

DESCRIPTION

DECORATIVE SHEET FOR INJECTION MOLDING

5 TECHNICAL FIELD

The present invention relates to a decorative sheet for injection molding, which has a base film comprising a polycarbonate resin containing a constituent unit able to be derived from a carbohydrate such as starch which is a biomass resource, is excellent in moldability, chemical resistance, deformation resistance, distortion resistance and whitening resistance, decorates a resin molded product and further provides hard coat properties such as abrasion resistance and high surface hardness.

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BACKGROUND ART

Heretofore, as means of decorating a resin molded product and providing hard coat properties such as abrasion resistance and high surface hardness, there has been known a method in which a decorative sheet for injection molding having a decorative layer on a base film and a hard coat layer as an outermost surface layer is bonded to a resin molded product at the time of molding. Although films made of various resins may be used as the base film, biaxially oriented aromatic polyester films and copolyester films are used from the viewpoints of physical properties and cost (refer to JP-A 2004-82565).

Although a decorative sheet for injection molding which has a biaxially oriented aromatic polyester film as the base film is excellent in chemical resistance and whitening resistance, it is unsatisfactory in terms of moldability such as deep drawability and shape follow-up property required to form a complicated shape and has a problem such as the occurrence of deformation or distortion

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after molding by residual stress generated by stretching the base film. Although a decorative sheet for injection molding which has a copolyester film as the base film is excellent in moldability, deformation resistance and distortion
5 resistance, its solvent resistance is so unsatisfactory that the flatness of the film surface is deteriorated and/or the film is whitened by the solvent used to form a decorative layer, an adhesive layer or a hard coat layer, and further it is crystallized or whitened by heat at the time of molding
10 or bonding it to a resin molded product.

Aromatic polyester resins and aromatic polycarbonate resins are generally manufactured from raw materials derived from oil resources. However, it has recently been worried about the depletion of oil resources, and the provision of
15 plastic molded articles manufactured from raw materials obtained from biomass resources such as plants has been desired. Since it has been feared that global warming by the increase and accumulation of the discharge amount of carbon dioxide would cause climate change, the development
20 of a plastic molded article material part produced from a plastic obtained from a plant-derived monomer which is "carbon neutral" even when it is disposed of after use has been desired. This demand is strong particularly from the field of large-sized molded articles.

25 It has been proposed to obtain a carbonate polymer through transesterification with diphenyl carbonate by using isosorbide as the plant-derived monomer (refer to the specification of English Laid-open Patent Application No. 1079686). However, the obtained carbonate polymer is brown
30 and not satisfactory as a molding material in terms of mechanical strength. There has also been proposed a polycarbonate obtained by copolymerizing bisphenol A as a carbonate copolymer of isosorbide and another dihydroxy compound (refer to JP-A 56-55425). Further, attempts are

being made to improve the rigidity of a homopolycarbonate composed of isosorbide by copolymerizing isosorbide and an aliphatic diol (refer to a pamphlet of International Laid-Open WO2004/111106). The mechanical strength and
5 chemical resistance of each of these polycarbonate materials are unsatisfactory for application in molded articles.

Although carbonate polymers comprising isosorbide have been proposed as described above, it cannot be said that the polymers are resins having good total balance among heat
10 resistance, mechanical strength, chemical resistance and flowability to be used for molded articles. What are disclosed by these documents are only glass transition temperature and basic mechanical properties and not characteristic properties such as chemical resistance which
15 is important for application in molded articles.

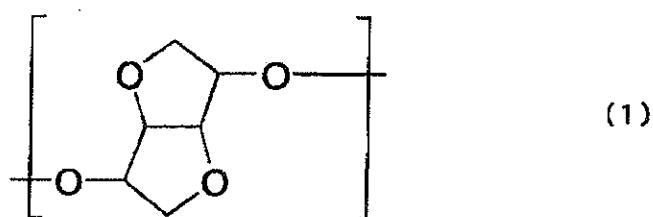
DISCLOSURE OF THE INVENTION

The inventors of the present invention have conducted intensive studies in view of the above problems and have found
20 that a decorative sheet for injection molding which has improved moldability, chemical resistance, deformation resistance and high surface hardness can be provided by using a polycarbonate resin comprising isosorbide which is a plant-derived monomer as the substrate of a base film. The
25 present invention has been accomplished based on this finding. Further, they have also found that a decorative sheet for injection molding which is excellent in deformation resistance, distortion resistance and whitening resistance is provided to decorate a resin molded product with a
30 decorative sheet for injection molding which has hard coat properties such as abrasion resistance and high surface hardness.

The above object can be attained by employing the following means. That is, according to the present invention,

there is provided a decorative sheet for injection molding, wherein a base film comprises a polycarbonate resin having a plant-derived ether diol residue, and a decorative layer is formed on at least one side of the base film.

5 The polycarbonate resin having a plant-derived ether diol residue, preferably comprises a plant-derived ether diol residue represented by the following formula (1) in an amount of 15 to 100 mol% based on the total of all the diol residues.



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The polycarbonate resin having a plant-derived ether diol residue may further comprise an aliphatic diol residue derived from an aliphatic dihydroxy compound.

15 This aliphatic dihydroxy compound is preferably a linear aliphatic diol or an alicyclic diol.

Further, the polycarbonate resin having a plant-derived ether diol residue may further comprise an aromatic diol residue derived from an aromatic dihydroxy compound.

20 The decorative sheet for injection molding of the present invention may further have an adhesive layer as an outermost surface layer.

25 The total thickness of the above base film is preferably 10 to 600 μm , and the base film is preferably an unstretched film.

30 The base film may be a multi-layer film having a layer (layer A) containing a resin composition which comprises a polycarbonate resin containing a plant-derived ether diol residue and a layer (layer B) containing an acrylic resin, wherein the layer B is formed on at least one side of the

layer A.

Alternatively, the base film may be a multi-layer film having a layer (layer A) containing a resin composition which comprises a polycarbonate resin containing a plant-derived ether diol residue and a layer (layer B) containing a resin composition which comprises a polycarbonate resin and a polyester-based thermoplastic elastomer, wherein the layer A is formed on at least one side of the layer B.

The haze of the base film is preferably not more than 10 %, and the total light transmittance of the base film is preferably not less than 85 %.

According to the present invention, there can be obtained a decorative sheet for injection molding which is excellent in moldability such as deep drawability and shape follow-up property, chemical resistance at the time of processing such as forming a decorative layer, deformation resistance and distortion resistance that it is rarely deformed and distorted after molding, and whitening resistance that the resin is rarely whitened at the time of injection molding, can decorate a resin molded product and is provided with hard coat properties such as abrasion resistance and high surface hardness.

BEST MODE FOR CARRYING OUT THE INVENTION

Preferred embodiments of the decorative sheet for injection molding of the present invention will be described hereinunder.

The decorative sheet for injection molding of the present invention has a decorative layer formed on at least one side of a base film and an adhesive layer as an outermost surface layer. That is, as for the constitution of the decorative sheet for injection molding of the present invention, the decorative sheet consists of three layers which are a base film, a decorative layer and an adhesive

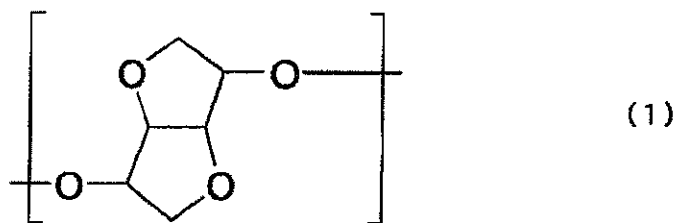
layer, three layers which are a decorative layer, a base film and an adhesive layer, or four layers which are a decorative layer, a base film, a decorative layer and an adhesive layer.

In the decorative sheet for injection molding of the present invention, a decorative layer is formed on at least one side of the base film, a hard coat layer is formed as one outermost surface layer, and an adhesive layer is formed as the other outermost surface layer. That is, the decorative sheet for injection molding of the present invention consists of four layers which are a hard coat layer, a base film, a decorative layer and an adhesive layer, four layers which are a hard coat layer, a decorative layer, a base film and an adhesive layer, or five layers which are a hard coat layer, a decorative layer, a base film, a decorative layer and an adhesive layer.

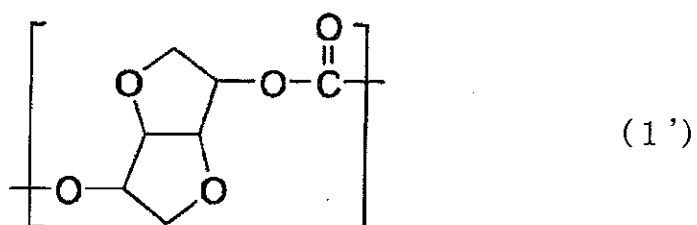
The base film used in the present invention is preferably used whether it is a single-layer film or a multi-layer film.

<base film>

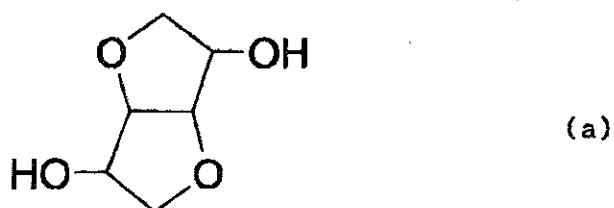
The base film used in the present invention comprises a polycarbonate resin which has a plant-derived ether diol residue, preferably a plant-derived ether diol residue represented by the following formula (1).



The polycarbonate resin has a plant-derived ether diol residue represented by the above formula (1) as a carbonate constituent unit represented by the following formula (1').

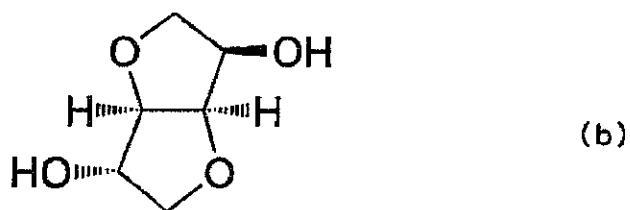


The above polycarbonate resin can be manufactured from an ether diol represented by the following formula (a) and a diester carbonate by melt polymerization.

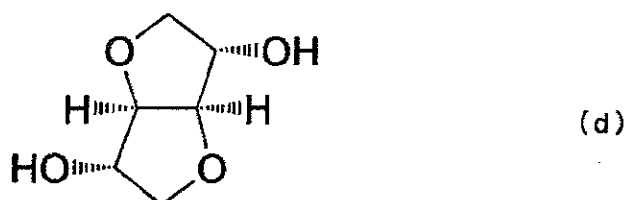
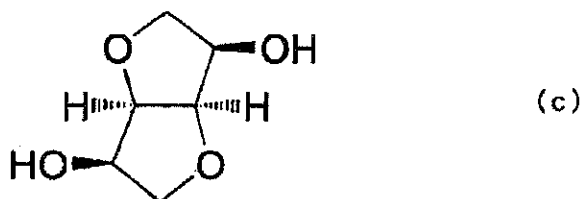


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Examples of the ether diol include isosorbide, isomannide and isoidide represented by the following formulas (b) (c) and (d), respectively.



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These carbohydrate-derived ether diols are also obtained from the biomass of the natural world and called "recyclable resources". Isosorbide is obtained by hydrogenating D-glucose obtained from starch and dehydrating the obtained hydrogenated product. The other ether diols are obtained by a similar reaction except for the starting material.

A polycarbonate resin containing a carbonate constituent unit derived from isosorbide(1,4;3,6-dianhydro-D-sorbitol) as the carbonate constituent unit represented by the above formula (1') is particularly preferred. Isosorbide is an ether diol which is easily produced from starch, can be acquired in abundance as a resource and superior to isomannide and isoidide in production ease, property and application range.

A polycarbonate containing a diol residue represented by the formula (1) in an amount of preferably 15 to 100 mol%, more preferably 30 to 100 mol%, much more preferably 40 to 100 mol%, particularly preferably 50 to 100 mol% based on the total of all the diol residues is preferred.

In the present invention, other diol compounds which can be used in combination with the plant-derived ether diol include linear aliphatic diol compounds, alicyclic diol compounds and aromatic dihydroxy compounds. They may be used alone or in combination.

The linear aliphatic diol compounds include ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 2-ethyl-1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, 1,10-decanediol, hydrogenated dilinoleyl glycol and hydrogenated dioleyl glycol. Out of these, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol and 1,10-decanediol are preferred. These linear aliphatic diols may be used alone or in combination

of two or more.

The alicyclic diols include cyclohexanediols such as 1,2-cyclohexanediol, 1,3-cyclohexanediol, 1,4-cyclohexanediol and 2-methyl-1,4-cyclohexanediol, 5 cyclohexanedimethanols such as 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol and 1,4-cyclohexanedimethanol, norbornane dimethanols such as 2,3-norbornane dimethanol and 2,5-dinorbornane dimethanol, tricyclodecane dimethanol, pentacyclopentadecane dimethanol, 1,3-adamantanediol, 10 2,2-adamantanediol, decalin dimethanol and 3,9-bis(2-hydroxy-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane. Out of these, 1,4-cyclohexane dimethanol, tricyclodecane dimethanol and 3,9-bis(2-hydroxy-1,1-dimethylethyl)-2,4,8,10- 15 tetraoxaspiro[5.5]undecane are preferred. These alicyclic diols may be used alone or in combination of two or more.

The aromatic dihydroxy compounds include 4'-biphenol, 3,3',5,5'-tetrafluoro-4,4'-biphenol, α,α' -bis(4-hydroxyphenyl)-o-diisopropylbenzene, 20 α,α' -bis(4-hydroxyphenyl)-m-diisopropylbenzene (commonly called "bisphenol M"), α,α' -bis(4-hydroxyphenyl)-p-diisopropylbenzene, α,α' -bis(4-hydroxyphenyl)-m-bis(1,1,1,3,3,3-hexafluoroisopropyl)benzene, 25 9,9-bis(4-hydroxyphenyl)fluorene, 9,9-bis(4-hydroxy-3-methylphenyl)fluorene, 9,9-bis(3-fluoro-4-hydroxyphenyl)fluorene, 9,9-bis(4-hydroxy-3-trifluoromethylphenyl)fluorene, 1,1-bis(4-hydroxyphenyl)cyclohexane, 30 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane, 1,1-bis(4-hydroxyphenyl)-4-isopropylcyclohexane, 1,1-bis(3-cyclohexyl-4-hydroxyphenyl)cyclohexane, 1,1-bis(4-hydroxyphenyl)cyclopentane, 1,1-bis(3-fluoro-4-hydroxyphenyl)cyclohexane,

- 1,1-bis(4-hydroxyphenyl)perfluorocyclohexane,
 4,4'-dihydroxydiphenyl ether,
 4,4'-dihydroxy-3,3'-dimethyldiphenyl ether,
 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxydiphenyl
 5 sulfoxide, 4,4'-dihydroxydiphenyl sulfide,
 3,3'-dimethyl-4,4'-dihydroxydiphenyl sulfide,
 3,3'-dimethyl-4,4'-dihydroxydiphenyl sulfone,
 4,4'-dihydroxydiphenyl sulfone,
 4,4'-dihydroxy-3,3'-diphenyl sulfide,
 10 4,4'-dihydroxy-3,3'-diphenyl sulfoxide,
 4,4'-dihydroxy-3,3'-diphenyl sulfone,
 1,1-bis(4-hydroxyphenyl)methane,
 1,1-bis(4-hydroxyphenyl)ethane,
 2,2-bis(4-hydroxyphenyl)propane (commonly called
 15 "bisphenol A"), 1,1-bis(4-hydroxyphenyl)-1-phenylethane,
 2,2-bis(4-hydroxy-3-methylphenyl)propane (commonly called
 "bisphenol C"), 2,2-bis(4-hydroxyphenyl)butane,
 2,2-bis(4-hydroxyphenyl)pentane,
 2,2-bis(4-hydroxy-3-phenylphenyl)propane,
 20 2,2-bis(3-isopropyl-4-hydroxyphenyl)propane,
 2,2-bis(3-tert-butyl-4-hydroxyphenyl)propane,
 2,2-bis(4-hydroxyphenyl)butane,
 4,4-bis(4-hydroxyphenyl)heptane,
 2,2-bis(4-hydroxyphenyl)octane,
 25 1,1-bis(4-hydroxyphenyl)-decane,
 1,1-bis(3-methyl-4-hydroxyphenyl)decane,
 1,1-bis(2,3-dimethyl-4-hydroxyphenyl)decane,
 2,2-bis(3-bromo-4-hydroxyphenyl)propane,
 bis(4-hydroxyphenyl)diphenylmethane,
 30 1,1-bis(4-hydroxyphenyl)-4-isopropylcyclohexane,
 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane
 (commonly called "bisphenol AF"),
 2,2-bis(4-hydroxy-3-methylphenyl)-1,1,1,3,3,3-hexafluoro
 propane,

- 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane,
 2,2-bis(3-fluoro-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane,
 5 2,2-bis(3,5-difluoro-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane,
 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane,
 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane,
 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane and
 10 2,2-bis(3-cyclohexyl-4-hydroxyphenyl)propane.

Out of these, bisphenol M,
 9,9-bis(4-hydroxy-3-methylphenyl)fluorene,
 1,1-bis(4-hydroxyphenyl)cyclohexane,
 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane,
 15 3,3'-dimethyl-4,4'-dihydroxydiphenyl sulfide, bisphenol A,
 bisphenol C, bisphenol AF and
 1,1-bis(4-hydroxyphenyl)decane are preferred. These
 aromatic diols may be used alone or in combination of two
 or more.

20 The above diol residue derived from another diol
 compound is contained in the polycarbonate resin in an amount
 of preferably 0 to 85 mol%, more preferably 0 to 70 mol%,
 much more preferably 0 to 60 mol%, particularly preferably
 0 to 50 mol% based on the total of all the diol residues.

25 The reaction temperature is preferably as low as
 possible to suppress the decomposition of the ether diol and
 obtain a resin which is rarely colored and has high viscosity.
 To promote the polymerization reaction properly, the
 polymerization temperature is preferably 180 to 280°C, more
 30 preferably 180 to 260°C.

A method in which the ether diol and the diester
 carbonate are heated under normal pressure to be pre-reacted
 with each other in the initial stage of the reaction, the
 pressure is gradually reduced, and the formed alcohol or

phenol is easily distilled off by reducing the pressure of the reaction system to 1.3×10^{-3} to 1.3×10^{-5} MPa in the latter stage of the reaction is preferred. The reaction time is preferably 0.5 to 4 hours.

5 The diester carbonate is an ester such as an aryl group or aralkyl group having 6 to 12 carbon atoms which may be substituted, or an alkyl group having 1 to 4 carbon atoms. Specific examples of the diester carbonate include diphenyl carbonate, bis(chlorophenyl)carbonate, m-cresyl carbonate,
10 dinaphthyl carbonate, bis(diphenyl)carbonate, dimethyl carbonate, diethyl carbonate and dibutyl carbonate. Out of these, diphenyl carbonate is particularly preferred from the viewpoints of reactivity and cost.

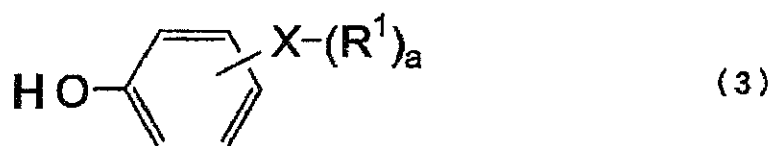
 The diester carbonate is preferably used in an amount
15 of 1.02 to 0.98 moles based on 1 mole of the ether diol. This molar ratio is more preferably 1.01 to 0.98, much more preferably 1.01 to 0.99. When the molar ratio of the diester carbonate is higher than 1.02, the carbonic acid ester residue functions as a terminal capping agent and a
20 sufficient polymerization degree is not obtained disadvantageously. When the molar ratio of the diester carbonate is lower than 0.98, a sufficient polymerization degree is not obtained as well disadvantageously.

 The polymerization catalyst is selected from alkali
25 metal compounds such as sodium hydroxide, potassium hydroxide, cesium hydroxide, sodium carbonate, potassium carbonate, cesium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, cesium hydrogen carbonate, and sodium salts, potassium salts and cesium salts of a dihydric
30 phenol; alkali earth metal compounds such as calcium hydroxide, barium hydroxide and magnesium hydroxide; and nitrogen-containing basic compounds such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, trimethylamine

and triethylamine. They may be used alone or in combination of two or more. A combination of a nitrogen-containing basic compound and an alkali metal compound is particularly preferred. A resin polymerized by using the catalyst is
 5 preferred because its 5 % weight loss temperature is kept fully high.

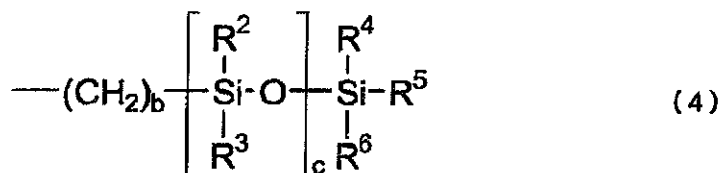
The amount of the polymerization catalyst is preferably selected from a range from 1×10^{-9} to 1×10^{-3} equivalent, more preferably from 1×10^{-8} to 5×10^{-4} equivalent
 10 based on 1 mole of the diester carbonate component. The reaction system is preferably maintained in an atmosphere of an inert gas to the raw materials, the reaction mixture and the reaction product, such as nitrogen. Examples of the inert gas except for nitrogen include argon. Further,
 15 additives such as an antioxidant may be added as required.

Although the obtained polycarbonate resin has a hydroxyl group or a diester carbonate residue at a terminal, a polycarbonate resin into which a terminal group has been introduced in limits that do not impair its characteristic
 20 properties may be used as the polycarbonate used as the polymer substrate of the base film of the present invention. The terminal group can be introduced by adding a monohydroxy compound at the time of polymerization. A hydroxyl compound represented by the following formula (2) or (3) is preferably
 25 used as the monohydroxy compound.



In the above formulas (2) and (3), R^1 is an alkyl group having 4 to 30 carbon atoms, an aralkyl group having 7 to 30

carbon atoms, perfluoroalkyl group having 4 to 30 carb atoms or organic siloxy group represented by the following formula (4), preferably an alkyl group having 4 to 20 carbon atoms, perfluoroalkyl group having 4 to 20 carbon atoms or the group of the above formula (4), particularly preferably an alkyl group having 8 to 20 carbon atoms or the group of the above formula (4).



X is at least one bond selected from the group consisting of single bond, ether bond, thioether bond, ester bond, amino bond and amide bond, preferably at least one bond selected from the group consisting of single bond, ether bond and ester bond, particularly preferably a single bond or an ester bond. "a" is an integer of 1 to 5, preferably 1 to 3, particularly preferably 1.

In the above formula (4), R^2 , R^3 , R^4 , R^5 and R^6 are each independently at least one group selected from the group consisting of alkyl group having 1 to 10 carbon atoms, cycloalkyl group having 6 to 20 carbon atoms, alkenyl group having 2 to 10 carbon atoms, aryl group having 6 to 10 carbon atoms and aralkyl group having 7 to 20 carbon atoms, preferably at least one group selected from the group consisting of alkyl group having 1 to 10 carbon atoms and aryl group having 6 to 10 carbon atoms, particular preferably at least one group selected from the group consisting of methyl group and phenyl group. "b" is an integer of 0 to 3, preferably 1 to 3, particularly preferably 2 to 3. "c" is an integer of 4 to 100, preferably 4 to 50, particularly preferably 8 to 50.

Since the polycarbonate resin used in the present invention has a carbonate constituent unit obtained from an

ether diol derived from a plant as a recyclable resource and represented by the above formula (a) in the main chain structure, the monohydroxy compound is also preferably a raw material obtained from a recyclable resource such as a plant.

- 5 Examples of the monohydroxy compound obtained from a plant include long-chain alkyl alcohols having 14 or more carbon atoms obtained from plant oil, such as cetanol, stearyl alcohol and behenyl alcohol.

The polycarbonate resin used as the polymer substrate
10 of the base film of the present invention has a biogenic matter content measured based on ASTM D6866 05 of preferably 25 to 100 %, more preferably 30 to 100 %.

The polycarbonate resin used as the above polymer substrate has a melt viscosity measured with a capillary
15 rheometer at 250°C of preferably 0.05×10^3 to 4.0×10^3 Pa·s, more preferably 0.1×10^3 to 3.0×10^3 Pa·s, particularly preferably 0.1×10^3 to 2.0×10^3 Pa·s at a shear rate of 600 sec^{-1} . When the melt viscosity falls within this range, the polycarbonate resin can be molded under a good condition
20 under which the decomposition of the polymer is suppressed and a molded article having excellent characteristic properties can be provided. When the melt viscosity is lower than the lower limit, if molding is possible, mechanical properties become unsatisfactory, when the melt viscosity
25 is higher than the upper limit, melt flowability becomes unsatisfactory, and when the molding temperature is raised, the decomposition of the polymer is accelerated.

The specific viscosity at 20°C of a solution prepared by dissolving 0.7 g of the polycarbonate resin used as the
30 substrate of the base film of the present invention in 100 ml of methylene chloride is 0.14 to 0.50. The lower limit of the specific viscosity is preferably 0.20, more preferably 0.22. The upper limit is preferably 0.45, more preferably 0.37, particularly preferably 0.35. When the specific

viscosity is lower than 0.14, it is difficult to provide satisfactory mechanical strength to the obtained base film and when the specific viscosity is higher than 0.50, melt flowability becomes too high with the result that the melt temperature having flowability required for molding becomes higher than the decomposition temperature.

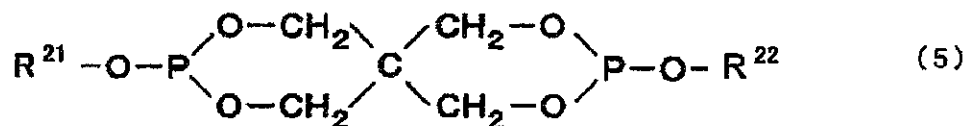
A mixture of polycarbonates may be contained in one layer, and the base film may be a multi-layer film. In this case, it is preferred that all the polycarbonates in use should satisfy the above requirements.

The lower limit of the glass transition temperature (T_g) of the polycarbonate resin used as the substrate of the base film of the present invention is preferably 80°C , more preferably 90°C or higher and the upper limit thereof is preferably 165°C . When T_g is lower than 80°C , the polycarbonate resin is inferior in heat resistance and when T_g is higher than 165°C , the polycarbonate resin is inferior in melt flowability at the time of molding and injection molding becomes impossible at a temperature range at which the decomposition of a polymer rarely occurs. T_g is measured by means of DSC (Model DSC2910 of TA Instruments Co., Ltd.

The lower limit of the 5 % weight loss temperature of the polycarbonate resin used as the substrate of the base film of the present invention is preferably 330°C , more preferably 340°C , much more preferably 350°C . When the 5 % weight loss temperature falls within the above range, the decomposition of the resin rarely occurs at the time of molding advantageously. To raise the 5 % weight loss temperature, the selection of a preferred compound as a melt polymerization catalyst is effective as described above. The 5 % weight loss temperature is measured by means of TGA (Model TGA2950) of TA Instruments Co., Ltd.

The polycarbonate resin constituting the base film of the present invention preferably contains a heat stabilizer

to obtain a better hue and stable flowability. The heat stabilizer preferably contains a phosphorus-based stabilizer, and a pentaerythritol type phosphite compound represented by the following formula (5) is preferred as the phosphorus-based stabilizer.



In the above formula, R^{21} and R^{22} are each independently a hydrogen atom, alkyl group having 1 to 20 carbon atoms, aryl or alkylaryl group having 6 to 20 carbon atoms, aralkyl group having 7 to 30 carbon atoms, cycloalkyl group having 4 to 20 carbon atoms or 2-(4-oxyphenyl)propyl-substituted aryl group having 15 to 25 carbon atoms. The cycloalkyl group and the aryl group may be substituted by an alkyl group.

Examples of the above pentaerythritol type phosphite compound include distearyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-ethylphenyl)pentaerythritol diphosphite, phenyl bisphenol A pentaerythritol diphosphite, bis(nonylphenyl)pentaerythritol diphosphite and dicyclohexyl pentaerythritol diphosphite. Out of these, distearyl pentaerythritol diphosphite and bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite are preferred.

Other phosphorus-based stabilizers except for pentaerythritol type phosphite compounds include phosphite compounds other than the above phosphite compounds, phosphate compounds, phosphonite compounds and phosphonate compounds.

The above phosphite compounds include triphenyl

phosphite, tris(nonylphenyl)phosphite, tridecyl phosphite,
 trioctyl phosphite, trioctadecyl phosphite,
 didecylmonophenyl phosphite, dioctylmonophenyl phosphite,
 diisopropylmonophenyl phosphite, monobutyldiphenyl
 5 phosphite, monodecyldiphenyl phosphite, monooctyldiphenyl
 phosphite, 2,2-methylenebis(4,6-di-tert-butylphenyl)octyl
 phosphite, tris(diethylphenyl)phosphite,
 tris(di-iso-propylphenyl)phosphite,
 tris(di-n-butylphenyl)phosphite,
 10 tris(2,4-di-tert-butylphenyl)phosphite and
 tris(2,6-di-tert-butylphenyl)phosphite.

Other phosphite compounds which react with a dihydric
 phenol to have a cyclic structure may also be used. Examples
 thereof include

15 2,2'-methylenebis(4,6-di-tert-butylphenyl)(2,4-di-tert-
 butylphenyl)phosphite,
 2,2'-methylenebis(4,6-di-tert-butylphenyl)(2-tert-butyl-
 4-methylphenyl)phosphite,
 2,2'-methylenebis(4-methyl-6-tert-butylphenyl)(2-tert-
 20 butyl-4-methylphenyl)phosphite and
 2,2'-ethylidenbis(4-methyl-6-tert-butylphenyl)(2-tert-
 butyl-4-methylphenyl phosphite.

The above phosphate compounds include tributyl
 phosphate, trimethyl phosphate, tricresyl phosphate,
 25 triphenyl phosphate, trichlorophenyl phosphate, triethyl
 phosphate, diphenylcresyl phosphate, diphenyl
 monoorthoxenyl phosphate, tributoxyethyl phosphate,
 dibutyl phosphate, dioctyl phosphate and diisopropyl
 phosphate. Out of these, triphenyl phosphate and trimethyl
 30 phosphate are preferred.

The above phosphonite compounds include
 tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene
 diphosponite,
 tetrakis(2,4-di-tert-butylphenyl)-4,3'-biphenylene

- diphosphonite,
 tetrakis(2,4-di-tert-butylphenyl)-3,3'-biphenylene
 diphosphonite,
 tetrakis(2,6-di-tert-butylphenyl)-4,4'-biphenylene
 5 diphosphonite,
 tetrakis(2,6-di-tert-butylphenyl)-4,3'-biphenylene
 diphosphonite,
 tetrakis(2,6-di-tert-butylphenyl)-3,3'-biphenylene
 diphosphonite,
 10 bis(2,4-di-tert-butylphenyl)-4-phenyl-phenyl phosphonite,
 bis(2,4-di-tert-butylphenyl)-3-phenyl-phenyl phosphonite,
 bis(2,6-di-n-butylphenyl)-3-phenyl-phenyl phosphonite,
 bis(2,6-di-tert-butylphenyl)-4-phenyl-phenyl phosphonite
 and bis(2,6-di-tert-butylphenyl)-3-phenyl-phenyl
 15 phosphonite. Out of these,
 tetrakis(di-tert-butylphenyl)-biphenylene diphosphonites
 and bis(di-tert-butylphenyl)-phenyl-phenyl phosphonites
 are preferred, and tetrakis(2,4-di-tert-butylphenyl)-
 biphenylene diphosphonites and
 20 bis(2,4-di-tert-butylphenyl)-phenyl-phenyl phosphonites
 are more preferred. These phosphite compounds may be and
 are preferably used in combination with a phosphite compound
 having an aryl group substituted by two or more of the above
 alkyl groups.
- 25 The above phosphonate compounds include dimethyl
 benzenephosphonate, diethyl benzenephosphonate and
 dipropyl benzenephosphonate.

The above phosphorus-based stabilizers may be used
 alone or in combination of two or more. It is preferred to
 30 use at least a pentaerythritol type phosphite compound in
 an effective amount. The phosphorus-based stabilizer is
 used in an amount of preferably 0.001 to 1 part by weight,
 more preferably 0.01 to 0.5 part by weight, much more
 preferably 0.01 to 0.3 part by weight based on 100 parts by

weight of the polycarbonate resin.

An antistatic agent is preferably added to or copolymerized with the polycarbonate resin used as the substrate of the base film of the present invention. The antistatic agent may be a known anionic, cationic, nonionic or amphoteric antistatic agent. Out of these, sodium alkylsulfonates and sodium alkylbenzenesulfonates all of which are anionic antistatic agents are preferably used from the viewpoint of heat resistance.

When the antistatic agent is added at the time of polymerization, an antioxidant is preferably added from the viewpoint of handling ease. Examples of the antioxidant include known antioxidants such as phenolic antioxidants, phosphite-based antioxidants and thioether-based antioxidants, and further mixtures thereof.

It is important that the base film of the present invention should be used as a film having a plane orientation coefficient of 0 to 0.05 from the viewpoint of moldability. The plane orientation coefficient is preferably 0 to 0.03. When the plane orientation coefficient is higher than 0.05, it may be difficult to form a molded product having a large molding drawing ratio. Thus, moldability may degrade disadvantageously. The term "plane orientation coefficient" as used herein means "fn" represented by the following equation (6) and indicates the orientation degree of a film.

Plane orientation coefficient: $fn = (N_x + N_y)/2 - N_z$ (6)

In the equation (6), N_x , N_y and N_z are the refractive indices of the base film in a film forming direction, width direction and thickness direction and can be measured by using an Abbe's refractometer, respectively. When the plane orientation coefficient is to be measured and the base film of the present invention is existent as a layer of the decorative sheet for injection molding, the surface layer

is filed off by using fine sandpaper to expose the base film, thereby making it possible to measure the refractive index of the base film. Similarly, when the base film itself is a laminate, the surface layer is filed off to exposure the layer to be measured for its refractive index, thereby making it possible to measure the refractive index of each layer.

When the measurement direction of the refractive index of the base film is unknown as the film forming direction of the base film is not known, the slow axis direction and the direction orthogonal to the slow axis direction are determined by confirming the slow axis direction by means of a phase difference measuring instrument such as the ellipsometer of JASCO Corporation or KOBRA of Oji Scientific Instruments Co., Ltd. The plane orientation coefficient can be obtained by measuring the refractive index by the above method, supposing that the obtained slow axis direction is the film forming direction and the direction orthogonal to the slow axis direction is the width direction.

Various kinds of particles can be added to the base film of the present invention according to purpose and use. The particles to be added are not particularly limited if they are inactive to the polycarbonate resin of the present invention. Examples of the particles include inorganic particles, organic particles, crosslinked polymer particles and internal particles formed in the polymerization system. These different kinds of particles may be used alone or in combination of two or more. The amount of the particles is preferably 0.01 to 10 wt%, more preferably 0.05 to 3 wt% based on the total weight of the base film.

In order to improve handling ease by providing slipperiness to the base film, the average particle diameter of the particles to be added is preferably 0.001 to 20 μm , more preferably 0.01 to 10 μm . When the average particle diameter is larger than 20 μm , a film defect is readily

produced, thereby causing the deterioration of moldability disadvantageously and when the average particle diameter is smaller than 0.001 μm , satisfactory slipperiness may not be obtained disadvantageously.

5 Examples of the inorganic particles include particles of carbonates such as calcium carbonate, magnesium carbonate and barium carbonate, sulfates such as calcium sulfate and barium sulfate, composite oxides such as kaolin and talc, phosphates such as lithium phosphate, calcium phosphate and
10 magnesium phosphate, oxides such as aluminum oxide, silicon oxide, titanium oxide and zirconium oxide, and salts such as lithium fluoride.

 Examples of the organic particles include particles of calcium oxalate and terephthalates of calcium, barium,
15 zinc, manganese and magnesium.

 Examples of the crosslinked polymer particles include particles of homopolymers and copolymers of a vinyl-based monomer such as divinyl benzene, styrene, acrylic acid or methacrylic acid. Other organic fine particles such as
20 polytetrafluoroethylene, benzoguanamine resin, thermosetting epoxy resin, unsaturated polyester resin, thermosetting urea resin and thermosetting phenolic resin particles are also preferably used.

 Known additives such as a flame retardant, a heat
25 stabilizer, an antioxidant, an ultraviolet absorbent, an antistatic agent, a plasticizer, a viscosity providing agent, an aliphatic acid ester, an organic lubricant such as wax, a defoaming agent such as polysiloxane, and a colorant such as a pigment or a dye can be mixed with the base film of the
30 present invention in suitable amounts as required.

 When a decorative layer, a hard coat layer or an adhesive layer is formed on the surface of the base film of the present invention, the surface of the base film may be subjected to a pre-treatment such as corona discharge

treatment, UV treatment or the application of an anchor coating agent in advance in order to improve its adhesion to each layer. As the anchor coating agent is preferably used at least one resin selected from the group consisting
5 of polyester resin, acrylic resin, acryl-modified polyester resin, polyurethane resin, polysiloxane and epoxy resin.

A decorative layer is formed on at least one side of the base film in the decorative sheet for injection molding of the present invention. The decorative layer used in the
10 present invention can take any form. For example, the decorative layer is a printed layer or a deposited layer which is directly formed on the base film, a colored resin layer which is formed on the base film, or a film layer which is decorated by printing or deposition. These layers are not
15 particularly limited.

Preferred examples of the binder resin material of the printed layer which is a type of decorative layer include polyurethane-based resins, vinyl-based resins, polyamide-based resins, polyester-based resins, acrylic
20 resin, polyvinyl acetal-based resins, polyester urethane-based resins, cellulose ester-based resins, alkyd-based resins and thermoplastic elastomer-based resins. Out of these resins, resins which can provide a soft film are particularly preferred. A color ink containing a
25 suitable color pigment or dye as a colorant is preferably mixed into the binder resin.

As means of forming the printed layer, offset printing, gravure printing and screen printing are preferably employed. When multi-color printing or gradation color is required,
30 offset printing and gravure printing are preferred. In the case of a single color, coating techniques such as gravure coating, roll coating and comma coating techniques may be employed. According to pattern, a printing technique in which a printed layer is formed on the entire surface of a

film or a printing technique in which a printed layer is partially formed may be employed.

The material for forming the deposited layer which is a type of decorative layer is preferably a metal such as aluminum, silicon, zinc, magnesium, copper, chromium or nickel chromium. From the viewpoints of design and cost, aluminum is more preferred but an alloy of two or more metal components may be used. As means of forming a metal thin film layer by deposition, an ordinary vacuum deposition method may be employed. In addition, a technique for activating an evaporated product by ion plating, sputtering or plasma may also be used. Chemical vapor deposition (so-called CVD) may also be used as a vapor deposition method in a broad sense. As evaporation sources for these, a resistance heating board system, radiation or high-frequency heating crucible system, or electron beam heating system may be used.

When the colored resin layer is to be laminated or formed on the base film as a type of decorative layer, a resin which has been colored by a dye, an organic pigment or an inorganic pigment as a colorant is formed by a coating technique or an extrusion lamination technique.

When the printed layer is formed as the decorative layer, the thickness of the decorative layer is not limited as long as the effect of the present invention is not impaired but preferably 0.01 to 100 μm from the viewpoint of moldability.

When the deposited layer is formed as the decorative layer, the thickness of the decorative layer is not limited as long as the effect of the present invention is not impaired but preferably 0.01 to 100 μm from the viewpoint of moldability.

When the resin layer is formed as the decorative layer, the thickness of the decorative layer is not limited as long as the effect of the present invention is not impaired but

preferably 0.01 to 100 μm from the viewpoint of moldability.

Even when a layer except for the printed layer, deposited layer and resin layer is used as the decorative layer, the thickness of the decorative layer is not limited
5 as long as the effect of the present invention is not impaired but preferably 0.01 to 100 μm from the viewpoint of moldability.

In the decorative sheet for injection molding of the present invention, it is desired that a hard coat layer should
10 be formed as an outermost surface layer. This hard coat layer is made of an acrylic resin, urethane-based resin, melamine-based resin, organic silicate compound, silicone-based resin or metal oxide. Silicone-based resin and acrylic resin are preferred from the viewpoints of
15 hardness and durability, and acrylic resin, especially active ray curable acrylic resin or thermosetting acrylic resin is more preferred from the viewpoints of curability, flexibility and productivity.

Various additives may be mixed into the hard coat layer
20 used in the present invention as required as long as the effect of the present invention is not impaired. For example, a stabilizer such as an antioxidant, an optical stabilizer or an ultraviolet absorbent, a surfactant, a leveling agent and an antistatic agent may be used.

25 To form the hard coat layer, off-line coating and in-line coating techniques may be employed.

In the off-line coating technique, a coating material for the coating layer comprising a thermosetting resin or an active ray curable resin as the main component is applied
30 to the base film. In the in-line coating technique, a coating material for the hard coat layer is applied in the step of forming the base film.

As means of applying a coating material containing a composition for forming the hard coat layer, various coating

techniques such as reverse coating, gravure coating, rod coating, bar coating, die coating and spray coating techniques may be employed.

Examples of the active ray used to cure the active ray curable resin include electromagnetic rays for polymerizing an acrylic vinyl group, such as ultraviolet rays (UV), electron rays and radiant rays (such as α -ray, β -ray and γ -ray). Practically, UV is easy and preferred. As UV sources may be used ultraviolet fluorescent lamps, low-pressure mercury lamps, high-pressure mercury lamps, super high-pressure mercury lamps, xenon lamps and carbon arc lamps. When the active ray is applied under a low-oxygen concentration, the active ray curable resin can be cured efficiently. Further, the electron ray system is advantageous because a photopolymerization initiator or an optical sensitizer does not need to be contained in the coating layer although equipment is expensive and must be operated in an inert gas atmosphere.

Heat required for the thermosetting of a thermosetting resin can be obtained by using a steam heater, an electric heater, an infrared heater or a far infrared heater to prepare air or inert gas heated at 140°C or higher and applying it to the substrate or the coating film by using a slit nozzle. Air heated at 200°C or higher is preferred, and nitrogen heated at 200°C or higher is more preferred as the curing speed is accelerated.

The thickness of the hard coat layer may be determined according to use but preferably 0.1 to 30 μm , more preferably 1 to 15 μm . When the thickness of the hard coat layer is smaller than 0.1 μm , if the layer is fully cured, the hard coat layer is unsatisfactory in terms of surface hardness and apt to be scratched as it is too thin. When the thickness is larger than 30 μm , the cured film is apt to be cracked by bending stress.

To provide adhesion between the resin to be molded and the decorative sheet for injection molding, an adhesive layer can be formed on the decorative sheet for injection molding of the present invention. When the hard coat layer is formed, the adhesive layer is formed on the outermost surface opposite to the hard coat layer formed surface. The material of the adhesive layer is preferably of a thermosensitive type or a pressure-sensitive type. When the resin to be molded by using the decorative sheet for injection molding is an acrylic resin, an acrylic resin is preferably used in the adhesive layer. When the resin to be molded by using the decorative sheet for injection molding is a polyphenylene oxide polystyrene-based resin, a polycarbonate-based resin, a styrene copolymer-based resin or a polystyrene-based resin, an acrylic resin, a polystyrene-based resin or a polyamide-based resin which has affinity for these resins is preferably used in the adhesive layer. When the resin to be molded by using the decorative sheet for injection molding is a polypropylene-based resin, a chlorinated polyolefin-based resin, a chlorinated ethylene-vinyl acetate copolymer-based resin, a cyclic rubber or a chromane indene-based resin is preferably used in the adhesive layer.

Known methods of forming the adhesive layer may be used, as exemplified by coating techniques such as roll coating, gravure coating and comma coating techniques, and printing techniques such as gravure printing and screen printing techniques.

The total thickness of the base film used in the present invention is preferably 10 to 600 μm , more preferably 20 to 400 μm , particularly preferably 40 to 300 μm . When the total thickness of the base film is smaller than 10 μm , the stiffness, film forming stability and flatness of the film deteriorate and the film readily creases at the time of molding disadvantageously. When the total thickness is larger than

600 μm , handling ease becomes worse and the degradation of moldability may occur in a case disadvantageously.

The base film of the present invention has a haze of preferably 0 to 10 %, more preferably 0 to 5 %, much more preferably 0 to 3 %, particularly preferably 0 to 2 %. When the haze of the base film is larger than 10 % and the base film is used as part of the decorative sheet for injection molding, visibility may deteriorate disadvantageously. Particularly when the decorative layer is formed on the adhesive layer side (opposite to the hard coat layer side) with the base film as the center, visibility may deteriorate disadvantageously. Although the haze is preferably as small as possible, it is difficult to reduce it to less than 0.1 % in fact.

The base film of the present invention has a total light transmittance of preferably 85 to 100 %, more preferably 90 to 100 %, particularly preferably 92 to 100 %. When the total light transmittance is lower than 85 % and the base film is used as the decorative sheet for injection molding, visibility may deteriorate. Particularly when the decorative layer is formed on the adhesive layer side (opposite to the hard coat layer side) with the base film as the center, visibility may deteriorate disadvantageously.

A description is subsequently given of a simultaneous injection-molding and decorating method which is the use purpose of the decorative sheet for injection molding of the present invention. The simultaneous injection-molding and decorating method is to decorate a resin molded product by arranging the decorative sheet for injection molding between a pair of molds, clamping the molds, filling a flowing resin into the cavity formed by these molds, solidifying the resin, and laminating the decorative sheet for injection molding on the surface of the resin molded product simultaneously with the molding of the resin molded product as described

in JP-B 50-19132. At this point, the hard coat layer side of the decorative sheet for injection molding is arranged in contact with the mold and the resin is poured into the adhesive layer side.

5 The simultaneous injection-molding and decorating method may be carried out in various ways. For example, the pre-molding of the decorative sheet for injection molding may or may not be carried out. The preheating of the decorative sheet for injection molding may or may not be
10 carried out. When pre-molding is carried out, the decorative sheet for injection molding is generally preheated.

 When the squeeze of the decorative sheet for injection molding is large, pre-molding is preferably carried out. When the squeeze of the decorative sheet for injection
15 molding is small, the decorative sheet for injection molding may be molded with the pressure of the resin in a flowing state to be injected. When the squeeze is small, the decorative sheet for injection molding may be molded with the pressure of the resin in a flowing state charged into
20 the mold simultaneously with the injection of the resin without pre-molding. When the decorative sheet for injection molding is to be molded with the resin pressure, the heat of the injected resin may be used without preheating the decorative sheet for injection molding. The pre-molding
25 of the decorative sheet for injection molding may be carried out by a method in which pre-molding is carried out by using an injection mold which is also used as a vacuum mold or a method in which the decorative sheet for injection molding is vacuum molded (off-line pre-molded) by using another
30 vacuum mold before the decorative sheet for injection molding is supplied between injection molds. The method in which the injection mold is also used as a vacuum mold is preferably used because pre-molding can be carried out efficiently and accurately. In the present invention, vacuum molding

includes vacuum pressure molding.

In the simultaneous injection-molding and decorating method, as the resin to be injection molded, a known resin may be used and the resin is not particularly limited. The resin to be injection molded is selected according to the required physical properties of a resin product of interest and cost. As long as the effect of the present invention is not impaired, two or more resins may be mixed together. Examples of the resin to be injection molded include, but are not limited to, acrylic resin, polyphenylene oxide polystyrene-based resin, polycarbonate-based resin, styrene copolymer-based resin, polystyrene-based resin and polypropylene-based resin.

The resin to be injection molded may be mixed with additives such as a heat-resistant stabilizer, an oxidation-resistant stabilizer, a weather-resistant stabilizer, an ultraviolet absorbent, an organic lubricant, a pigment, a dye, organic or inorganic fine particles, a filler and a nucleating agent as required.

A decorative molded article in which the decorative sheet for injection molding is laminated on the resin molded product becomes a molded article which is excellent in hard coat properties such as abrasion resistance and high surface hardness as well as the visibility of the decorative layer.

Examples

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting. The measurement of physical properties in Reference Examples, Examples and Comparative Examples was carried out as follows.

(1) Specific viscosity

A pellet was dissolved in methylene chloride to a concentration of about 0.7 g/dL to measure the specific

viscosity of the resulting solution at 20°C with an Ostwald's viscosimeter (RIGO AUTO VISCOSIMETER TYPE VMR-0525·PC). The specific viscosity (η_{sp}) is obtained from the following equation.

5 $\eta_{sp} = t/t_0 - 1$

t : flow time of a specimen solution

t_0 : flow time of a solvent alone

(2) Glass transition temperature

This was measured with the DSC (Model DSC2910) of TA
10 Instruments Co., Ltd.

(3) Thickness and layer thickness

To measure the thickness of the whole film, a dial gauge was used to measure the thickness of each sample cut out from the film at 5 arbitrary sites so as to obtain the average
15 value of these measurement data.

(4) Plane orientation coefficient (f_n)

The refractive index in the film forming direction (N_x), the refractive index in the width direction (N_y) and the refractive index in the thickness direction (N_z) of the
20 surface of the base film were measured by using sodium D line (wavelength of 589 nm) as a light source, methylene iodide as an intermediate liquid and the DR-M2 Abbe refractometer of Atago Co., Ltd. equipped with polarization eyepiece lenses so as to calculate the plane orientation coefficient (f_n)
25 from the following equation (6).

Plane orientation coefficient $f_n = (N_x + N_y)/2 - N_z$ (6)

(5) Total light transmittance and haze

The total light transmittance and haze were measured by using the NDH-200 (D65 light source) of Nippon Denshoku
30 Industries Co., Ltd. The measurement was made 5 times and the average value of the measurement data was used as a measurement value.

(6) Solvent resistance of base film

After 3 ml of each of methyl ethyl ketone, methyl

isobutyl ketone and toluene was dropped on different spots of the haze measurement portion of the base film and left for 6 hours, the solvent was cleaned off to judge a change before and after the dropping of the solvent visually.

5 ○: not changed by all the solvents

△: not ○ and not ×

×: whitened and dissolved by all the solvents

(7) Heat moldability of decorative sheet for injection molding

10 The heat moldability of the decorative sheet for injection molding at 100 to 200°C was evaluated by using a cup type vacuum molding machine. The transferability of each corner portion, thickness uniformity and the existence of whitening were evaluated by using a cylindrical cup-like mold
15 having a diameter of 50 mm, a depth of 50 mm and a fixed diameter in the depth direction.

○: transferability, thickness uniformity and whitening resistance are excellent

×: NG in any one of them

20 (8) Toughness of decorative sheet for injection molding

For the evaluation of heat moldability by a vacuum molding machine, whether the film was cracked or broken when it was stretched in a mold shape and removed from the mold was judged based on the following criteria.

25 Excellent: when the film is removed, it is not cracked or broken

Cracked: when the film is removed, the film is cracked or broken

(9) Deformation resistance and distortion resistance of decorative sheet for injection molding
30

The deformation and distortion of the decorative sheet for injection molding after molding were evaluated visually by using the above cup type vacuum molding machine.

(10) Abrasion resistance of decorative sheet for injection

molding

The surface of the hard coat layer of the decorative sheet for injection molding was rubbed with Steel Wool #0000 10 times, wherein one reciprocation of rubbing counts as 1 times, under a load of $1,000 \text{ g/cm}^2$ to judge its abrasion resistance visually.

(11) Pencil hardness of decorative sheet for injection molding

This was measured in accordance with JIS K-5400. The measurement was made 5 times to obtain the average value of the measurement data. A decorative sheet having a pencil hardness of HB or more was accepted.

(12) Adhesion between decorative sheet for injection molding and resin molded product

Cuts as deep as the resin molded product were made in a grid form on the surface of the decorative sheet laminated on the decorated resin molded product. Then an adhesion test was made by putting "Cellotape" (registered trademark) adhesive cellophane tape (24 mm wide, for industrial use) of Nichiban Co., Ltd. on the cuts and stripping the tape by hand to observe and judge the existence of peeling visually.

Example 1

1,608 parts by weight (11 moles) of isosorbide and 2,356 parts by weight (11 moles) of diphenyl carbonate were fed to a reactor, and 1.0 part by weight (1×10^{-4} mole based on 1 mole of the diphenyl carbonate component) of tetramethylammonium hydroxide as a polymerization catalyst and 1.1×10^{-3} part by weight (0.25×10^{-6} mole based on 1 mole of the diphenyl carbonate component) of sodium hydroxide were fed to the reactor to carry out a melt reaction by heating at 180°C under normal pressure in a nitrogen atmosphere.

The inside pressure of the reactor was gradually reduced to $13.3 \times 10^{-3} \text{ MPa}$ over 30 minutes under agitation

while the formed phenol was distilled off. After the reaction was carried out in this state for 20 minutes, the temperature was raised to 200°C, the pressure was gradually reduced over 20 minutes to carry out the reaction at 4.00
5 $\times 10^{-3}$ MPa for 20 minutes while the phenol was distilled off, and the temperature was further raised to 220°C to carry out the reaction for 30 minutes and then to 250°C to carry out the reaction for another 30 minutes.

Thereafter, the pressure was gradually reduced to
10 continue the reaction at 2.67×10^{-3} MPa for 10 minutes and at 1.33×10^{-3} MPa for 10 minutes, and when the pressure was further reduced to 4.00×10^{-5} MPa, the temperature was gradually raised to 260°C to carry out the reaction at 260°C and 6.66×10^{-5} MPa for 1 hour in the end. The polymer after
15 the reaction was pelletized. The obtained polymer had a specific viscosity of 0.26 and a glass transition temperature of 163°C.

After the obtained polycarbonate resin was dried, melt film formation was carried out by using a 40 mm-diameter
20 single-screw extrusion film forming machine to obtain a film. The cylinder temperature of the extruder was kept at a range of 220 to 260°C, static electricity was applied to the both ends of a sheet extruded from a slit die by using a needle-like edge pinning device, and the sheet was brought into close
25 contact with a casting drum (surface temperature was adjusted to 150°C) to be solidified by cooling from a molten state so as to obtain the base film having a thickness of 100 μm of the present invention. The plane orientation coefficient, total light transmittance, haze, solvent
30 resistance and pencil hardness of the film were evaluated, and the results are shown in Table 1.

Example 2

The melt polymerization of a polycarbonate resin was

carried out in the same manner as in Example 1 except that 66.42 parts by weight (0.45 mole) of isosorbide, 11.52 parts by weight (0.15 mole) of 1,3-propanediol (PD) and 129.81 parts by weight (0.61 mole) of diphenyl carbonate were fed to a reactor and 1.0 part by weight (1×10^{-4} mole based on 1 mole of the diphenyl carbonate component) of tetramethylammonium hydroxide as a polymerization catalyst and 1.1×10^{-3} part by weight (0.25×10^{-6} mole based on 1 mole of the diphenyl carbonate component) of sodium hydroxide were used. The obtained polymer had a specific viscosity of 0.25 and a glass transition temperature of 116°C.

A base film was obtained from the obtained polycarbonate resin in the same manner as in Example 1. The plane orientation coefficient, total light transmittance, haze, solvent resistance and pencil hardness of the film were evaluated, and the results are shown in Table 1.

Example 3

The melt polymerization of a polycarbonate resin was carried out in the same manner as in Example 1 except that 731 parts by weight (5.0 moles) of isosorbide, 720 parts by weight (5.0 moles) of 1,4-cyclohexane dimethanol (CHDM) and 2,142 parts by weight (10 moles) of diphenyl carbonate were fed to a reactor and 1.0 part by weight (1×10^{-4} mole based on 1 mole of the diphenyl carbonate component) of tetramethylammonium hydroxide as a polymerization catalyst and 1.1×10^{-3} part by weight (0.25×10^{-6} mole based on 1 mole of the diphenyl carbonate component) of sodium hydroxide were used. The obtained polymer had a specific viscosity of 0.35 and a glass transition temperature of 104°C.

A base film was obtained from the obtained polycarbonate resin in the same manner as in Example 1. The plane orientation coefficient, total light transmittance, haze, solvent resistance and pencil hardness of the film were

evaluated, and the results are shown in Table 1.

Example 4

The melt polymerization of a polycarbonate resin was carried out in the same manner as in Example 1 except that 1,169 parts by weight (8.0 moles) of isosorbide, 653 parts by weight (2.0 moles) of 1,1-bis(4-hydroxyphenyl)decane (may be abbreviated as DED hereinafter) and 2,142 parts by weight (10 moles) of diphenyl carbonate were fed to a reactor and 1.0 part by weight (1×10^{-4} mole based on 1 mole of the diphenyl carbonate component) of tetramethylammonium hydroxide as a polymerization catalyst and 1.1×10^{-3} part by weight (0.25×10^{-6} mole based on 1 mole of the diphenyl carbonate component) of sodium hydroxide were used. The obtained polymer had a specific viscosity of 0.25 and a glass transition temperature of 110°C . A base film was obtained from the obtained polycarbonate resin in the same manner as in Example 1. The plane orientation coefficient, total light transmittance, haze, solvent resistance and pencil hardness of the film were evaluated, and the results are shown in Table 1.

Example 5

The melt polymerization of a polycarbonate was carried out in the same manner as in Example 1 except that 1,023 parts by weight (7.0 moles) of isosorbide, 432 parts by weight (3.0 moles) of 1,4-cyclohexane dimethanol, 2,142 parts by weight (10 moles) of diphenyl carbonate and 54 parts by weight (0.20 mole) of stearyl alcohol were fed to a reactor and 1.0 part by weight (1×10^{-4} mole based on 1 mole of the diphenyl carbonate component) of tetramethylammonium hydroxide as a polymerization catalyst and 1.1×10^{-3} part by weight (0.25×10^{-6} mole based on 1 mole of the diphenyl carbonate component) of sodium hydroxide were used. The obtained

polymer had a specific viscosity of 0.30 and a glass transition temperature of 114°C.

A base film was obtained from the obtained polycarbonate resin in the same manner as in Example 1. The plane orientation coefficient, total light transmittance, haze, solvent resistance and pencil hardness of the film were evaluated, and the results are shown in Table 1.

Example 6

The melt polymerization of a polycarbonate was carried out in the same manner as in Example 1 except that 1,169 parts by weight (8.0 moles) of isosorbide, 2,142 parts by weight (10 moles) of diphenyl carbonate and 236 parts by weight (2 moles) of hexanediol (HD) were fed to a reactor and 1.0 part by weight (1×10^{-4} mole based on 1 mole of the diphenyl carbonate component) of tetramethylammonium hydroxide as a polymerization catalyst and 1.1×10^{-3} part by weight (0.25×10^{-6} mole based on 1 mole of the diphenyl carbonate component) of sodium hydroxide were used. The obtained polymer had a specific viscosity of 0.27, a glass transition temperature of 111°C and a 5 % weight loss temperature of 348°C.

A base film was obtained from the obtained polycarbonate resin in the same manner as in Example 1. The plane orientation coefficient, total light transmittance, haze, solvent resistance and pencil hardness of the film were evaluated, and the results are shown in Table 1.

Example 7

(molding material A)

The polycarbonate resin obtained in Example 6 was prepared.

(molding material B)

Acrylic resin (Acrypet VH001 of Mitsubishi Rayon Co.,

Ltd.; standard grade) was prepared as molding material B for the layer B.

(co-extrusion)

The molding material A and the molding material B were
5 each extruded from a 300 mm-wide T die at a cylinder
temperature of 230 to 250°C (molding material A) and 240 to
270°C (molding material B) by using a single-screw extruder
having a screw diameter of 40 mm in accordance with a feed
block system, one side of each of the molten resins was brought
10 into contact with a cooling roll to be cooled, and then a
multi-layer film having a width of 200 mm and consisting of
layer B, layer A and layer B was formed. The plane
orientation coefficient, total light transmittance, haze,
solvent resistance, pencil hardness, heat moldability and
15 toughness of the film were evaluated, and the results are
shown in Table 2.

Example 8

(molding material A)

20 The polycarbonate resin obtained in Example 6 was
prepared.

(molding material B)

Preparation Example 1 (production of polyester-based
thermoplastic elastomer)

25 175 parts by weight of dimethyl isophthalate, 23 parts
by weight of dimethyl sebacate and 140 parts by weight of
hexamethylene glycol were subjected to a transesterification
reaction by using a dibutyltin diacetate catalyst and
polycondensed under reduced pressure to obtain an amorphous
30 polyester (soft segment) which had an intrinsic viscosity
of 1.06 and did not show any heat absorption peak caused by
the melting of a crystal in DSC measurement.

A pellet (hard segment) of polybutylene terephthalate
having an intrinsic viscosity of 0.98 obtained by

polycondensation was dried, 107 parts of this pellet was added to this polyester so as to carry out a reaction at 240°C for 45 minutes, and 0.1 part of phenylphosphonic acid was added to terminate the reaction. The obtained polymer had
5 a melting point of 190°C and an intrinsic viscosity of 0.93.

A polycarbonate resin pellet (Panlite L-1250 of Teijin Chemicals Ltd., viscosity average molecular weight of 23,700) and the polyester-based thermoplastic elastomer produced above were pre-dried in advance and mixed together
10 in a weight ratio of 90/10 (100/11.1) (parts by weight) of polycarbonate resin/polyester-based thermoplastic elastomer by means of a twin-cylinder mixer, and the resulting mixture was extruded at a cylinder temperature of 260°C by using a double-screw extruder to be pelletized so
15 as to obtain a molding material A for the layer A. The glass transition temperature of the molding material A was 111°C.

(co-extrusion)

The molding material A and the molding material B were
20 each extruded from a 300 mm-wide T die at a cylinder temperature of 230 to 250°C (molding material A) and 240 to 270°C (molding material B) by using a single-screw extruder having a screw diameter of 40 mm in accordance with the feed block system, one side of each of the molten resins was brought
25 into contact with a cooling roll to be cooled, and then a multi-layer film having a width of 200 mm and consisting of layer A, layer B and layer A was formed. The plane orientation coefficient, total light transmittance, haze, solvent resistance, pencil hardness, heat moldability and
30 toughness of the film were evaluated, and the results are shown in Table 2.

[decorative layer]

"NT-Hiramic" (registered trademark) 701R White of

Dainichiseika Color & Chemicals Mfg. Co., Ltd. was mixed with a mixed solution of ethyl acetate, methyl ethyl ketone and isopropyl alcohol in a weight ratio of 2:2:1 to adjust its printing viscosity to 15 seconds (Zahn Cup #3), and the base
5 film was printed with a pattern by a gravure printing technique and dried in a 70°C oven for 10 seconds to form a 35 µm-thick decorative layer.

[hard coat layer]

10 An active ray curable resin comprising 67 wt% of dipentaerythritol hexaacrylate, 29 wt% of N-vinylpyrrolidone and 4 wt% of 1-hydroxycyclohexylphenyl ketone was diluted with a 1/1 mixed solution of toluene and ethyl acetate to a concentration of 50 wt%, applied to the
15 base film or the decorative layer by a die coating technique, dried in a 70°C oven for 2 minutes and irradiated with ultraviolet light from a high-pressure mercury lamp having an irradiation intensity of 80 W/cm and set at a height of 9 cm from the surface to be coated for 15 seconds to be cured
20 so as to form a hard coat layer having a thickness of 5 µm.

[adhesive layer]

A resin comprising 98 wt% of "Oribine" (registered trademark) BPS-1109 acrylic adhesive of Toyo Ink Chemical
25 Industry Co., Ltd. and 2 wt% of "Oribine" (registered trademark) BHS-8515 isocyanate-based curing agent of Toyo Ink Chemical Industry Co., Ltd. was diluted with ethyl acetate to a concentration of 50 wt%, applied to the base film or the decorative layer by a gravure coating technique
30 and dried in a 70°C oven for 10 seconds to form an adhesive layer having a thickness of 30 µm.

Example 9

A decorative layer was formed on the surface in contact

with the casting drum of the base film produced in Example 2, and an adhesive layer was formed on the decorative layer. Further, a hard coat layer was formed on the surface not in contact with the casting drum of the base film to obtain the decorative sheet for injection molding of the present invention. The methods of forming the decorative layer, the adhesive layer and the hard coat layer are as described above.

Then, the obtained decorative sheet for injection molding was heated at 80°C and formed into a cup-like molded product at 85°C by using a cylindrical cup mold having a diameter of 50 mm, a depth of 50 mm and a fixed diameter in the depth direction and a vacuum molding machine, and methacrylic resin ("Sumipex" (registered trademark) LG35 ABS resin of Sumitomo Chemical Co., Ltd.) heated at 250°C was injected into the cup-like molded product as a molding resin. After the methacrylic acid was solidified by cooling, the cup-like molded product was taken out from the mold to obtain a decorative molded product having the decorative sheet for injection molding of the present invention which was laminated on the resin molded product. The decorative sheet was excellent in moldability (transferability, thickness uniformity), had no problem with deformation resistance and distortion resistance after molding and was not whitened. The surface hardness of the hard coat layer measured by a steel wool test was high without a scratch, and there was no problem with the adhesion of the sheet without peeling.

Example 10

A decorative sheet for injection molding was obtained from the base film produced in Example 5 in the same manner as in Example 9. The decorative sheet was excellent in moldability (transferability, thickness uniformity), had no problem with deformation resistance and distortion resistance after molding and was not whitened. The surface

hardness of the hard coat layer measured by a steel wool test was high without a scratch, and there was no problem with the adhesion of the sheet without peeling.

Then, a cup-like molded article was produced by using the obtained decorative sheet for injection molding in the same manner as in Example 9 to obtain a decorative molded article having the decorative sheet for injection molding of the present invention which was laminated on the resin molded product.

10

Example 11

A decorative sheet for injection molding was obtained from the base film produced in Example 6 in the same manner as in Example 9. The decorative sheet was excellent in moldability (transferability, thickness uniformity), had no problem with deformation resistance and distortion resistance after molding and was not whitened. The surface hardness of the hard coat layer measured by a steel wool test was high without a scratch, and there was no problem with the adhesion of the sheet without peeling.

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Then, a cup-like molded article was produced by using the obtained decorative sheet for injection molding in the same manner as in Example 9 to obtain a decorative molded article having the decorative sheet for injection molding of the present invention which was laminated on the resin molded product.

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Comparative Example 1

Film formation was carried out by using polyethylene terephthalate polymer (PET) in the same manner as in Example 1, and the obtained film was stretched to 3.0 times in the longitudinal direction at 95°C with rolls and to 3.1 times in the transverse direction at 115°C with a tenter, relaxed 5 % at 200°C and heat set for 5 seconds to obtain a base film

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having a thickness of 9 μm . The plane orientation coefficient, total light transmittance, haze, solvent resistance and pencil hardness of the film were evaluated, and the results are shown in Table 1.

5 The decorative sheet for injection molding of the present invention was obtained by using this base film in the same manner as in Example 9. Although the whitening of the decorative sheet was not seen, the decorative sheet was nonuniform in thickness and its warp deformation was seen.
10 The surface hardness of the hard coat layer measured by a steel wool test was high without a scratch. There was no problem with the adhesion of the decorative sheet without peeling.

 A decorative molded article having the decorative
15 sheet for injection molding of the present invention which was laminated on a resin molded product was obtained in the same manner in Example 9 by using the obtained decorative sheet for injection molding.

20 Comparative Example 2

 Film formation was carried out by using a polycarbonate resin pellet (Panlite L-1250 of Teijin Chemicals Ltd., viscosity average molecular weight of 23,700) in the same manner as in Example 1 to form a base film.

25 The plane orientation coefficient, total light transmittance, haze, solvent resistance, pencil hardness, heat moldability and toughness of the film were evaluated, and the results are shown in Tables 1 and 2.

 Then, a decorative molded article having the
30 decorative sheet for injection molding of the present invention which was laminated on a resin molded product was obtained in the same manner as in Example 9 by using the obtained decorative sheet for injection molding.

 Although the whitening of the decorative sheet was not

seen, the surface of the hard coat layer was easily scratched in a steel wool test. There was no problem with the adhesion of the decorative sheet without peeling.

5 Comparative Example 3

Film formation was carried out by using acrylic resin (Acrypet VH001 of Mitsubishi Rayon Co., Ltd.; standard grade) in the same manner as in Example 1 to form a base film.

10 The plane orientation coefficient, total light transmittance, haze, solvent resistance, heat moldability and toughness of the film were evaluated, and the results are shown in Table 2.

Then, a decorative molded article having the decorative sheet for injection molding of the present
15 invention which was laminated on a resin molded product was obtained in the same manner as in Example 9 by using the obtained decorative sheet for injection molding.

Although the whitening of the decorative sheet was not seen and the surface of the hard coat layer measured by a
20 steel wool test was high without a scratch, the decorative sheet was easily broken when it was taken from the mold. There was no problem with the adhesion of the decorative sheet without peeling.

Table 1

	ISS	Diol	Monoalcohol	Specific viscosity	Tg	Plane orientation coefficient	Total light transmittance (%)	Haze (%)	Solvent resistance	Pencil hardness
Ex.1	100	0		0.26	163	0.000	93	0.4	O	H
Ex.2	75	PD 25		0.25	116	0.000	92	0.5	O	F
Ex.3	50	CHDM 50		0.35	104	0.000	92	0.5	Δ	F
Ex.4	80	DED 20		0.25	110	0.000	93	0.4	O	H
Ex.5	70	CHDM 30	Stearyl alcohol 2	0.3	114	0.000	92	0.5	O	H
Ex.6	80	HD 20		0.27	111	0.000	92	0.3	O	H
C. Ex.1	Stretched PET	—	—	—	—	0.160	91	7	O	H
C. Ex.2	PC	-	-	-	150	0.000	90	0.3	x	2B

Ex.: Example C.Ex.: Comparative Example

Table 2

	Molding material A	Molding material B	Constitution	Plane orientation coefficient	Total light transmittance	Haze (%)	Solvent resistance	Heat moldability	Toughness	Pencil hardness
Ex. 7	Ex. 6	PMMA	Layer B/A/B 3-layer of 2 kinds	0.000	92	0.4	O	O	Satisfactory	2H
Ex. 8	Ex. 6	PC+ Thermoplastic elastomer	A/B/A 3-layer of 2 kinds	0.000	91	0.2	O	O	Satisfactory	HB
C. Ex. 1	Stretched PET	—	Single layer	0.160	91	7	O	x	Satisfactory	H
C. Ex. 2	PC	—	Single layer	0.000	90	0.3	x	x	Satisfactory	2B
C. Ex. 3	PMMA	—	Single layer	0.000	92	1.0	O	O	cracked	HB

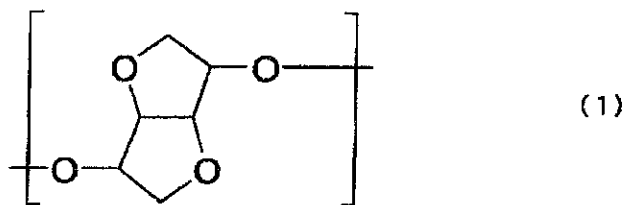
Ex.: Example C.Ex.: Comparative Example

As described above, the present invention can provide a decorative sheet for injection molding which comprises a polycarbonate resin containing a constituent unit able to be derived from a carbohydrate such as starch which is a biomass resource as the substrate of a base film and is excellent in abrasion resistance, high surface hardness, moldability, chemical resistance, deformation resistance, distortion resistance and whitening resistance.

A decorative molded article obtained by using the decorative sheet for injection molding of the present invention is used and useful as an electric/electronic part, an information communication part or a car part.

CLAIMS

1. A decorative sheet for injection molding, which comprises a base film comprising a polycarbonate resin having a plant-derived ether diol residue and a decorative layer formed on at least one side of the base film.
2. The decorative sheet for injection molding according to claim 1, wherein the polycarbonate resin having a plant-derived ether diol residue comprises a plant-derived ether diol residue represented by the following formula (1) in an amount of 15 to 100 mol% based on the total of all diol residues.



3. The decorative sheet for injection molding according to claim 1 or 2, wherein the polycarbonate resin having a plant-derived ether diol residue further comprises an aliphatic diol residue derived from an aliphatic dihydroxy compound.
4. The decorative sheet for injection molding according to claim 3, wherein the aliphatic dihydroxy compound is a linear aliphatic diol.
5. The decorative sheet for injection molding according to claim 3, wherein the aliphatic dihydroxy compound is an alicyclic diol.
6. The decorative sheet for injection molding according to any one of claims 1 to 3, wherein the polycarbonate resin

having a plant-derived ether diol residue further comprises an aromatic diol residue derived from an aromatic dihydroxy compound.

- 5 7. The decorative sheet for injection molding according to claim 1, wherein a decorative layer is formed on at least one side of the base film and an adhesive layer is formed on one outermost surface.
- 10 8. The decorative sheet for injection molding according to claim 1, wherein the base film comprises a polycarbonate resin having a plant-derived ether diol residue, a decorative layer is formed on at least one side of the base film, a hard coat layer is formed as one outermost surface layer, and an adhesive layer is formed as the other
15 outermost surface layer.
9. The decorative sheet for injection molding according to claim 1, wherein the total thickness of the base film
20 is 10 μm to 600 μm .
10. The decorative sheet for injection molding according to claim 1, wherein the base film has a layer (layer A) comprising a resin composition comprising a polycarbonate resin having a plant-derived ether diol residue and a layer
25 (layer B) comprising an acrylic resin and is a multi-layer film having the layer B on at least one side of the layer A.
- 30 11. The decorative sheet for injection molding according to claim 1, wherein the base film has a layer (layer A) comprising a resin composition comprising a polycarbonate resin having a plant-derived ether diol residue and a layer (layer B) comprising a resin composition comprising a

polycarbonate resin and a polyester-based thermoplastic elastomer and is a multi-layer film having the layer A on at least one side of the layer B.

5 12. The decorative sheet for injection molding according to claim 1, wherein the base film is an unstretched film.

13. The decorative sheet for injection molding according to claim 1, wherein the haze of the base film is 0 to 10 %.

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14. The decorative sheet for injection molding according to claim 1, wherein the total light transmittance of the base film is 85 to 100 %.