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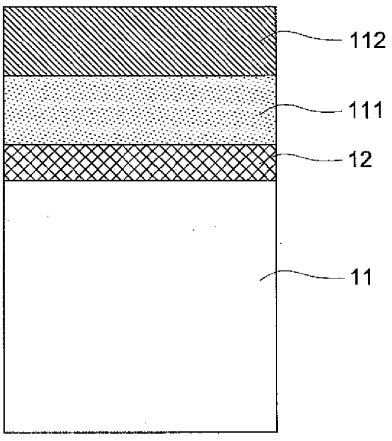
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(54) TRANSPARENT BARRIER SHEET AND PRODUCTION METHOD OF TRANSPARENT BARRIER SHEET

(57) Disclosed is a transparent barrier sheet **characterized by** comprising at least one transparent inorganic thin film layer and at least one transparent organic thin film layer on a base sheet on which a transparent primer layer is arranged. This transparent barrier sheet is also **characterized in that** the transparent organic thin film layer is formed by polymerizing a composition containing a compound having an oxetane ring and a compound having an oxirane ring. This transparent barrier sheet is excellent in gas barrier property and bending resistance. Also disclosed is a method for producing such a transparent barrier sheet.

FIG. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to a transparent barrier sheet for packaging employed in the packaging fields of foods and medicines, or a transparent barrier sheet employed for members related to electronic equipment, a transparent barrier sheet at extremely low permeability of gases such as oxygen or water vapor, and a production method of the same.

BACKGROUND ART

[0002] In recent years, in order to confirm contents, transparent packaging materials have been sought for packaging foods and medicines. Further, in order to minimize effects of permeated oxygen, water vapor, and other gases which adversely affect the content, gas barrier properties are demanded to maintain function and properties of packaged goods. Conventionally, when a high degree of gas barrier properties is demanded, packaging materials have been employed in which foil composed of metals such as aluminum is employed as a gas barring layer. However, the above packaging materials, which employ metal foil as a gas barrier, exhibit a high degree of gas barrier properties, which are not affected by temperature and humidly but have resulted in problems in which it is not possible to confirm contents through the packing material and it is not possible to use a metal detector during inspection.

[0003] Consequently, in recent years, in order to enhance the performance, have been developed and proposed, for example, are transparent barrier materials which are prepared in such a manner that a sputtered layer of metal oxides such as silicon oxide or aluminum oxide are provided on one side of a plastic substrate. However, in order to enhance the gas barrier properties, when the thickness of such inorganic material layer is increased beyond a certain value, cracking is induced due to insufficient flexibility and plasticity, whereby the gas barrier properties are degraded.

[0004] Further, in order to overcome the above drawbacks, it is proposed to realize excellent gas barrier properties by applying a thin organic layer of a cross-linked structure together with a thin inorganic layer onto a transparent plastic substrate (refer, for example, to Patent Documents 1 and 2).

[0005] In such a transparent barrier sheet, commonly, after coating polymerizable monomers or providing the same on a substrate via deposition, a thin organic layer is formed via cross-linking the monomers, employing light or heat. However, the thin organic layer prepared by cross-linking monomers having radically polymerizable unsaturated double bonds, represented by (meth)acryl based monomers, which is provided employing these methods, commonly exhibits large contraction ratio after polymerization compared to one prior to polymerization, whereby the resulting transparent barrier sheet occasionally results in curling, and gas barrier properties is occasionally degraded due to cracking, caused by poor bending resistance since the resulting thin organic layer is brittle.

[0006] Consequently, in order to overcome the above concerns, thin organic layers utilizing cationically polymerizable monomers are proposed (refer, for example, to Patent Documents 3 - 5). The bending resistance of the resulting thin organic layer itself is improved compared to those prepared by radical polymerization, but is still not at a satisfactory level. However, at present, including a close contact between the substrate sheet and the thin layer, at present, a practical satisfaction has not yet been attained. Further, when the thin organic layer is formed via coating, the thin inorganic layer occasionally results in defects, whereby problems occasionally occur in which the resulting gas barrier properties is degraded.

(Patent Document 1) Japanese Patent Publication Open to Public Inspection (hereinafter referred to as JP-A) No. 2003-276115

(Patent Document 2) JP-A No. 2003-300273

(Patent Document 3) JP-A No. 2003-251731

(Patent Document 4) JP-A No. 2004-524958

(Patent Document 5) JP-A No. 2005-125731

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] The present invention was achieved to overcome the above conventional technical problems. An object of the present invention is to provide a transparent barrier sheet which exhibits excellent gas barrier properties and excellent bending resistance, and a production method thereof.

MEANS TO SOLVE THE PROBLEMS

[0008] The above object of the present invention is accomplished employing the following embodiments.

(1) A transparent barrier sheet comprising:

a substrate sheet having thereon a transparent primer layer;
a transparent inorganic thin layer; and
a transparent organic thin layer,
wherein the transparent organic thin layer is formed by polymerizing a composition comprising:

a compound having an oxetane ring; and
a compound having an oxirane ring.

(2) A transparent barrier sheet of the above-described in item 1,
wherein the compound having an oxetane ring comprises at least two oxetane rings in the molecule.
(3) A transparent barrier sheet of the above-described in items 1 or 2,
wherein the compound having an oxirane ring comprises at least two oxirane rings in the molecule.
(4) A transparent barrier sheet of the above-described in any one of items 1 to 3,
wherein the composition to form the transparent organic thin layer further comprises a compound having a group selected from the group consisting of an alkenyl ether group, an allene ether group, a ketene acetal group, a tetrahydrofuran group, an oxepane group, a single ring acetal group, a double ring acetal group, a lactone group; a cyclic orthoester group and a cyclic carbonate group.
(5) A transparent barrier sheet of the above-described in any one of items 1 to 4,
wherein the transparent inorganic thin layer and the transparent organic thin layer are provided in that order on the transparent primer layer of the substrate sheet.
(6) A transparent barrier sheet of the above-described in item 5,
wherein a second transparent inorganic thin layer is further provided on the transparent organic thin layer.
(7) A transparent barrier sheet of the above-described in any one of items 1 to 4,
wherein a second transparent inorganic thin layer; and a second transparent organic thin layer are provided in that order on the substrate sheet having thereon the transparent primer layer, whereby at lease two units each composed of a transparent inorganic thin layer and a transparent organic thin layer are formed on the substrate sheet.
(8) A transparent barrier sheet of the above-described in any one of items 1 to 7,
wherein a thickness of the transparent organic thin layer is from 50 nm to 5.0 μm.
(9) A method of producing a transparent barrier sheet comprising the steps of:

forming a transparent inorganic thin layer on a substrate sheet having thereon a primer layer employing a catalytic chemical vapor deposition method, a reactive plasma deposition method or an electron cyclotron resonance plasma deposition method; and
forming a transparent organic thin layer.

(10) A method of producing a transparent barrier sheet of the above-described in item 9,
wherein the transparent organic thin layer is formed by the steps of:

depositing on the transparent inorganic thin layer vapors of:

a compound having an oxetane ring;
a compound having an oxirane ring; and
a polymerization initiator,

polymerizing the deposited vapors by irradiating with actinic rays or by heating.

(11) A method of producing a transparent barrier sheet of the above-described in items 9 or 10,
wherein a maximum attained temperature T (in K) of the substrate sheet is controlled to be in the range of 243 to 383 K during the formations of the transparent inorganic thin layer and the transparent organic thin layer.
(12) A method of producing a transparent barrier sheet of the above-described in item 11,

wherein the maximum attained temperature T (in K) of the substrate sheet is controlled to satisfy Formula (1):

Formula (1)

$$1.21 \leq (T \times S)/1000 \leq 460$$

wherein S (in second) represents a required time to form the transparent inorganic thin layer and the transparent organic thin layer.

EFFECTS OF THE INVENTION

[0009] Based on the present invention, it was possible to provide a transparent barrier sheet which exhibited excellent gas barrier properties and excellent bending resistance and the production method thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

Fig. 1 is a schematic sectional view of a transparent barrier sheet incorporating one unit of a transparent thin inorganic layer/transparent thin organic layer on a substrate sheet provided with a transparent primer layer.
Fig. 2 is a schematic sectional view of a transparent barrier sheet incorporating two units of a transparent thin inorganic layer/transparent thin organic layer on a substrate sheet provided with a transparent primer layer.
Fig. 3 is a schematic sectional view of a transparent barrier sheet incorporating 5 units of a transparent thin inorganic layer/transparent thin organic layer on a substrate sheet provided with a transparent primer layer.
Fig. 4 is a schematic sectional view of a transparent barrier sheet incorporating two units of a transparent thin inorganic layer/transparent thin organic layer on both sides of a substrate sheet coated with a transparent primer layer on both aforesaid sides.
Fig. 5 is a schematic sectional view of a transparent barrier sheet incorporating a transparent thin inorganic layer/transparent thin organic layer/transparent thin inorganic layer on a substrate sheet provided with a transparent primer layer.
Fig. 6 is a view showing a casting apparatus employing a catalytic chemical vapor deposition method.

DESCRIPTION OF SYMBOLS

[0011]

11, 21, 31, 41, 61: substrate sheet
12, 22, 32, 42, 42', 62: transparent primer layer
111, 211, 221, 311, 321, 331, 341, 351, 411, 411', 421, 421',
611, 621: transparent thin inorganic layer 112, 212, 222, 312, 322, 332, 342, 352, 412, 412', 422, 422',
612: transparent thin organic layer
50: vacuum vessel
51: substrate sheet provided with a transparent primer layer
52: holding mechanism
53: cooling mechanism
54: heater (tungsten)
55: gas inlet
56: hydrogen gas source
57: ammonia gas source
58: silane gas source
59: shielding member
501: driving device for shielding member
502: heating electric source for heater
503: vacuum pump
504: cooling source
505: device for inlet
506: space
V56, V57, V58: on-off valve

PREFERRED EMBODIMENTS TO CARRY OUT THE INVENTION

[0012] The transparent barrier sheet of the present invention and the production method thereof will now be detailed.

(Transparent Barrier Sheet)

[0013] The transparent barrier sheet of the present invention incorporates a substrate sheet coated with a transparent primer layer having thereon at least one thin transparent inorganic layer, and at least one thin transparent organic layer. Each of the constituting materials of the transparent sheet of the present invention will now be described. The visible light transmittance of the transparent barrier sheet of the present invention is 50 - 95%.

[0014] Substrate sheets employed in the present invention may be used without any particular limitation as long as they result in neither dimensional deformation when the following production method is employed, nor curling after coating of a thin layer. Listed as resins to form the sheet may, for example, be polyester based resins such as polyethylene terephthalate (PET), or polyethylene naphthalate; polyolefin based resins such as polyethylene or polypropylene; styrene based resins such as polystyrene or acrylonitrile-styrene copolymers; acryl based resins such as polymethyl methacrylate or methacrylic acid-maleic acid copolymers; cellulose based resins such as triacetyl cellulose; vinyl based resins such as polyvinyl chloride; imido based resins such as polyimide, fluorinate polyimide, or polyetherimide; amido based resins such as nylon 6, nylon 66, or MXD nylon 6; polycarbonate resins composed of bisphenol A, bisphenol Z, or 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane; polyacrylate resins, fluororesins; polyethersulfone resins; polysulfone resins; polyether ketone resins; or alicyclic polyolefin resins such as alicyclic polyolefin, or alicyclic olefin copolymers.

[0015] Substrate sheets include those which have been stretched or not stretched as long as the object of the present invention is not adversely affected, and preferred are those which exhibit sufficient mechanical strength and dimensional stability. Of these, biaxially stretched polyethylene terephthalate or polyethylene naphthalate is preferred for the use of thin substrate sheets. On the other hand, when substrate sheets are relatively thick, the above-cited polyester based resins such as polyethylene terephthalate or polyethylene naphthalate, polyarylate resins, polyether sulfone resins, polycarbonate resins, or alicyclic polyolefin resins are preferred in view of dimensional stability, chemical resistance, and heat resistance.

[0016] Further, if desired, various additives may be added to substrate sheets of the present invention in a range which does not adversely affect the present invention. Cited as such additives may, for example, be plasticizers, dyes and pigments, antistatic agents, UV absorbers, antioxidants, minute inorganic particles, peeling enhancing agents, leveling agents, inorganic layer-shaped silicates, and lubricants.

[0017] The thickness of the substrates may be appropriately varied depending on the use of the transparent barrier sheet of the present invention. Further, when considering suitability of a packaging material, other than a single resin sheet, it is possible to select and employ appropriate sheets laminated with a different quality sheet. However, when considering machinability during formation of the transparent thin inorganic layer and the thin transparent organic layer described below, in practice, the thickness is preferably in the range of 6 - 400 μm, but is most preferably in the range of 25 - 100 μm. When employed for electronic devices such as liquid crystal display elements, dye type solar batteries, organic or inorganic ELs, electronic paper, or fuel cells, appropriate thickness is chosen based on various uses. Of these, when employed as a substitute of a glass substrate, the substrate is prepared according to glass substrate specifications, and after production, the thickness is preferably in the range of relatively thick 50 - 800 μm, but is most preferably in the range of 50 - 400 μm in order to match with the process for the glass substrate.

[0018] Further, when mass productivity of the transparent barrier sheets of the present invention is considered, it is preferable to prepare them in the form of a continuous long-length film so that it is feasible to continuously form the thin transparent inorganic layer and the thin transparent organic layer onto the substrate sheet.

[0019] Subsequently, a transparent primer layer, coated onto the substrate sheet, will now be described.

[0020] The transparent primer layer applied onto the substrate sheet is provided to enhance adhesion to the thin layer applied thereon and to secure the flatness of the surface of the applied thin layer. By providing the above transparent primer layer, it is possible to minimize defects of the thin transparent inorganic layer due to projections and foreign matter on the substrate sheet, to enhance adhesion between the substrate sheet and the thin transparent inorganic layer, and further, it is possible to prepare a transparent barrier sheet which exhibits excellent bending resistance.

[0021] It is also possible to prepare the transparent primer layer via coating of a resin liquid coating composition prepared by dissolving resins in various solvents and subsequently drying the coating. Further, after drying, if desired, a cross-linking reaction may be performed. Further, it is also possible to preferably employ a layer which is prepared as follows. Any of metal alkoxides, UV radiation curing resins, electron beam curing resins, or heat curing resins is coated in the absence of solvents, or a coating composition prepared by diluting any of the above with solvents is coated, subsequently dried, and cured.

[0022] Resins, which are employed to prepare a liquid resin coating composition for the above-mentioned transparent primer layer, upon being dissolved in various solvents, include polyester based resins, urethane based resins, acryl

based resins, styrene based resins, cellulose based resins, polyvinyl acetal based resins, and vinyl chloride based resins. It is possible to select and employ any appropriate one(s) from these.

[0023] Further listed as metal alkoxides are those metals with alcohol such as methyl alcohol, ethyl alcohol, or isopropyl alcohol, and listed as metals may be silicon, titanium, or zirconium.

[0024] As UV radiation curable resins or electron beam curable resins, other than compounds such as styrene based monomers or compounds having an unsaturated double bond in the molecule such as acryl based monomers, selected and employed may be any suitable one(s) from compounds having an oxetane ring, which are employed to form the thin transparent organic layer described below, and compounds having an oxirane ring, or compounds having an alkenyl ether group, an allene ether group, a ketene acetal group, a tetrahydrofuran group, an oxepane group, a single ring acetal group, a double ring acetal group, a lactone group, a cyclic orthoester group, or a cyclic carbonate group. A composition prepared by combining the above compounds with cross-linking agents is applied onto substrate sheet to form a layer followed by curing, whereby it is possible to form a transparent primer layer.

[0025] Further, heat curable resins are suitably selected from combinations with compounds or resins having an oxirane ring and an amino group, combinations of acid anhydrides with compounds or resins having an amino group, or combinations of compounds or resins having hydroxyl group with compounds or resins having an isocyanate group, other than heat curing resins such as phenol resins, epoxy resins, melamine resins, urea resins, unsaturated polyester, or alkyd resins, which are widely employed, and then employed.

[0026] The above transparent primer layer may be composed of a single layer or a plurality of layers. The thickness is commonly in the range of 0.05 - 5.0 μm, but is preferably in the range of 0.1 - 2.0 μm.

[0027] The thin transparent inorganic layer and the thin transparent organic layer applied onto the transparent primer layer of the substrate sheet coated with the transparent primer layer will now be detailed.

[0028] The thin transparent inorganic layers according to the present invention may be employed without particular limitation as long as they exhibit gas barrier properties and are transparent. Specific examples which form the thin inorganic layer include oxides incorporating at least one of Si, Al, In, Sn, Zn, Mg, Ca, K, Sn, Na, B, Ti, Pb, Zr, Y, In, Ce, and Ta, or nitrides and oxidized nitrides. Suitable ones may be selected and then employed. Further, when employed to confirm contents or applied to electronic devices, those, which have not clear maximum absorption wavelength in the visible region, are preferred.

[0029] Of these, employed as inorganic oxides may be oxides of metals such as silicon (Si), aluminum (Al), Zinc (Zn), magnesium (Mg), calcium (Ca), potassium (K), tin (Sn), sodium (Na), boron (B), titanium (Ti), lead (Pb), zirconium (Zr), Yttrium (Y), or Indium (In).

[0030] Of these, metal oxides are represented by MO_x (in which M represents a metal element, and each value of X differs in the range depending on the metal element), such as SiO_x, AlO_x, or MgO_x. Further, with regard to the range of the X value, the possible value range is as follows; $0 < X \leq 2$ for silicon (Si), $0 < X \leq 1$ for aluminum (Al), $0 < X \leq 1$ for zinc (Zn), $0 < X \leq 1$ for magnesium (Mg), $0 < X \leq 1$ for calcium (Ca), $0 < X \leq 0.5$ for potassium (K), $0 < X \leq 2$ for tin (Sn), $0 < X \leq 0.5$ for sodium (Na), $0 < X \leq 1.5$ for boron (B), $0 < X \leq 2$ for titanium (Ti), $0 < X \leq 1$ for lead (Pb), $0 < X \leq 2$ for zirconium (Zr), $0 < X \leq 1.5$ for yttrium (Y), and $0 < X \leq 1$ for indium (In). In the present invention, in terms of gas barrier properties, oxides of silicon (Si) and aluminum (Al) are preferred. In such a case, it is preferable to employ silicon oxide (SiO_x) in the range of $1.0 \leq X \leq 2.0$ and aluminum oxide (AlO_x) in the range of $0.5 \leq X \leq 1.5$.

[0031] In view of transparency as an inorganic nitride, silicon nitrides are preferred. Further, as such mixtures, silicon nitride oxides are preferred. Silicon nitride oxide is represented by SiO_xN_y. When enhancement of close contact capability is manly intended, it is preferable that an oxygen-rich layer is formed resulting in $1 < x < 2$ and $0 < y < 1$. When enhancement of water vapor barrier properties is mainly intended, it is preferable that a nitrogen-rich layer is formed resulting in $0 < x < 0.8$ and $0.8 < y < 1.3$.

[0032] The thickness of thin transparent inorganic layers is commonly 10 - 1,000 nm, but is preferably 20 - 1,000 nm to assure desired barrier properties.

[0033] The thin transparent organic layer will now be detailed.

[0034] The thin transparent organic layer according to the present invention is featured to be a thin layer which is formed via polymerization of compositions incorporating oxetane ring containing compounds and oxirane ring containing compounds.

[0035] Examples of the above compounds having a oxetane ring include those described in JP-A Nos. 5-170763, 5-371224, 6-16804, 7-17958, 7-173279, 8-245783, 8-301859, 10-237056, 10-330485, 11-106380, 11-130766, 11-228558, 11-246510, 11-246540, 11-246541, 11-322735, 2000-1482, 2000-26546, 2000-191652, 2000-302774, 2000-336133, 2001-31664, 2001-31665, 2001-31666, 2001-40085, 2003-81958, 2003-89693, 2001-163882, 2001-226365, 2001-278874, 2001-278875, 2001-302651, 2001-342194, 2002-20376, 2002-80581, 2002-193965, 2002-241489, 2002-275171, 2002-275172, 2002-322268, 2003-2881, 2003-12662, 2003-81958, 2004-91347, 2004-149486, 2004-262817, 2005-125731, 2005-171122, 2005-238446, 2005-239573, and 2005-336349, and Japanese Patent Publication Open to Public Inspection under PCT Application) No. 11-500422. These compounds may be employed individually or in combinations of at least two types.

[0036] Further employed as compounds having an oxirane ring may be various types of compounds. Specific examples include resins, the terminals of which are modified with a glycidyl group, such as aliphatic polyglycidyl ether, polyalkylene glycol diglycidyl ether, tertiary carboxylic acid monoglycidyl ether, polycondensation products of bisphenol A with epichlorohydrine, polycondensation products of hydrogenated bisphenol A with epichlorohydrine, polycondensation products of brominated bisphenol A with epichlorohydrine, and polycondensation products of bisphenol F with epichlorohydrine, as well as glycidyl modified phenol novolak resins, glycidyl modified o-cresol novolak resins, 3,4-epoxycyclohexenylmethyl-3',4'-epoxycyclohexane carboxylate, 3,4-epoxy-4-methylcyclohexenylmethyl-3',4'-epoxy-4'-methylcyclohexane carboxylate, 1,2-bis(3,4-epoxy-4-methylcyclohexycenylcarbonyloxy)ethane, and dipentane dioxide. Further, it is also possible to suitably employ the compounds described on pages 778 - 787 of "11290 no Kagaku Shohin (11290 Chemical Products)", Kagaku Kogyo Nippo-Sha, and the compounds described in JP-A No. 2003-341003.

[0037] With regard to the above compounds having oxetane ring(s) or oxirane ring(s), in order to retard variation of bending resistance due to ambient temperature around the thin transparent organic layer formed via polymerization, it is preferable that at least either of the above-mentioned compounds is one having at least two oxetane rings in the molecule or one having at least two oxirane rings in the molecule.

[0038] Further, in the present invention, to polymerize compounds having oxetane rings and compounds having oxirane rings via exposure to actinic radiation or heating, other than those, polymerization initiators are incorporated in the composition as an essential component.

[0039] Listed as polymerization initiators to polymerize the compounds according to the present invention may be photopolymerization initiators or heat polymerization initiators which allow the oxetane ring and the oxirane ring to undergo cationic polymerization. Of these, photopolymerization initiators may be employed without particular limitation as long as they can generate Brϕnsted acid or Lewis acid. For example, cationic photopolymerization initiators employed in chemical amplification type photoresists and light carving resins (refer to pages 187 - 192 of "imagine yo Yuuki Zairyo (Organic Materials for Imaging"), edited by Yuuki Electronics Zairyo Kenkyuu Kai, Bunshin Shuppan, (1993)), may, if suitable, be selected and then employed.

[0040] Specific examples of such cationic photopolymerization initiators include s-triazine compounds substituted with a trihalomethyl group, such as 2,4,6-tris(trichloromethyl)-1,3,5-triazine, 2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, and the compounds described in JP-A No. 2-306247; iron arene complexes such as [η6-i-propylbensene] or [η5-cyclopentadienyl]iron hexafluorophosphate; onium salts such as diphenyliodonium hexafluorophosphate, diphenyliodonium hexafluoroantimonate, triphenylsulfonium hexafluorophosphate, triphenyltellurium hexafluoroarylcyanate, or diphenyl-4-thiophenoxysulfonium hexafluoroantimonate; and aryldiazonium salts, diazoketone, o-nitrobenzyl ester, sulfonic acid ester, disulfone derivatives, imidosulfonate derivatives, and silanol-aluminum complexes described in JP-A No. 62-57646. Further, any of those described in JP-A Nos. 5-107999, 5-181271, 8-16080, 8-305262, 2000-47552, 2003-66816; U.S. Patent No. 5,759,721, and European Patent No. 1,029,258 may, if suitable, be selected and then employed.

[0041] Further, without particular limitation, employed as the cationic heat polymerization initiators may be onium salts such as sulfonium salts, ammonium salts, or phosphonium salts and silanol-aluminum complexes. Of these, listed as cationic heat polymerization initiators, when other essential components result in no problem while heated at equal to or higher than 150 °C, are the benzylsulfonium salts described in JP-A Nos. 58-37003 and 63-223002, the trialkylsulfonium salts described in JP-A No. 56-152833, and the compounds described in JP-A Nos. 63-8365, 63-8366, 1-83060, 1-290658, 2-1470, 2-196812, 2-232253, 3-17101, 3-47164, 3-48654, 3-145459, 3-200761, 3-237107, 4-1177, 4-210673, 8-188569, 8-188570, 11-29609, 11-255739, and 2001-55374. These cationic heat polymerization initiators may be employed individually or in combinations of at least two types.

[0042] The amount of above polymerization initiators, when the amount of compounds having oxetane rings and compounds having oxirane rings is to be 100 parts by weight, is commonly in the range of 0.01 - 30 parts by weight, but is preferably in the range of 0.05 - 20 parts by weight.

[0043] Further, the thickness of the thin transparent organic layer is commonly 50 nm - 5.0 μm, but is preferably 50 nm - 2.0 μm in terms of achieving flatness and bending resistance.

[0044] Further, in the present invention, other than the above compounds having oxetane rings and compounds having oxirane rings, to regulate viscosity of compositions and to control the polymerization reaction, added may be compounds having an alkenyl ether group, an allene ether group, a ketene acetal group, a tetrahydrofuran group, an oxepane group, a single ring acetal group, a double ring acetal group, a lactone group, a cyclic orthoester group, or a cyclic carbonate group. Those having any of the above functional group(s) may be employed without particular limitation. Of these, compounds having an alkenyl ether group include hydroxyethyl vinyl ether, hydroxylbutyl vinyl ether, dodecyl vinyl ether, propenylether propylene carbonate, and cyclohexyl vinyl ether. Cited as compounds having at least two vinyl ether groups may be cyclohexane dimethanol divinyl ether, triethylene glycol divinyl ether, and novolak type divinyl ether.

[0045] In the present invention, it is preferable that a thin transparent inorganic layer and a thin transparent organic layer are applied in the stated order onto the substrate sheet coated with the transparent primer layer, since defects such as cracking are minimized when external stress is applied to the thin transparent inorganic layer coated to secure

gas barrier properties. Consequently, in order to secure gas barrier properties, it is preferable that a thin transparent inorganic layer is further applied onto the thin transparent organic layer.

[0046] In order to enhance gas barrier properties and bending resistance at high temperature and high humidity, when a thin transparent inorganic layer and a thin transparent organic layer are regarded as one unit, it is preferable that at least two such units are applied onto the transparent primer layer on the substrate sheet coated with the transparent primer layer. Numbers of coated units are commonly 2 - 10 units, but are preferably 2 - 5 units.

[0047] In the above case in which a plurality of units is applied, when it is necessary to consider abrasion resistance, it is preferable that the thickness of the thin transparent organic layer, which is to be the uppermost layer, is more than that of the lower thin transparent organic layer. In such a case, it is preferable to satisfy the following relationship;

$$1 < R2/R1 \leq 10$$

wherein R1 represent the maximum layer thickness of the lower transparent organic layer, while R2 represents the thickness of the uppermost thin transparent organic layer. Further, the thickness of the thin transparent inorganic layer and the thin transparent organic layer, other than the uppermost thin transparent organic layer, are as follows. The thickness of the thin transparent inorganic layer is commonly 10 - 1,000 nm, but is preferably 20 - 500 nm. The thickness of the thin transparent organic layer is commonly 50 nm - 2.0 μm, but is preferably 50 nm - 1.0 μm.

[0048] Further, in the transparent barrier sheet of the present invention, other than the above-mentioned essential layers, if desirable, coated may be functional layers such as an antistatic layer, an adhesion layer, an electrically conductive layer, an antireflection layer, an ultraviolet radiation protective layer. Coated location may be suitably selected in response to the use.

(Production Method of Transparent Barrier Sheet)

[0049] Figs. 1 - 5 are schematic sectional views of the transparent barrier sheets of the present invention. However, if embodiments are in the range of the present invention, the present invention is not limited to these embodiments.

[0050] Fig. 1 shows that coated onto substrate sheet 11 are transparent primer layer 12, thin transparent inorganic layer 111, and thin transparent organic layer 112 in the stated order. Fig. 2 shows that when thin transparent inorganic layer 211 and thin transparent organic layer 212 are regarded as one unit, two units are applied onto transparent primer layer 22 of substrate sheet 21 coated with transparent primer layer 22. Fig. 3 shows that 5 units are coated compared to two units in Fig. 2. Fig. 4 shows that both sides of a substrate sheet are coated with transparent primer layers 42 and 42'. Fig. 5 shows that transparent primer layer 62, thin transparent inorganic layer 611, thin transparent organic layer 612, and thin transparent inorganic layer 621 are applied in the stated order onto substrate sheet 61.

[0051] Transparent primer layer composition is prepared by blending the above-mentioned transparent primer layer forming components or if desirable, dissolving them in solvents or dispersing them.

[0052] When a dispersion is required to form a liquid coating composition, it is possible to select any of the suitable homogenizers known in the art, such as a two-roller mill, a three-roller mill, a ball mill, a pebble mall, a COBOL mill, a tron mill, a sand mill, a sand grinder, a SQEVARI attritor, a high speed impeller homogenizer, a high speed stone mill, a high speed impact mill, DISPER, a high speed mixer, a homogenizer, an ultrasonic homogenizer, an open kneader, or a continuous kneader, and then employed.

[0053] Further listed as solvents to employ for dissolution, when required: are water; ketones such as methyl ethyl ketone, methyl isobutyl ketone, or cyclohexanone; alcohols such as ethyl alcohol, n-propyl alcohol, or isopropyl alcohol; aliphatic hydrocarbons such as heptane or cyclohexane; aromatics such as toluene or xylene; glycols such as ethylene glycol or diethylene glycol; ether alcohols such as ethylene glycol monomethyl ether; ethers such as tetrahydrofuran, 1,3-dioxysolan or 1,4-dioxane; and halogen compounds such as dichloromethane or chloroform.

[0054] It is possible to apply the transparent primer layer forming composition, prepared as above, onto a substrate sheet, employing, for example, a roller coating method, a gravure roller coating method, a direct gravure roller coating method, an air doctor coating method, a rod coating method, a kiss roller coating method, a squeezing roller coating method, a reverse roller coating method, a curtain flow coating method, a fountain method, a transfer coating method, a spray coating method, a dip coating method, or other appropriate methods. Subsequently, the resulting coating is heat-dried, followed by an aging treatment, whereby it is possible to apply a transparent primer layer onto a substrate sheet.

[0055] Further, in the present invention, when the transparent primer layer forming composition is applied onto a substrate sheet, it is preferable that after performing a suitable surface treatment selected from a flame treatment, an ozone treatment, a glow discharge treatment, a corona discharge treatment, a plasma treatment, a vacuum ultraviolet radiation exposure treatment, an electron beam exposure treatment, or a radiation exposure treatment, the transparent

primer layer forming composition is applied onto a substrate sheet. By treating the surface of the substrate sheet as described above, it is possible to enhance adhesion between the substrate sheet and the transparent primer layer.

[0056] When the employed transparent primer layer forming components are the same as the thin transparent organic layer forming compositions, the same method as used to coat the thin transparent organic layer, to be described below, may be employed.

[0057] The forming method of the thin transparent inorganic layer formed on the transparent primer layer will now be detailed.

[0058] Listed as forming methods of the thin transparent inorganic layer may, for example, be a vacuum deposition method, a sputtering method, an ion plating method, a reactive plasma deposition method, an method employing an electron cyclotron resonance plasma, a plasma chemical vapor deposition method, a thermochemical vapor deposition method, a photochemical vapor deposition method, a catalytic chemical vapor deposition method, and a vacuum ultraviolet radiation chemical vapor deposition method. Of these methods, it is preferable that the thin transparent inorganic layer is formed employing at least one of the catalytic chemical vapor deposition method (namely a Cat-CPD method), the reactive plasma deposition method (namely an RPD method), and the electron cyclotron resonance (ECR) plasma deposition method, which result in a layer exhibiting a relatively flat and smooth surface due to relatively little surface roughness on the formed thin transparent inorganic layer.

[0059] A specific method and deposition device of the above catalytic chemical vapor deposition method may suitably be selected from those described, for example, in JP-A Nos. 2002-69644, 2002-69646, 2002-299259, 2004-211160, 2004-217966, 2004-292877, 2004-315899, and 2005-179693, and may then be employed upon improvement of the shape suitable for the purpose of the present invention.

[0060] Further, a specific method and deposition device of the reactive plasma vapor deposition method may suitably be selected from those described, for example, in JP-A Nos. 2001-262323, 2001-295031, 2001-348660, 2001-348662, 2002-30426, 2002-53950, 2002-60929, 2002-115049, 2002-180240, 2002-217131, 2002-249871, 2003-105526, 2004-76025, and 2005-34831, and may then be employed upon improvement of the shape suitable for the purpose of the present invention.

[0061] Still further, a specific method and deposition device of the ECR plasma deposition method may suitably be selected from those described, for example, on pages 152 - 154 and 226 in Tatsuo Asagi, "Hakumaku Sakusei no Kiso (Basis of Thin Layer Formation)" (published by Nikkan Kogyo Shinbun Sha, March 1996), and in JP-A Nos. 3-197682, 4-216628, 4-257224, 4-311036, 5-70955, 5-90247, 5-9742, 5-117867, 5-129281, 5-171435, 6-244175, 6-280000, 7-263359, 7-335575, 8-78333, 9-17598, 2003-129236, 2003-303698, and 2005-307222, and may then be employed upon improvement of the shape suitable for the purpose of the present invention.

[0062] Further, employed as the deposition method of the thin transparent organic layer formed on the above-mentioned thin transparent inorganic layer may be a coating when the above primer layer is formed, or a deposition method. However, in the transparent barrier sheet of the present invention, it is preferable to employ the deposition method so that the thin transparent inorganic layer, functioning as a barrier layer, is not damaged.

[0063] More specifically, when photopolymerization initiators are employed as a polymerization initiator after depositing a composition incorporating compounds having oxetane rings and compounds having oxirane rings as an essential component onto the thin transparent inorganic layer, via exposure to actinic radiation such as ultraviolet radiation, visible light, or near infrared radiation capable of allowing the polymerization initiators to initiate polymerization, it is possible to form a thin transparent organic layer upon polymerizing the compounds having oxetane rings and the compounds having oxirane rings.

[0064] Further, when heat polymerization initiators are employed as a polymerization initiator, polymerization reaction is initiated from the heat polymerization initiators while heated, whereby it is possible to form the thin transparent organic layer via polymerizing compounds having oxetane rings and compounds having oxirane rings.

[0065] When a thin transparent inorganic layer and a thin transparent organic layer are continuously applied onto a film-type substrate sheet, or when productivity is the main concern, it is preferable to employ photopolymerization initiators which tend to simplify the polymerization process.

[0066] In order to deposit a composition incorporating compounds having oxetane rings and compounds having oxirane rings as an essential component, deposition conditions may be set for each of the compounds. Further, when no polymerization reaction proceeds during layer formation via deposition and no problem occurs due to some difference in the deposition rate via monomers, deposition conditions may be set for the mixture of compositions.

[0067] A specific method and layer forming device of the above-mentioned deposition method may suitably be selected from those described, for example, in JP-A Nos. 5-125520, 6-316757, 7-26023, 9-272703, 9-31115, 10-92800, 10-168559, 10-289902, 11-172418, 2000-87224, 2000-127186, 2000-348971, 2003-3250, 2003276115, 2003-300273, 2003-322859, 2003-335880, 2003-341003, 2005-14483, 2005-125731, and 2005-178010, as well as in Japanese Patent Publication Open to Public Inspection (under PCT Application) Nos. 8-503099, 2001-508089, 2001-518561, and 2004-524958, and may then be employed upon improvement of the shape suitable for the purpose of the present invention.

[0068] Further, to minimize thermal deformation of substrate sheets during preparation of the transparent barrier sheet

of the present invention, it is preferable to regulate the maximum attained temperature T, in K of the substrate sheet to the range of 242 - 383 K, but is more preferably to regulate it to the range of 243 - 333 K. Further, it is more preferable that maximum attained temperatures T (in K) of the substrate sheet is within the range represented by following Formula (3):

$$\text{Formula (3)} \quad 0.46 \leq T/Tg \leq 0.98$$

wherein Tg (in K) represents the glass transition temperature of the resin employed in the substrate sheet.

[0069] Further, when a rolled film product is employed as a substrate sheet employed to form a transparent barrier sheet, tension is applied to the unwinding side and the winding side during casting, and a thin transparent inorganic layer and a thin transparent organic layer are cast while being conveyed. In such a case, rather than casting in the form of substrate sheets, due to occasional cases in which thermal deformation of the substrate sheet is enhanced, it is preferable to satisfy the conditions of following Formula (1) wherein T (in K) represents a maximum attained temperature and S (in seconds) represents the casting time, so that it is possible to produce transparent barrier sheets of minimal defects. Further, it is preferable to satisfy the conditions of Formula (2) since it is possible to produce transparent barrier sheets with fewer defects. Maximum attained temperature T (in K) of the substrate sheet during formation of the thin transparent organic layer and the thin transparent inorganic layer and casting time S (in seconds), as described herein, relate to the process forming single layer. When the thin transparent organic layer and the thin transparent inorganic layer are superposed to form a plurality of layers, above T and S represent casting conditions of each of the single layers. Further, casting time, as described herein, represents the casting time at a certain point of the substrate sheet.

$$\text{Formula (1)} \quad 1.21 \leq (T \times S)/1000 \leq 460$$

$$\text{Formula (2)} \quad 1.21 \leq (T \times S)/1000 \leq 350$$

[0070] On the other hand, in the transparent barrier sheet of the present invention, other than the above-mentioned essential layers, functional layers such as an antistatic layer, an adhesion layer, an antireflection layer, an ultraviolet radiation protective layer or a near infrared radiation protective layer, which are provided to meet requirements, may be coated via suitable selection of the coating method employed for the above-mentioned transparent primer layer, thin transparent inorganic layer or thin transparent organic layer.

EXAMPLES

[0071] The barrier sheet of the present invention will now be described with reference to specific examples, however the present invention is not limited thereto. "Parts" represent parts by weight unless otherwise specified.

Example 1

(Preparation of Transparent Barrier Sheets 1-A - 1-F)

[0072] As a substrate sheet coated with a 100 μm thick transparent primer layer on both sides, a biaxially stretched polyethylene terephthalate (COSMOSHINE A-4300, produced by TOYOBO Co., Ltd.) was prepared. A 10 °C cooling plate was placed on the reverse side of the substrate. Subsequently, a thin transparent inorganic layer composed of a silicon oxide was formed under layer forming conditions of a discharge electric current of 120 A and a layer forming pressure of 0.1 Pa, as well as under an ambient gas condition of argon : oxygen = 1 : 5 while employing silicon as a solid target, employing a reactive type plasma vapor deposition apparatus (a small sized plasma layer forming apparatus: compatible with 370 x 480 mm, produced by Sumitomo Heavy Industries, Ltd.).

[0073] On the reverse of the substrate sheet coated with the transparent primer layer having thereon the above thin transparent inorganic layer, placed was a 10 °C cooling plate and loaded in a vacuum tank. Separately, a thin transparent organic layer forming composition was prepared by completely dissolving 40 parts of 3,4-epoxycyclohexenylmethyl-3', 4'-epoxycyclohexane carboxylate, 59 parts of di[1-ethyl(3-oxetanyl)]methyl ether, and 1 part of hexafluoroantimonate allyliodonium. After lowering the pressure in the tank to an order of 10^{-4} Pa, the resulting composition was introduced

into an organic deposition source. Subsequently, heating the resistor was initiated, and when impurities were completely vaporized, the deposition shutter was opened, whereby a thin transparent organic layer was deposited. Thereafter, UV at an integral radiation of 500 mJ/cm^2 was exposed to form a thin transparent organic layer, whereby each of Transparent Barrier Sheets 1-A - 1-F was prepared.

[0074] Table 1 shows the layer thickness and the layer forming time during layer formation of the resulting thin transparent inorganic and organic layers, and the maximum attained temperature T (in K) of the substrate sheet. Maximum attained temperature T (in K) during layer formation was determined as follows. A thermo-label was adhered onto the surface of the formed layer and after forming the thin layer, the temperature was confirmed.

[0075] Resulting transparent barrier sheets were evaluated for gas barrier properties and bending resistance, as described below. Table 1 shows the results.

(Preparation of Transparent Barrier Sheets R-1A and R-1B)

[0076] A biaxially stretched polyethylene terephthalate (COSMOSHINE A-4300 produced by TOYOBO Co., Ltd.) film having a thickness of 125 μm as a substrate sheet, provided with a transparent primer layer on both sides, was placed in a vacuum tank. After lowering the pressure to an order of 10^{-4} Pa, a thin transparent inorganic layer having a thickness of 60 nm composed of silicon oxide was formed employing the electron beam deposition method while using silicon oxide as a target.

[0077] Thereafter, in the state in which the degree of vacuum in the vacuum tank was stabilized in an order of 10^{-4} Pa, heating the resistor was initiated. When vaporization of impurities was completed, the deposition shutter was opened and a thin transparent inorganic layer was deposited employing an uncured resin composed of one part of a photopolymerization initiator (IRUGACURE 907, produced by Ciba Specialty Chemicals Co.) to 100 parts of bifunctional dicyclopentadienyl diacrylate as an organic deposition source.

[0078] After closing the deposition shutter, the UV lamp shutter was opened, and the monomers were cured at an integral radiation of 500 mJ/cm^2. By forming the thin transparent organic layer, described as above, Transparent Barrier Sheets R-1A and R-1B were prepared and employed as a comparative example.

[0079] Table 1 shows the thickness of the resulting thin Transparent inorganic and organic layers, the layer forming time during layer formation, and the maximum attained temperature T (in K) of the substrate sheet during layer formation. Maximum attained temperature T (in K) during layer formation was determined as follows. A thermo-label was adhered onto the surface of the formed layer and after forming the thin layer, the temperature was confirmed.

[0080] The transparent barrier sheets, prepared as above, were evaluated for gas barrier properties and bending resistance, as described below. Table 1 shows the results.

(Evaluation of Gas Barrier Properties)

(Evaluation of Water Vapor Barrier Properties)

[0081] Water vapor barrier properties of each of the transparent barrier sheets, prepared via the above method, were determined at 35 °C and 90% relative humidity, employing a water vapor permeability meter (OXTRAN 2/21, produced by MOCON Co.). Table 1 shows the results.

(Evaluation of Oxygen Barrier Properties)

[0082] Oxygen permeability of each of the transparent barrier sheets, prepared via the above method, was determined at 35 °C and 0% relative humidity, employing an oxygen permeability meter (PERMATRAN-W 3/32, produced by MOCON Co.). Table 1 shows the results.

(Evaluation of Bending Resistance)

[0083] Each of the transparent barrier sheets, prepared via the above method, was repeatedly bent 20 times to an angle of 180 degrees along a 30 mmϕ stainless steel rod while the thin layer was oriented to the outer side. The above sheet was evaluated in the same manner as for water vapor barrier properties.

Table 1

			Inv.	Inv.	Inv.	Inv.	Inv.	Inv.	Comp.	Comp.
Transparent Barrier Sheet No.			1-A	1-B	1-C	1-D	1-F	1-E	R-1A	R-1B
Glass Transition Temperature of Substrate Sheet Component		Tg[K]	340	340	340	340	340	340	340	340
Thin Transparent Inorganic Layer	Layer Thickness	[nm]	60	100	150	200	200	200	60	60
	Maximum Attained Temperature	T[K]	288	288	288	293	288	293	333	333
	Layer Firming Time	S (seconds)	20	30	45	60	60	60	60	60
		T x S/1000 (K·second)	5.76	8.64	13.0	17.6	17.3	17.6	19.98	19.98
Thin Transparent Organic Layer	Layer Thickness	[nm]	100	200	250	400	300	500	500	1000
	Maximum Attained Temperature	T[K]	288	288	293	298	293	298	298	318
	Layer Forming Time	S (seconds)	75	150	188	300	225	375	375	750
		T x S/1000 (K·second)	21.6	43.2	54.9	89.4	65.925	112	112	238.5
Evaluation of Gas Barrier Properties	Water Vapor Permeability	(g/m^2·24hr· 35 °C·90%)	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	0.07	0.05
	Oxygen Permeability	(ml/m^2·24hr· 35 °C·0%)	0.04	0.02	<0.01	<0.01	<0.01	<0.01	0.11	0.08
Evaluation of Bending Resistance	Water Vapor Permeability	(g/m^2·24hr· 35 °C·90%)	0.06	0.04	0.03	0.02	0.02	0.02	0.14	0.12
Inv.: Present Invention, Comp.: comparative example										

[0084] As can be seen from Table 1, Transparent Barrier Sheets 1-A - 1-F exhibited superior gas barrier properties and bending resistance to Comparative Barrier Sheets R-1A and R-1B.

Example 2

(Preparation of Transparent Barrier Sheets 2-A - 2-F)

[0085] As a substrate sheet coated with a 125 μm thick transparent primer layer on both sides, a biaxially stretched polyethylene terephthalate (COSMOSHINE A-4300, produced by TOYOBO Co., Ltd.) film was prepared. Subsequently, each of Transparent Barrier Sheets 2-A - 2-F was produced by forming a thin transparent inorganic layer and a thin transparent organic layer, employing the methods described in following 1) and 2).

1) Preparation of the thin transparent inorganic layer: The deposition apparatus, shown in Fig. 6, was employed, utilizing the catalytic chemical vapor deposition method. Transparent primer layer coated substrate sheet 51 came into close contact with holding mechanism 52 as a substrate holder and placed in vacuum vessel 50. Thereafter, the pressure in the vacuum vessel 50 was reduced to at most 2 x 10^{-4} Pa, employing vacuum pump 503, and subsequently, holding mechanism 52, as a substrate holder, was cooled to 0 °C.
Subsequently, on-off valve V56 for hydrogen gas source 56 was opened and on-off valve V57 for ammonia gas source 57 was also opened, followed by introduction of hydrogen gas and ammonia gas into vacuum vessel 50. In order to decompose and activate these introduced gases, linear heater 54 arranged between gas inlet 55 and transparent primer layer coated substrate sheet 51 was heated to 1,800 °C.
Subsequently, shielding member 59, arranged between heater 54 and transparent primer layer coated substrate sheet 51, was opened, whereby the surface of transparent primer layer coated substrate sheet 51 was exposed to decomposition active spices of hydrogen gas and ammonia gas over 20 second.
Thereafter, while maintaining heater 54 at 1,800 °C, shielding member 59 was temporarily closed, and on-off valve V58 for silane gas source 58 was opened, followed by introduction of silane gas into vacuum vessel 50. Thereafter, shielding member was again opened, and 60 nm thick silicon nitride layer was formed on the surface of transparent primer layer coated substrate sheet 51.
2) Preparation of thin transparent organic layer: A 10 °C cooling plate was placed on the reverse side of a substrate the thin transparent inorganic layer and was placed in a vacuum tank. The pressure of the vacuum tank was reduced to an order of 10^{-4} Pa. Separately, the thin transparent organic layer forming composition, described in Table 2, was introduced into the organic deposition source, followed by initiation resistor heating. When impurities were completely evaporated, the deposition shutter was opened, whereby a thin transparent organic layer was deposited. Thereafter, UV at an integral radiation of 500 mL/cm^2 was emitted, whereby a thin transparent organic layer was formed.

[0086] Table 2 shows the thickness of the resulting thin transparent inorganic layer and thin transparent organic layer, the deposition time during deposition, and maximum attained temperature T (in K) of the substrate sheet during deposition.
[0087] The resulting transparent barrier sheet was evaluated for gas barrier properties and bending resistance, employing the same methods as in Example 1. Table 2 shows the results.

(Preparation of Transparent Barrier Sheets R-2A and R-2B)

[0088] Transparent Barrier Sheets R-2A and R-2B were prepared employing the same method as for Transparent Barrier Sheets R-1A and R-1B prepared in Example 1.
[0089] Table 2 shows the thickness of the resulting thin transparent inorganic layer and thin transparent organic layer, the deposition time during deposition, and maximum attained temperature T (in K) of the substrate sheet during deposition. Maximum attained temperature during layer formation was determined as follows. A thermo-label was adhered onto the surface of the formed layer and after forming the thin layer, temperature T (in K) was confirmed.
[0090] The resulting transparent barrier sheet was evaluated for gas barrier properties and bending resistance, employing the same methods as in Example 1. Table 2 shows the results.
[0091] Further, each of the compounds described in Table 2 is the following compound, and the ratio refers to the ratio by weight.

(Compounds having Oxetane Ring)

[0092]

O1 di[1-ethyl(3-oxetanyl)]methyl ether

O2: 1,4-bis{[(3-ethyl-3-oxetanyl)methoxy]methyl}benzene
O3: 3-ethyl-3-hydroxymethyloxetane

(Compounds having Oxirane Ring)

[0093]

E1: 3,4-epoxycyclohexenylmethyl-3',4'-epoxycyclohexane carboxylate
E2: 1,4-butanediol glycidyl ether
E3: 1,2-bis(3,4-epoxy-4-methylcyclohexenylcarboxy)ethane

(Photopolymerization Initiators)

[0094]

I1: diallyliodinium hexafluoroantimonate
I2: diphenyl-4-thiophenoxysulfonium hexafluoroantimonate

[0095] When formation of the thin transparent inorganic layer and the thin transparent organic layer of above 1) and 2) is referred as one cycle, the number of cycles described in Table 2 was repeated.

Table 2

			Inv.	Inv.	Inv.	Inv.	Inv.	Inv.	Comp.	Comp.
Transparent Barrier Sheet No.			2-A	2-B	2-C	2-D	2-E	2-F	R-2A	R-2B
Glass Transition Temperature of Substrate Sheet Component		Tg(K)	340	340	340	340	340	340	340	340
Thin Transparent Inorganic Layer	Layer Thickness	[nm]	60	60	60	60	60	60	60	60
	Maximum Attained Temperature	T[K]	298	298	298	298	298	298	333	333
	Layer Forming Time	*4	900	900	900	900	900	900	60	60
		*1	268	268	268	268	268	268	19.98	20.0
Thin Transparent Organic Layer	Thin Organic layer Composition	Type	O1/E1/I2	O1/E1/I2	O1/E1/I2	O1/E2/I2	O2/E3/I1	O2/E3I/I1	*	*
		Ratio	50/48/2	50/48/2	50/48/2	60/38/2	40/58/2	5.81/40/2		
	Layer Thickness	[nm]	100	200	300	300	250	250	500	1000
	Maximum Attained Temperature	T [K]	288	288	298	298	293	293	298	318
	Layer Forming Time	*4	85	175	260	260	220	220	375	750
		*1	24.5	50.4	77	77	64.5	64.5	112	238.5
Evaluation of Gas Barrier Properties	Water Vapor Permeability	*2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.07	0.05
	Oxygen Permeability	*3	0.02	0.02	0.02	0.02	0.02	0.02	0.11	0.07
Evaluation of Bending Resistance	Water Vapor Permeability	*2	0.02	0.02	0.02	0.02	0,02	0.02	0.14	0.12

Inv.: Present Invention, Comp.: Comparative Example, *: Dicyclopentadienyl acrylate
*1: T x S/1000 (K·second), *2: (g/m^2·24hr·35 °C·90%), *3: (ml/m^2·24hr·35 °C·0%),
*4: S (seconds)

[0096] As can be seen from Table 2, Barrier Sheets 2-A - 2-F of the present invention exhibited the desired gas barrier properties as well as desired bending resistance contrary to Comparative Barrier Sheets R-2A and R-2B.

Example 3

(Preparation of Transparent Barrier Sheets 3-A - 3-F)

[0097] One side of a 75 μm thick biaxially stretched polyethylene terephthalate film (LUMILAR-T60, produced by Toray Industries, Inc.), as a substrate sheet, was subjected to corona discharge treatment. Onto the corona discharged surface, a coating composition prepared by blending 98 parts of di[1-ethyl(3-oxetanyl)]methyl ether and 2 parts of diphenyl-4-thiophenoxysulfonium hexafluoroantimonate, as a polymerization initiator, was applied to reach a coating thickness of 0.5 μm. Thereafter, ultraviolet radiation in an amount which allowed the composition to sufficiently undergo reaction in the atmosphere to result in curing, was emitted employing an ultraviolet radiation exposure device (being a UV curing device incorporating a conveyer, produced by Iwasaki Electric Co., Ltd.), whereby a transparent primer layer was formed.

[0098] Subsequently, Thin Transparent Inorganic Layer A and Thin Transparent Organic Layer B described in following 3) and 4) were applied onto the substrate sheet having thereon the above transparent primer layer to result in the layer configuration described in Table 3, whereby Transparent Barrier Sheets 3-A - 3-F were prepared.

3) Preparation of Thin Transparent Inorganic Layer A: While placing a 10 °C cooling plate on the reverse side of a sheet, a thin transparent inorganic layer composed of silicon nitride oxide was formed employing an ECR plasma deposition apparatus (AFTECH ER-1200, produced by NTT Afty Corp.) in the following manner. Silicon was employed as a solid target. Layer forming conditions were at a microwave power of 500 W, an RF power of 500W, and a layer forming pressure of 0.9 Pa, while gas introduction conditions were at an argon flow rate of 40 sccm and at a gas mixture of nitrogen/oxygen = 8/2 of 0.5 sccm.
Further, the composition ratio of the resulting thin transparent inorganic layer, determined via XPS (X-ray photo-electron spectroscopy) was Si : O : N = 1.00 : 0.18 : 1.21.
4) Preparation of Thin Transparent Inorganic Layer B: On the reverse side of a sheet placed was a 10 °C cooling plate and loaded into a vacuum tank. Separately, a thin transparent organic layer forming composition was prepared by completely dissolving 30 parts of 3,4-epoxycyclohexenylmethyl-3',4'-epoxycyclohexane carboxylate, 69 parts of di[1-ethyl(3-oxetanyl)]methyl ether, and 1 part of diallyliodonium hexafluoroantimonate. After lowering the pressure in the tank to an order of 10^{-4} Pa, the resulting composition was fed into an organic deposition source. Subsequently, heating the resistor was initiated, and when impurities were completely vaporized, the deposition shutter was opened, whereby a thin transparent organic layer was deposited. Thereafter, UV at an integral radiation of 500 mJ/cm^2 was emitted to form a thin transparent organic layer, whereby a thin transparent organic layer was formed.

[0099] Table 3 shows the thickness of the resulting thin transparent inorganic layer and thin transparent organic layer, the deposition time during deposition, and maximum attained temperature T (in K) of the substrate sheet during deposition. Maximum attained temperature during layer formation was determined as follows. A thermo-label was adhered onto the surface of the formed layer and after forming the thin layer, temperature T (in K) was confirmed.

[0100] The resulting transparent barrier sheet was evaluated for gas barrier properties and bending resistance, employing the same methods as in Example 1. Table 3 shows the results.

(Preparation of Transparent Barrier Sheet R-3)

[0101] A 75 μm thick biaxially stretched polyethylene terephthalate film (LUMILAR-T60, produced by Toray Industries, Inc.), as a substrate sheet, was placed in a vacuum tank. After reducing the pressure to an order of 10^{-4} Pa, 60 nm thick Thin Transparent Inorganic Layer D composed of silicon oxide was formed via the electron beam deposition method, employing silicon oxide as a target. Thereafter, in the state in which the degree of vacuum was stabilized in an order of 10^{-4} Pa, resistor heating was initiated employing an uncured resin composed of one part of a photopolymerization initiator (IRUGACURE 907, produced by Ciba Specialty Chemicals Co.) and 100 parts of bifunctional dicyclopentadienyl diacrylate. When impurities were completely evaporated, the deposition shutter was opened, whereby 500 nm Thin Transparent Organic Layer E was deposited. Further, Thin Transparent Inorganic Layer D and Thin Transparent Organic Layer E were successively formed on Thin Transparent Organic Layer E, whereby comparative Transparent Barrier Sheet R-3 was prepared.

[0102] Table 3 shows the thickness of the resulting thin transparent inorganic layer and thin transparent organic layer, the layer forming time during layer formation, and maximum attained temperature T (in K) of the substrate sheet during layer formation. Maximum attained temperature during layer formation was determined as follows. A thermo-label was

adhered onto the surface of the formed layer and after forming the thin layer, temperature T (in K) was confirmed.

[0103] The resulting transparent barrier sheet was evaluated for gas barrier properties and bending resistance, employing the same methods as in Example 1. Table 3 shows the results.

Table 3

			Inv.	Inv.	Inv.	Inv.	Inv.	Inv.	Comp.
Transparent Barrier Sheet No.			3-A	3-B	3-C	3-D	3-E	3-F	R-3
Glass Transition Temperature of Substrate Sheet Component		Tg[K]	340	340	340	340	340	340	340
Thin Transparent Inorganic Layer	Layer Thickness	[nm]	60	60	60	100	100	100	60
	Maximum Attained Temperature	T[K]	288	288	288	293	293	293	333
	Layer Forming Time	*1	720	720	720	1200	1200	1200	60
		*2	207	207	207	352	352	352	19.98
Thin Transparent Organic Layer	Layer Thickness	[nm]	100	100	100	150	120	120	500
	Maximum Attained Temperature	T[K]	288	288	288	288	288	288	298
	Layer Forming Time	*1	75	75	75	115	90	90	375
		*2	21.6	21.6	21.6	33.1	25.9	25.9	112
Layer Configuration			C/A/B	C/A/B/A	C/A/B/A/B	C/A/B	C/A/B/A/B	C/A/B/A/ B/A/B	C/D/E/D/E
Evaluation of Gas Barrier Properties	Water Vapor Permeability	*3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.03
	Oxygen Permeability	*4	0.02	<0.01	<0.01	0.02	<0.01	<0.01	0.06
Evaluation of Bending Resistance	Water Vapor Permeability	*3	0.02	<0.01	<0.01	0.02	<0.01	<0.01	0.08

Inv.: Present Invention, Comp.: Comparative Example, *1: S (seconds),
*2: T x S/1000 (K·second), *3: (g/m^2·24hr·35 °C·90%), *4: (ml/m^2·24hr·35 °C·0%)

[0104] As can be seen from Table 3, Barrier Sheets 3-A - 3-F of the present invention exhibited the desired gas barrier properties as well as desired bending resistance contrary to Comparative Barrier Sheet R-3.

Claims

1. A transparent barrier sheet comprising:

a substrate sheet having thereon a transparent primer layer;
a transparent inorganic thin layer; and
a transparent organic thin layer,
wherein the transparent organic thin layer is formed by polymerizing a composition comprising:

a compound having an oxetane ring; and
a compound having an oxirane ring.

2. The transparent barrier sheet of claim 1,
wherein the compound having an oxetane ring comprises at least two oxetane rings in the molecule.

3. The transparent barrier sheet of claims 1 or 2,
wherein the compound having an oxirane ring comprises at least two oxirane rings in the molecule.

4. The transparent barrier sheet of any one of claims 1 to 3,
wherein the composition to form the transparent organic thin layer further comprises a compound having a group selected from the group consisting of an alkenyl ether group, an allene ether group, a ketene acetal group, a tetrahydrofuran group, an oxepane group, a single ring acetal group, a double ring acetal group, a lactone group, a cyclic orthoester group and a cyclic carbonate group.

5. The transparent barrier sheet of any one of claims 1 to 4,
wherein the transparent inorganic thin layer and the transparent organic thin layer are provided in that order on the transparent primer layer of the substrate sheet.

6. The transparent barrier sheet of claim 5,
wherein a second transparent inorganic thin layer is further provided on the transparent organic thin layer.

7. The transparent barrier sheet of any one of claims 1 to 4,
wherein a second transparent inorganic thin layer; and a second transparent organic thin layer are provided in that order on the substrate sheet having thereon the transparent primer layer, whereby at lease two units each composed of a transparent inorganic thin layer and a transparent organic thin layer are formed on the substrate sheet.

8. The transparent barrier sheet of any one of claims 1 to 7,
wherein a thickness of the transparent organic thin layer is from 50 nm to 5.0 μm.

9. A method of producing a transparent barrier sheet comprising the steps of:

forming a transparent inorganic thin layer on a substrate sheet having thereon a primer layer employing a catalytic chemical vapor deposition method, a reactive plasma deposition method or an electron cyclotron resonance plasma deposition method; and
forming a transparent organic thin layer.

10. The method of producing a transparent barrier sheet of claim 9,
wherein the transparent organic thin layer is formed by the steps of:

depositing on the transparent inorganic thin layer vapors of:

a compound having an oxetane ring;
a compound having an oxirane ring; and
a polymerization initiator,

polymerizing the deposited vapors by irradiating with actinic rays or by heating.

11. The method of producing a transparent barrier sheet of claims 9 or 10, wherein a maximum attained temperature T (in K) of the substrate sheet is controlled to be in the range of 243 to 383 K during the formations of the transparent inorganic thin layer and the transparent organic thin layer.

12. The method of producing a transparent barrier sheet of claim 11, wherein the maximum attained temperature T (in K) of the substrate sheet is controlled to satisfy Formula (1):

Formula (1)

$$1.21 \leq (T \times S)/1000 \leq 460$$

wherein S (in second) represents a required time to form the transparent inorganic thin layer and the transparent organic thin layer.

FIG. 1

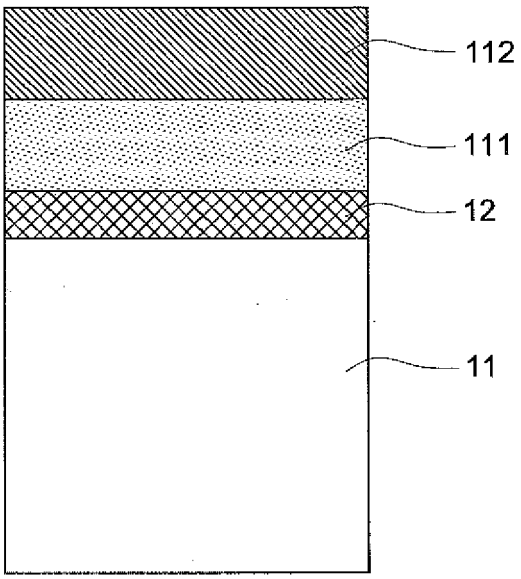


FIG. 2

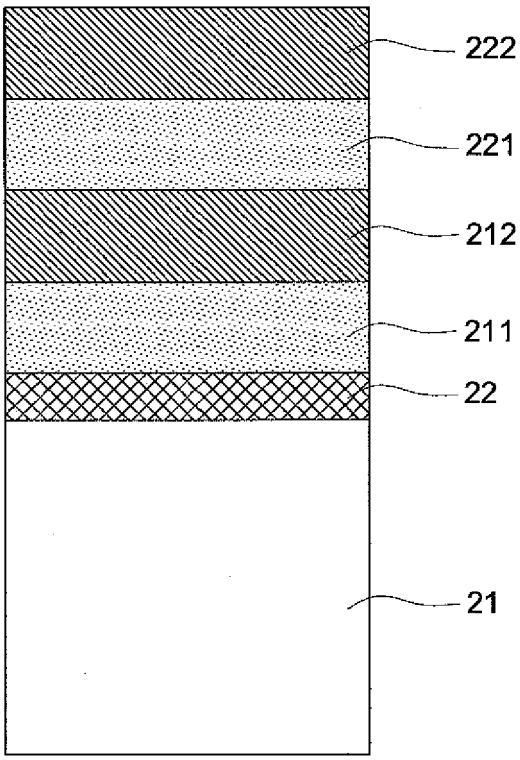


FIG. 3

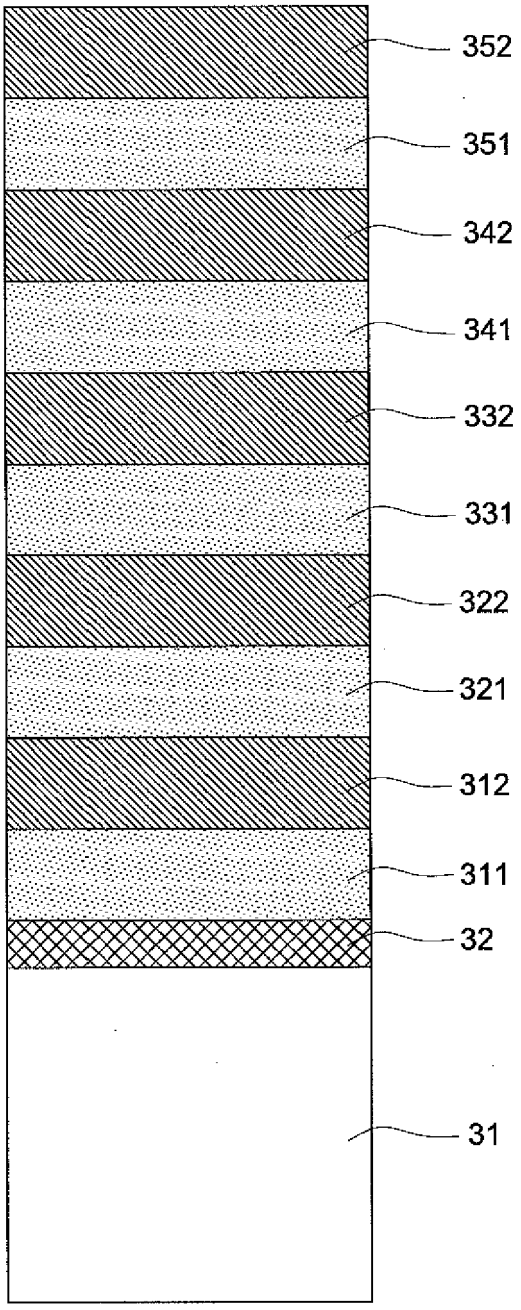


FIG. 4

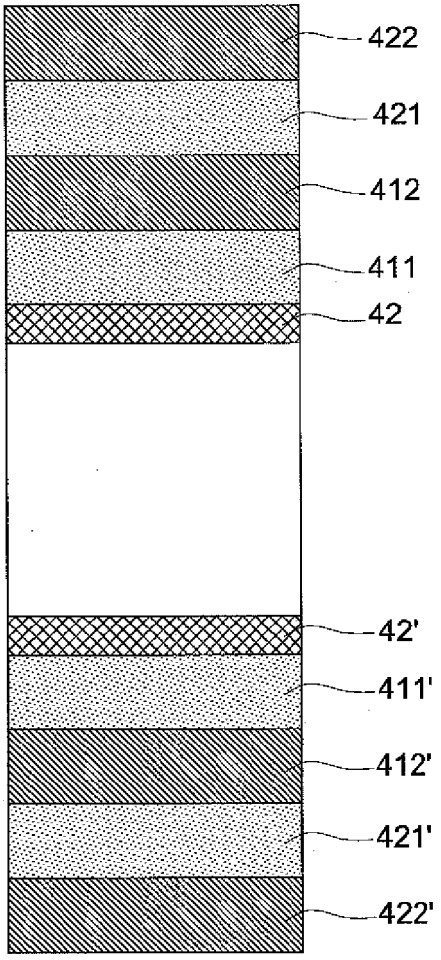


FIG. 5

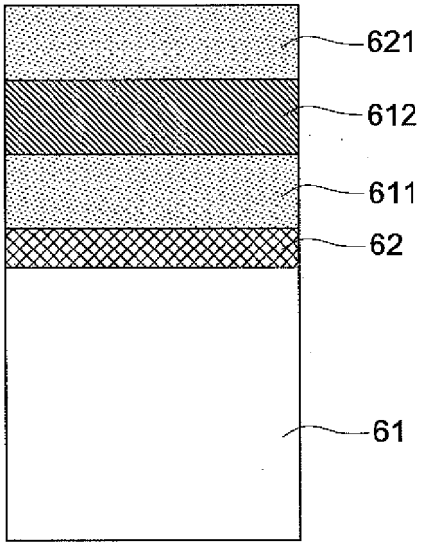
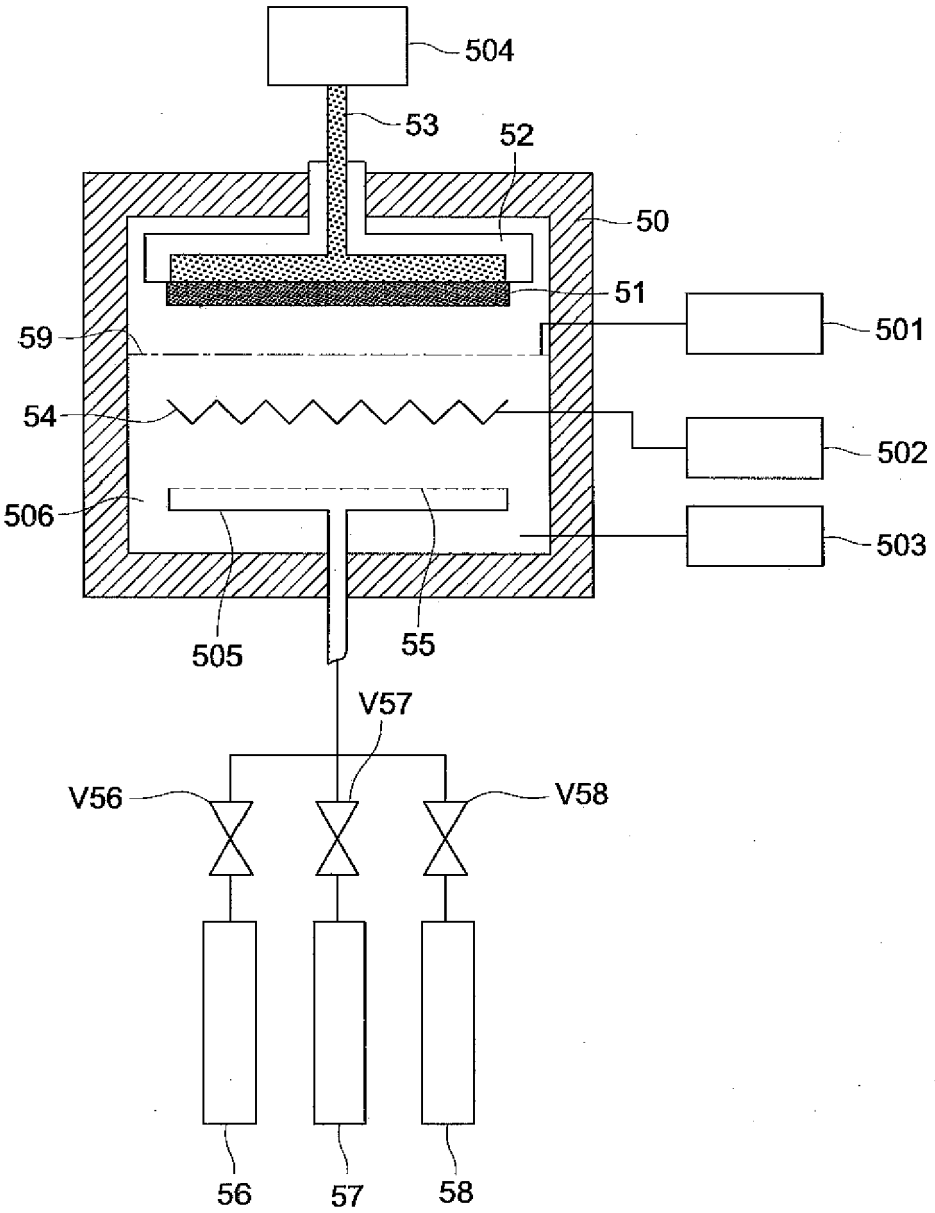


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/053904

A. CLASSIFICATION OF SUBJECT MATTER
B32B9/00(2006.01)i, *B65D65/40*(2006.01)i, *B65D81/24*(2006.01)i, *C23C14/06*(2006.01)i, *C23C16/42*(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B32B1/00-43/00, B65D65/40, B65D81/24, C23C14/06, C23C16/42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2007
Kokai Jitsuyo Shinan Koho 1971-2007 Toroku Jitsuyo Shinan Koho 1994-2007

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
11 May, 2007 (11.05.07)	22 May, 2007 (22.05.07)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
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