra identificado en el estado de la técnica tal como se puede comprobar de la lectura de los documentos seleccionados como relevantes para este estudio.

Comentarios respecto al estado de la técnica

Después de realizar la investigación del estado de la técnica para el presente caso, se encontraron diversas propuestas de laminados de barrera de gas que tienen transparencia en vista de la incorporación de óxidos como el de aluminio, que ya no incluyen laminas metálicas para aumentar la barrera a gases, que incluyen compuestos organosilanos para disminuir la porosidad de la película y que incluyen compuestos de silicio como agentes de acoplamiento para mejorar las propiedades de adhesión entre las películas del laminado, sobre todo cuando hay películas orgánicas e inorgánicas.

A continuación se realiza una descripción resumida de los documentos seleccionados como relevantes para el presente estudio:

- En el documento **EP0646611** (D1) se divulga un material laminado de barrera de gas que comprende un sustrato; una capa delgada de deposición de vapor de barrera y una capa de recubrimiento, las cuales son laminadas en ese orden.

  La capa de deposición de vapor de barrera contiene un compuesto inorgánico como óxido de aluminio y la capa de cubrimiento se forma por revestimiento, calentamiento y secado sobre la capa del compuesto inorgánico, la cual comprende un polímero soluble en agua con un grupo hidroxilo y un alcóxido tal como tetraetoxisilano o sus hidrolizados (Folio 119, resumen; Folio 120, reivindicaciones 6, 8, 9, 11, 12, 13, 16).

- En el documento **US20010031811** (D2) se divulgan películas transparentes que comprenden un material polimérico orgánico (sustrato de resina) y una capa de recubrimiento formada por revestimiento y secado de una composición que incluye una mezcla de glicidoxialquilalcoxisilano (compuesto de silicio que cabe dentro de la definición de la fórmula 2) o sus hidrolizados, alquilalcoxisilanos, tetraalcoxisilanos (compuestos de silicio de que caben dentro de la definición de la fórmula 3); un polímero soluble en agua con un grupo hidroxilo; un surfactante; alcohol alifático; ácido soluble en agua y agua (Folio 121, resumen; Folio 122, párrafos 2, 3; Folio 123, párrafos 22 a 24, 28, 29; Folio 124, párrafo 53, Folio 125, reivindicaciones 1, 2, 4; Folio 126, reivindicaciones 16, 17).

- En el documento **US5942320** (D3) se divulga una película compuesta de barrera a gas que comprende una capa base, una capa de enlace formada sobre por lo menos un lado de dicha capa base, una capa inorgánica sobre la capa de enlace, una capa de resina barrera a gas que contiene agente silano de acoplamiento y formada sobre la capa inorgánica.

  De este documento se desea resaltar la naturaleza química del agente silano de acoplamiento; D3 enseña que dicho agente tiene la fórmula

  $Y\text{-}R_n\text{-}SiX_3$

  Donde Y puede ser un grupo funcional como un grupo epoxi, un grupo vinil o un grupo metacriloil; R representa un residuo de hidrocarburo y X indica el mismo o diferente grupo alcoxi, siendo n= 1 o 0. X puede ser grupo metoxi o etoxi.

  Agentes de acoplamiento con grupo vinil pueden ser por ejemplo viniltrimetoxisilano, viniltrietoxisilano; entre los que tienen grupo metacriloil se encuentra por ejemplo, 2-metacriloiloxietiltrimetoxisilano, 2-metacriloiloxietiltrietoxisilano, 3-acriloiloxipropiltrimetoxisilano (Resumen; Columnas 13, 14; Reivindicaciones 16, 17).

- En el documento **JP08099390** (D4) se divulga la existencia de una película laminada de barrera a gases que tiene buena resistencia al agua caliente, que soporta tratamientos de retorta.

  De este documento se quiere resaltar la incorporación de compuestos organosilanos como agentes de acoplamiento, entre los cuales se encuentra el tetraetoxisilano: $Si(OR^1)_4$, agentes de acoplamiento como gama-glicidoxipropiltrimetoxisilano, beta - (3, 4 – epoxi ciclohexil) etil trimetoxisilano, compuestos que caben dentro de la definición de la fórmula (2) para n=1 (D3; párrafos 34, 36)

<u>La Solución Técnica</u>

La Película Laminada de Barrera de Gas (Reivindicaciones 1 a 11)

- De acuerdo con la reivindicación 1 se entiende que el principio técnico sobre el cual se fundamenta la propuesta consiste en desarrollar una película multicapa con propiedades de barrera, que comprenda un sustrato de resina, una capa de deposición de barrera de gas que tiene un compuesto inorgánico, y una capa de cubrimiento que contiene un polímero soluble en agua con grupo hidroxilo, un compuesto de silicio de fórmula (1) y un compuesto de silicio de fórmula (2). No obstante, en D1 se divulga un material laminado de barrera de gas con una estructura de capas y naturaleza química equivalente.

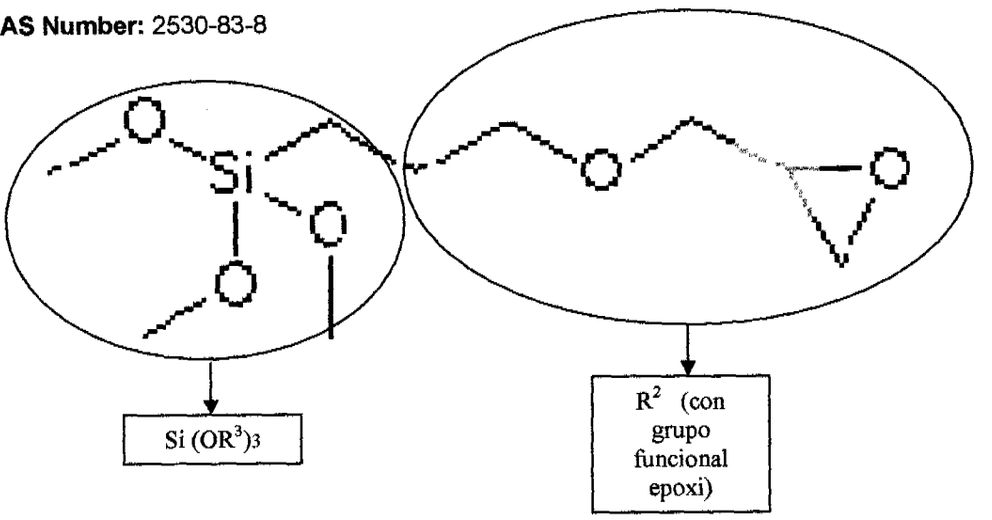
  La diferencia entre la invención de la solicitud y D1 corresponde a la incorporación del compuesto de silicio de fórmula (2) o sus hidrolizados de la capa de cubrimiento dado que en D1 no se mencionan. Sin embargo, D2 **sí sugiere una capa de cubrimiento que sí cabe dentro de la definición dada con la fórmula estructural (2)**.

  Para demostrarlo, tomemos como ejemplo, uno de los agentes de acoplamiento que sugiere el estado de la técnica representado por D2:

Gama-glicidoxipropiltrimetoxisilano (D2; Reivindicación 4)

La fórmula estructural de dicho componente es:

CAS Number: 2530-83-8



Ahora bien, al analizar dicha fórmula estructural se puede observar que coindice con la siguiente fórmula química:

$$(R^2 - Si\ (OR^3)_3)_n \Big|_{n=1}$$

Por lo tanto, incorporar un agente de acoplamiento como el de la fórmula (2) no es algo sorprendente sobre todo cuando se quiere mejorar la adhesión. Esto mismo se puede comprobar al analizar de manera independiente D3 o D4. En estos documentos también se incorporan agentes de acoplamiento que pueden definirse con la misma fórmula (2).

Entonces, si un técnico de nivel medio versado en la materia se basa en D1 y tiene acceso a enseñanzas de agentes de acoplamiento de fórmula (2) como D2, D3 o D4, podría desarrollar películas de barrera a gas equivalentes a las de la solicitud en estudio.

Cabe resaltar, que se decidió la incorporación de los documentos D3 y D4 adicionales, para demostrar que el estado de la técnica está conformado por numerosos documentos que contienen enseñanzas sobre la incorporación de agentes de acoplamiento organosilanos para mejorar las propiedades de adhesión en laminados de barrera de gas, de modo que esto muestra claramente una tendencia normal a utilizarlos, por lo que dicha característica técnica podría ser derivada de manera obvia del estado del arte por un técnico que espera mejorar las propiedades físicas de los laminados de barrera de gas.

Así las cosas, proponer un producto como el de la solicitud en estudio, no parece generar un efecto sorprendente que evidencie un salto tecnológico respecto a lo conocido. Por ello, se puede afirmar que no tiene nivel inventivo y no cumple con el requisito del artículo 18 de la Decisión 486.

6. Conclusión

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	Documento N°	Reivindicaciones afectadas	Requisito que afecta
D1	EP0646611	1 – 11	Nivel Inventivo
D2	US20010031811		
D1	EP0646611	1 – 11	Nivel Inventivo
D3	US5942320		
D1	EP0646611	1 – 11	Nivel Inventivo
D4	JP08-099390		

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de **60 días** contados a partir de la fecha de notificación de la presente comunicación. **En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.**

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.

ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha 05 Jun

CONCEPTO TÉCNICO	EXAMINADOR TÉCNICO
No. 1276	Código No. 202042