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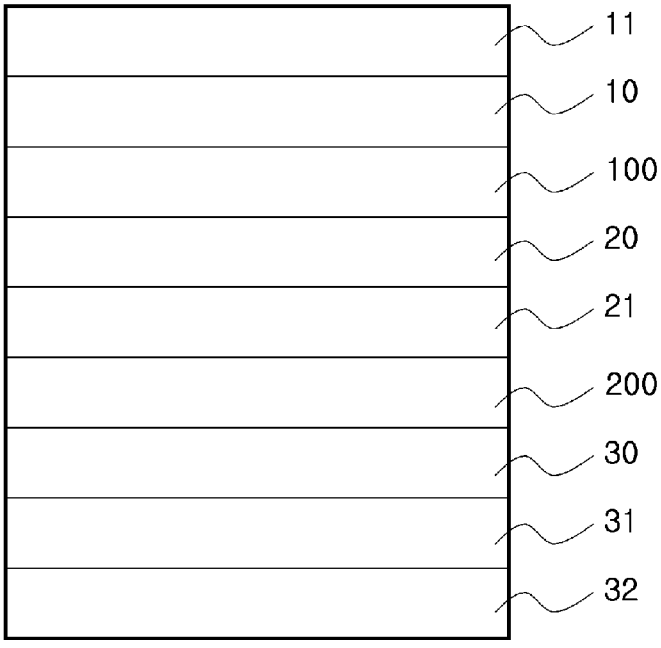
(54) Title: PROTECTIVE FILM

(57) Abstract: Provided is a protective film including two or more transparent plastic substrates having a functional coating layer formed thereon and laminated successively by way of adhesive layers.

[Fig. 2]



WO 2012/002706 A2

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Description

Title of Invention: PROTECTIVE FILM

Technical Field

[I] The following disclosure relates to a protective film including a functional coating layer and, more particularly, to a protective film having excellent total transmittance and low water permeability.

[2] The disclosure also relates to a protective film for a touch screen type e-book.

[3]

Background Art

[4] In general, e-paper refers to a display having properties very similar to paper, and is a next-generation display by which writing, deleting and storing of data are performed freely in addition to simple information display.

[5] Based on the principle of e-paper, e-books have also been developed. The e-books primarily include a driving film formed on glass and a protective film for protecting the same.

[6] In addition, as the e-book industry continuously develops, e-books need not only to display information but also provide various functions such as freely writing, deleting and storing data, in order to be competitive on the market. To more easily utilize such functions, touch screens have been applied to e-books. A touch screen type e-book needs a protective film to allow the e-book to stably and firmly operate even under contaminative environment.

[7] Under such circumstances, protective films for e-books or touch screen type e-books are required to have favorable physical properties including, for example, impact-cushioning property, humidity resistance and UV resistance. Therefore, there is still a need for developing such protective films.

[8]

Disclosure of Invention

Technical Problem

[9] In one general aspect, the present invention provides a protective film for e-books, which has high humidity resistance and excellent UV protectability.

[10] In another general aspect, the present invention provides a protective film having anti-scratch and anti-glare functions.

[II] In another aspect, the present invention provides a protective film having excellent total light transmittance (hereinafter, 'total transmittance').

[12] In another aspect, the present invention provides a protective film including a third adhesive layer and a release film, which may be combined with a substrate such as a

front panel laminate (FPL) without an alternative adhesive coating process and have excellent adhesiveness, enabling improvement in workability.

[13] In a still further aspect, the present invention provides a protective film for a touch screen type product requiring strict physical properties.

Solution to Problem

[14] Embodiments of the present invention relate to a protective film for e-books.

[15] In order to accomplish the above objects of the present invention, there is provided a protective film which includes; an anti-glare coating layer, a first transparent plastic substrate, a first adhesive layer, a second transparent plastic substrate, a first silicon oxide coating layer (SiO_x, wherein x ranges from 1.0 to 2.0), a second adhesive layer, a second silicon oxide coating layer (SiO_x, wherein x ranges from 1.0 to 2.0), a third transparent plastic substrate, an acrylic resin coating layer, a third adhesive layer and a release film laminated in sequential order, thereby having a total transmittance of 89 to 91%, a moisture vapor transmission rate (MVTR) of 0.02 to 0.06 g/m^2.day and a haze of 6 to 10%.

[16] According to another embodiment, there is provided a protective film, which includes; an anti-glare coating layer, a first transparent plastic substrate, a first adhesive layer, a second transparent plastic substrate, a first silicon oxide coating layer (SiO_x, wherein x ranges from 1.0 to 2.0), a second adhesive layer, a third transparent plastic substrate, a second silicon oxide coating layer (SiO_x, wherein x ranges from 1.0 to 2.0) and an acrylic resin coating layer laminated in sequential order, thereby having a total transmittance of 89 to 91%, a moisture vapor transmission rate (MVTR) of 0.01 g/m^2.day or lower and a haze of 6 to 10%.

[17] More particularly, the protective film according to one embodiment of the present invention is characterized by the order of laminating individual layers such that an anti-glare layer is formed on the outermost side to perform an anti-glare function and to prevent scratch generation. In addition, a first silicon oxide coating layer may face and be adhered to a second silicon oxide coating layer to decrease moisture permeability, thus providing a protective film suitable for e-books.

[18] In addition, a second transparent plastic substrate having the first silicon oxide coating layer formed thereon may be combined with a third transparent plastic substrate having the second silicon oxide coating layer formed thereon, through a second adhesive layer. Further, it can be seen that moisture permeability may be unexpectedly decreased when laminating the first silicon oxide coating layer (SiO_x, wherein x ranges from 1.0 to 2.0), the second adhesive layer, the third transparent plastic substrate and the second silicon oxide coating layer (SiO_x, wherein x ranges from 1.0 to 2.0) in sequential order. Specifically, when the lamination is performed by the

foregoing lamination order according to the present invention, unexpected effects such as the MVTR of 0.01 g/m^2.day or lower, may be rendered. Since a driving device of the e-book, *i.e.,* an electronic ink (e-ink) may produce displays near black as the MVTR is lowered, such MVTR is an important parameter for the protective film used for e-books. The present invention may retain relatively low MVTR, thus improving performance of a protective film for e-books.

[19] Moreover, using an acrylic resin coating layer may enable production of a protective film having excellent total transmittance.

[20] According to another embodiment, there is provided a protective film fabricated by providing a third adhesive layer on the top of the acrylic resin coating layer and laminating a release film on the top of the third adhesive layer, so as to improve workability in post treatment. The release film is removed during post treatment and, after peeling off the release film, the third adhesive layer is adhered to the substrate. Therefore, the protective film may be attached to the substrate without an alternative adhesive coating process. Specifically, when an adhesive composition comprising specific components with predetermined contents thereof is used to prepare the third adhesive layer, various beneficial effects such as improved adhesion to FPL as a substrate for post treatment, no transcription to the substrate, no influence upon total transmittance, and improved shrinkage, which in turn noticeably enhances workability, as compared to conventional adhesion processes of applying an adhesive under the conditions of 60°C x 95% relative humidity (R.H.) x 168 hours.

[21] It was found that the protective film of the present invention is characterized by a thickness as well as a lamination order thereof and, by adjusting each layer to a predetermined thickness, a protective film having improved moisture permeability may be provided. The present invention has been completed under the foregoing findings. The protective film fabricated with the thickness in the lamination order described herein may have a moisture permeability of 0.5 g/m^2.day or lower, UV transmittance of 2.0% or lower, a total transmittance of 89 to 91%, an MVTR of 0.06 g/m^2.day or lower and a haze of 6 to 10%, under the conditions of 38+2°C and 100% R.H. (KS M 3088:2004).

[22] The protective film of the present invention has desired moisture permeability suitable for e-books, and may induce little change in e-ink over time and prevent film ageing.

[23] The advantages, features and aspects of the invention will become apparent from the following description of embodiments with reference to the accompanying drawings, which is set forth hereinafter, without particular limitation thereto.

[24] As shown in FIG. 1, the protective film according to one embodiment of the present invention includes a first transparent plastic substrate 10, an anti-glare coating layer 11 formed on one surface of the first transparent plastic substrate, a second transparent

plastic substrate 20, a first silicon oxide (SiO_x, wherein x is 1.0-2.0) coating layer 21 formed on one surface of the second transparent plastic substrate, a third transparent plastic substrate 30, a second silicon oxide (SiO_x, wherein x is 1.0-2.0) coating layer 31 formed on one surface of the third transparent plastic substrate, and an acrylic resin coating layer 32 formed on the opposite side of the second silicon oxide (SiO_x, wherein x is 1.0-2.0) coating layer 31, wherein the first transparent plastic substrate 10 and the second transparent plastic substrate 20 face each other and are adhered to each other through a first adhesive layer 100, and the first silicon oxide coating layer 21 and the second silicon oxide coating layer 31 face each other and are adhered to each other through a second adhesive layer 200. Thereafter, an adhesive composition comprising 1 to 3 parts by weight of an epoxy curing agent, 0.01 to 1 parts by weight of a silane coupling agent and 1 to 20 parts by weight of a solvent, based on 100 parts by weight of an acryl based two-component curable adhesive, is applied to the top of the acrylic resin coating layer 32 to form a third adhesive layer, followed by laminating a release film on the top of the third adhesive layer, thereby fabricating the protective film.

[25] The protective film according to the above embodiment has moisture permeability of 0.5 g/m^2.day or lower under the conditions of 38+2°C and 100% R.H (KS M 3088:2004) and, preferably, 0.01 to 0.4 g/m^2.day. In addition, the foregoing film may have a UV transmittance of 2.0% or lower and, preferably, 0.1 to 1.8%, a total transmittance of 89 to 91%, an MVTR of 0.02 to 0.06 g/m^2.day and a haze of 6 to 10%.

[26] As shown in FIG. 2, the protective film according to another embodiment of the present invention includes a first transparent plastic substrate 10, an anti-glare coating layer 11 formed on one surface of the first transparent plastic substrate, a second transparent plastic substrate 20, a first silicon oxide (SiO_x, wherein x is 1.0-2.0) coating layer 21 formed on one surface of the second transparent plastic substrate, a third transparent plastic substrate 30, a second silicon oxide (SiO_x, wherein x is 1.0-2.0) coating layer 31 formed on one surface of the third transparent plastic substrate, and an acrylic resin coating layer 32 formed on the top of the second silicon oxide (SiO_x, wherein x is 1.0-2.0) coating layer 31, wherein the first transparent plastic substrate 10 and the second transparent plastic substrate 20 face each other and are adhered to each other through a first adhesive layer 100, and the first silicon oxide coating layer 21 and the third transparent plastic substrate 30 face each other and are adhered to each other through a second adhesive layer 200, thereby fabricating the protective film having improved moisture permeability.

[27] The protective film according to the above embodiment has moisture permeability of 0.5 g/m^2.day or lower under the conditions of 38+2°C and 100% R.H (KS M 3088:2004) and, preferably, 0.01 to 0.4 g/m^2.day. In addition, the foregoing film may have a UV transmittance of 2.0% or lower and, preferably, 0.1 to 1.8%, a total trans-

mittance of 89 to 91%, an MVTR of 0.01 g/m^2.day or lower and, preferably, 0.001 to 0.01 g/m^2.day, and a haze of 6 to 10%.

[28] Hereinafter, technical configurations of the present invention will be described detail.

[29] In one embodiment, the first transparent plastic substrate 10, the second transparent plastic substrate 20 or the third transparent plastic film 30 may be made of a plastic material having a light transmittance of 90% or higher. For example, polyethylene terephthalate resin, polyethylene terephthalate resin, polyethylene naphthalate resin, or the like may be used and, in addition, oriented materials thereof may also be used.

[30] The first transparent plastic substrate 10 serves as a support for the protective film, and may have a thickness of 50-250 ㎛, preferably 100-188 ㎛, without being particularly limited thereto. Such a thickness is sufficient to make the first transparent plastic substrate serve as a support, prevents damages to the outer appearance, and allows the first transparent plastic substrate to maintain flexibility.

[31] The second transparent plastic substrate 20 and the third transparent plastic substrate 30 each serve as a support for the silicon oxide coating layer, and may have a thickness of 10-50 ㎛, preferably 12-30 ㎛, without being particularly limited thereto. Such a thickness is suitable to make the substrates serve as a support during oxide deposition and prevents damages (e.g., wrinkle generation) to the outer appearance.

[32] The anti-glare coating layer 11 may include a hard resin, such as an acrylic urethane resin or siloxane resin, in combination with silicone beads, and provides an anti-glare effect and an anti-scratch effect. However, if the anti-glare coating layer 11 is too thin, sufficient hardness cannot be obtained. On the other hand, if the anti-glare coating layer 11 is too thick, cracks may be caused. The anti-glare coating layer 11 may have a thickness of 3-5 ㎛ to also prevent curling.

[33] The first silicon oxide coating layer 21 or the second silicon oxide coating layer 31 may be formed through vacuum deposition. The silicon oxide (SiO_x, wherein x is 1.0-2.0) coating layer may have low transparency when x is less than 1.0, resulting in a light transmittance of 90% or lower. On the other hand, the silicon oxide coating layer may be cracked when x is greater than 2.0. For these reasons, x may be defined in the foregoing range. The silicon oxide coating layer may have a thickness of 300-l,000Å more preferably 400-800Åto realize good moisture resistance and a clear color.

[34] The first adhesive layer 100 may be an acrylic resin adhesive composition including a UV protecting agent. The first adhesive layer 100 may have a light transmittance of 90% or higher, a haze of 1% or lower, and a shear storage modulus of 10^3-10^5 Pa. If the adhesive layer has a light transmittance of 90% or lower or a haze of 1% or lower, a display fabricated using the protective film that is provided with such an adhesive layer may have poor clearness. When the adhesive layer has a shear storage modulus less than 10^3 Pa, a problem in assembling the display may occur because the adhesive layer

protrudes out from an assembled display upon blanking. On the other hand, if the shear storage modulus is greater than 10^5 Pa, the adhesive layer shows low adhesiveness, resulting in poor durability and weak impact-absorbing property.

[35] In addition, the adhesive composition may further include 0.5 to 5 parts by weight of a triazole-based UV protecting agent, based on the solid content of the resin, to ensure UV protectability over a wide range of wavelengths. When the triazole-based UV protecting agent is used in an amount less than 0.5 parts by weight, the UV transmittance may rapidly increase after the QUV test, thus causing damages to the driving layers of e-book and degradation in the response rates. On the other hand, if the triazole-based UV protecting agent is used in an amount greater than 5 parts by weight, it may cause a change in the color index after the QUV test. The triazole-based UV protecting agent used herein may be, for example, benzotriazole, methylene bis(hydroxyphenyl benzotriazole) derivatives, hydroxylphenyl benzotriazole, or the like. Besides the above UV protecting agent, other trazine-based UV protecting agents, anti-oxidants, thermal stabilizers, fluorescent whitening agents, etc. may be further added, if necessary. These additives may be added in amounts where they cause no deterioration in physical properties of a coating film. Preferably, they are added in an amount of 0.5-5 parts by weight based on the solid content of the resin. The triazine-based UV protecting agent may include, for example; hydroxyphenyl triazine, 2,4,6-tris(diethyl-4'-aminobenzalmalonate)-s-triazine, 2,4,6-tris(diisopropyl 4'-aminobenzalmalonate)-s-triazine, 2,4,6-tris(dimethyl 4'-aminobenzalmalonate)-s-triazine, 2,4,6-tris(ethyl α-cyano-4-aminosinamate)-s-triazine, 2,4,6-tris[(3'-benzotriazole-2-yl-2'-hydroxy-5'-methyl)phenylamino]-s-triazine, 2,4,6-tris[(3'-benzotriazole-2-yl-2'-hydroxy-5'-ter-octyl)phenylamino]-s-triazine, etc. In addition, the anti-oxidants, thermal stabilizers and/or fluorescent whitening agents disclosed therein are not particularly limited so long as they are commonly available in the conventional art.

[36] The adhesive composition used in the first adhesive layer may further include a crosslinking agent in addition to the acrylic resin. Due to the incorporation of the crosslinking agent, the resin may be crosslinked, thereby improving the heat resistance and water resistance. The crosslinking agent used herein may include one reactive to the functional groups of the acrylic resin. Particular examples of the crosslinking agent include peroxides, isocyanate-based crosslinking agents, epoxy-based crosslinking agents, metal chelate-based crosslinking agents, melamine-based crosslinking agents, aziridine-based crosslinking agents, metal salts, or the like. Such crosslinking agents may be used alone or in combination with two or more thereof. Among these, isocyanate-based crosslinking agents are preferably used to provide good adhesion.

Particular examples of such isocyanate-based crosslinking agents include diisocyanates such as tolylene diisocyanate, diphenylmethane diisocyanate, xylene diisocyanate, isophorone diisocyanate or hexamethylene diisocyanate, as well as various polyol-modified diisocyanate adducts, polyisocyanate compounds having isocyanurate rings, biuret forms or allophanate forms, or the like. In addition, aliphatic or alicyclic isocyanate compounds may be used as the isocyanate-based crosslinking agents in applications requiring transparency. This is because aromatic isocyanate compounds may cause coloration in the adhesive layer after curing. The crosslinking agent may be generally used in an amount of 0.01-10.0 parts by weight, preferably 0.05-5.0 parts by weight based on 100 parts by weight of the acrylic adhesive. If the amount of the crosslinking agent exceeds 10.0 parts by weight, excessive crosslinking may occur which reduces the tackiness after drying and decreases adhesion after the lamination with a transparent plastic substrate, resulting in poor durability. On the other hand, if the amount of the crosslinking agent is less than 0.01 parts by weight, the adhesive may be cured insufficiently, resulting in degradation of the water resistance.

[37] The first adhesive layer 100 is formed by applying the adhesive composition onto a support, followed by drying. Since the adhesive includes a crosslinking agent, thermal treatment of the adhesive layer enables crosslinking. The crosslinking may be carried out simultaneously with drying at the temperature where the solvent is dried. Otherwise, separate crosslinking operation may be performed after the drying. The adhesive layer may be aged to regulate the crosslinking of the adhesive layer.

[38] In one embodiment of the present invention, the first adhesive layer 100 serves to improve the impact-absorbing property between the first transparent plastic substrate and the second transparent plastic substrate. To facilitate the impact-absorbing function, the first adhesive layer 100 may have a shear storage modulus of 10^3-10^5 Pa.

[39] The second adhesive layer 200 may be formed using a urethane adhesive having excellent adhesion to silicon oxide.

[40] The adhesive composition used in the first adhesive layer or the second adhesive layer may be used in the form of a liquid composition. Particular examples of the solvent used herein may include methyl ethyl ketone, acetone, ethyl acetate, tetrahydrofuran, dioxane, cyclohexanone, n-hexane, toluene, xylene, methanol, ethanol, n-propanol, isopropanol, water, etc. Such solvents may be used alone or in combination with two or more thereof. The solvent may be the solvent previously used for polymerization or at least one solvent added to allow uniform application of the adhesive layers, other than the polymerization solvent.

[41] In one embodiment of the present invention, the third adhesive layer 300 serves to adhere the protective film of the present invention to the substrate. In order to facilitate adhesion to the substrate after post treatment, an adhesive composition including 1-3

parts by weight of an epoxy-based curing agent, 0.01-1 parts by weight of a silane-based coupling agent and 1-20 parts by weight of a solvent, based on 100 parts by weight of acryl based two-component curable adhesive, may be applied to a dry coating thickness of 30-60/㎛ onto the substrate.

[42] The acryl based two-component curable adhesive may comprise 20-30 wt.% of acrylic resin, 1-5 wt.% of C1-C20 alkyl acrylate and a solvent. More particularly, the foregoing adhesive may include 20-30 wt.% of acrylic resin, 1-5 wt.% of n-butyl acrylate, and a solvent comprising 20-30 wt.% of toluene, 20-30 wt.% of acetone, 10-20 wt.% of ethyl acetate and 10-20 wt.% of methylethylketone. As a practical example, EG 655 (trade name, available from Toyo Ink Inc.) may be used.

[43] The epoxy based curing agent may be used in an amount of 1-3 parts by weight in terms of solid content, to exhibit excellent adhesiveness and prevent transcription thereof to the substrate. BXX-5627 (trade name, available from Toyo Ink Inc.) may be practically used without particular limitation.

[44] The silane based coupling agent may be used to improve adhesiveness and, for example, BXX-320 of Toyo Ink Inc. may be used, without particular limitation. An amount of a silane based coupling agent may range from 0.01 to 1 part by weight.

[45] The solvent may be methylethylketone, ethyl acetate, etc. and used in an amount of 1-20 parts by weight, improving coatability.

[46] In one embodiment of the present invention, an acrylic resin coating layer 32 provided on the third transparent plastic substrate 30 may improve a total transmittance. A coating solution forming the acrylic resin coating layer may be prepared using any one composition, without particular limitation of constitutional composition thereof, so long as the composition can improve adhesiveness of the coating layer. More particularly, the coating solution may be an acrylic resin composition including 10-15 wt.% of an acryl based binder resin, 0.01-1 wt.% of a wetting agent, 0.1-2 wt.% of particles, 0.1-3 wt.% of a curing catalyst, 0.01-1 wt.% of an anti-oxidant, 80-85 wt.% of water and 1-5 wt.% of an organic solvent.

[47] The acryl based binder resin may be one prepared by polymerization of at least one selected from a group consisting of acrylic acid, methacrylic acid methyl acrylate, ethyl acrylate, n-acrylate, ethyl methacrylate, acrylamide, butlacrylate, glicidyl methacrylate, etc. The acrylic resin may have T_g at 40-50°C, which is a preferable curing rate. Moreover, the acryl based binder resin may have a refractive index of 1.4-4.5, preferably, 1.44-1.45, thus preferably compensating the transmittance.

[48] The particles may be inorganic or organic particles to increase light diffusiveness caused by difference in refractive index, thus leading to enhancement of total transmittance. The particles used herein may include, for example; anti-blocking inorganic particles such as harden calcium carbonate (CaO), colloidal silica particles, barium

sulfate ($BaS0_4$), sodium oxide ($Na0_2$), sodium sulfate (Na_2S0_4), kaolin, talc, etc., silicone resin, cross-linked acrylate resin and polystyrene resin such as cross-linked divinylbenzene polymethacrylate, cross-linked polymethacrylate, etc., organic particles such as benzoguanamine-formaldehyde resin, benzoguanamine-melamine-formaldehyde resin, melamine-formaldehyde resin, etc. More preferably, the particles have an average particle diameter of 150-200nm to attain excellent dispersibility and coatability.

[49] The curing catalyst may be epoxy, isocyanate, etc. The organic solvent may improve wettability and comprise, for example, isopropyl alcohol, propanol, etc.

[50] In one embodiment of the present invention, the acryl based resin composition may have 1-15 wt.% of solid content and a viscosity of 20 cps (25°C) or lower. If the solid content is less than 1 wt.%, a wet coating amount should be increased to have a desired coating thickness and a great amount of energy may be required to dry the coating layer, thus increasing production cost. If the solid content exceeds 15 wt.%, a viscosity is raised to 15 cps (25°C) or higher, resulting in reduction of coatability. Further, a dry coating thickness of the acrylic resin coating layer 32 preferably ranges from 70 to 90nm to minimize variation in the refractive index of a protective film.

[51] In one embodiment of the present invention, the release film 40 may be any conventional film available in the art, without being particularly limited thereto. More particularly, a release film formed of a silicon release agent applied onto one surface of a polyethylene terephthalate film may be used since it is easily peeled off and conveniently transported.

[52]

Advantageous Effects of Invention

[53] As is apparent from the foregoing description, a protective film according to the present invention has low moisture permeability to minimize change in the e-ink over time, when the protective film is used as a protective film for e-books, and also has low UV transmittance to prevent ageing of a driving film.

[54] The protective film of the present invention may provide a protective film having a total transmittance of at least 89%.

[55] The present invention may provide a protective film by removing a release film, without an alternative adhesive coating process during post treatment, which has various advantages, for example; high adhesion to a substrate, enhanced workability, no transcription to the substrate, low shrinkage and no reduction in total transmittance of the protective film.

[56] The protective film disclosed herein may be applied not only to e-books but also to various fields, including household electronic appliances, cars, communication in-

struments, display devices, such as a PDA, or the like.

[57]

Brief Description of Drawings

[58] The above and other objects, features and advantages of the present invention will become apparent from the following description of preferred embodiments given in conjunction with the accompanying drawings, in which:

[59] FIG. 1 illustrates a protective film according to one embodiment of the present invention; and

[60] FIG. 2 illustrates a protective film according to another embodiment of the present invention.

[61]

[62] [Detailed Description of Main Elements]

[63] 10: first transparent plastic substrate

[64] 11: anti-glare coating layer

[65] 20: second transparent plastic substrate

[66] 21: first silicon oxide coating layer

[67] 30: third transparent plastic substrate

[68] 31: second silicon oxide coating layer

[69] 32: acrylic resin coating layer

[70] 40 : release film

[71] 100: first adhesive layer

[72] 200: second adhesive layer

[73] 300: third adhesive layer

[74]

Mode for the Invention

[75] The examples and experiments will now be described. The following examples and experiments are for illustrative purposes only and not intended to limit the scope of this disclosure.

[76] In the following examples, physical properties of protective films are measured as follows.

[77] 1) Water Permeability

[78] Water permeability of a film is measured according to KS M3088:2004 (38+2°C, 100% R.H.).

[79] Fail: water permeability > 0.5

[80] Pass: water permeability $\leq$ 0.5

[81] 2) UV Transmittance

[82] UV transmittance of a film is measured using Verian, Cary 5000 UV-Visible Spec-

trophotometer.

[83] - UV transmittance (%) before QUV: UV transmittance is measured over the whole range of UV wavelengths (200-300 nm), after a protective film is prepared, and the anti-glare coating layer of the first transparent plastic is allowed to face the UV light source. The highest UV transmittance value is taken from the measured range.

[84] Fail: UV transmittance > 2.0

[85] Pass: UV transmittance ≤ 2.0

[86] - UV transmittance (%) after QUV: the surface of the first transparent plastic substrate is allowed to face the light source in a QUV chamber equipped with a lamp emitting the light with UVB wavelengths after a protective film is prepared, and then the protective film is allowed to stand for 100 hours. Then, UV transmittance is measured in a UV wavelength range of 200-300 nm using a UV transmittance measuring system. The highest UV transmittance value is taken from the measured range.

[87] Fail: UV transmittance > 2.0

[88] Pass: UV transmittance ≤ 2.0

[89] 3) Shear Storage Modulus

[90] The adhesive composition used for producing the protective film is dissolved into a solvent, the resultant solution is applied to a Teflon sheet through a solvent casting process, and the solvent is allowed to evaporate to obtain a 1 mm-thickness film as only the adhesive layer. The adhesive film is loaded in the middle of a fixed lower plate and a rotatable upper plate using a rheometer (Rheometrics, RMS), and variations in the shear force are measured depending on frequency (moving angle of the upper plate per unit time). Herein, data are obtained under a strain of 5% over a range of 1-100 radian/sec, and the storage modulus value at 10 radian/sec is taken as the reference value.

[91] 4) Coating Thickness

[92] A thickness measuring device is used to measure the thickness of a coating layer.

[93] 5) Appearance

[94] Film appearance is determined by the naked eye. A film that shows no specific feature is evaluated as 'paass' and a film having wrinkles is evaluated as 'fail'.

[95] 6) Light transmittance of Protective Film and Total transmittance (%)

[96] Light transmittance is taken as the total transmittance measured by 300A model available from Nippon Denshoku Co. A protective film having a light transmittance of 88% or higher is evaluated as 'excellent', a protective film having a light transmittance of 60-88% is evaluated as 'good', and a protective film having a light transmittance less than 60% is evaluated as 'poor'.

[97] 7) Haze

[98] Haze and light transmittance are measured in visible regions using a hazemeter (TOYOSEIKI, Japan) according to ASTM D1003.

[99] 8) Moisture Vapor Transmission Rate (MVTR)

[100] An amount of moisture transmission for 24 hours is measured by PERMATRAN-W® Model 398 (Mocon, United States) under the conditions of 38°C x 100% R.H., for 24 hours.

[101] 9) Workability

[102] Each of the protective films prepared in Examples and Comparative Examples is laminated on a cell. When failure occurs, the protective film must be peeled off. In this case, it is determined whether the protective film is easily released. Further, it is determined whether the adhesive residue of the third adhesive layer remains on FPL surface after peeling off the protective film.

[103] 10) Adhesiveness (n=5)

[104] After cutting a film into a piece having a length of 20mm x a width of 25mm, the cut piece is subjected to measurement of adhesiveness using INSTRON 3365 Model.

[105] 11) Shrinkage

[106] A sample having a size of 150mmxl50mm is laminated on a glass and subjected to reliability test under the conditions of 60°C x 95% R.H. x 168 hours, followed by measuring a shrunk length of the third adhesive layer. If the length is 1.5mm or less, the sample is evaluated as good.

[107]

[108] [Example 1]

[109] Fabrication of First Transparent Plastic Substrate Having Anti-Glare Coating Layer

[110] A polyethylene terephthalate film (HI IF available from Kolon) having a thickness of 188 ㎛ and a width of 1,000 mm was provided. Next, 5 parts by weight of silica beads (Shinetsu Chemical, X-52-854) were added to and mixed with 100 parts by weight of an acrylic urethane resin (DAI NIPPON PRINTING, UNIDIK 17-824-9) to prepare a composition for an anti-glare layer. The composition was applied to one surface of the polyethylene terephthalate film, dried at 100°C for 3 minutes, and irradiated immediately with UV rays using two ozone type high-pressure mercury lamps (80W/cm, 15 cm light collection type). As a result, an anti-glare layer having a thickness of 5 ㎛ was formed.

[Ill] Fabrication _of_Second _Transparent _Plastic _Substrate _Having _First _Silicon _Oxide Coating _Layer

[112] A SiOi.5 coating layer having a thickness of 500 was provided onto a polyethylene terephthalate film (Kolon, FQOO) having a thickness of 12 ㎛ and a width of 1,000 mm through vacuum deposition.

[113] Fabrication _of_Third _Transparent _Plastic _Substrate _Having _Second _Silicon _Oxide De-

position Layer and Acrylic Resin Coating Layer

[114] A SiOi.5 coating layer having a thickness of 500Å was provided onto a polyethylene terephthalate film (Kolon, FQOO) having a thickness of 12 ㎛ and a width of 1,000 mm via vacuum deposition.

[115] 12.5g of an acryl binder (refractive index: 1.44, glass transition temperature: 48°C), O.lg of a silicon based wetting agent (TEGO Co., polyestersiloxane copolymer), 0.4g of colloidal silica particles having an average particle diameter of 200nm, 0.83g of a curing catalyst (ammonium thiocyanate based), 0.2g of an anti-oxidant (benzotriazol based), 80.97g of water and 5g of isopropyl alcohol were mixed together, thereby preparing an acrylic resin composition having a solid content of 5% and a viscosity of 30 cps.

[116] The prepared acrylic resin composition was applied in a dry coating thickness of 80nm onto one surface facing the other surface on which the silicon oxide coating layer was formed.

[117] Preparation of First Adhesive Composition

[118] First, 0.3 parts by weight of an isocyanate crosslinking agent (Soken Chemistry, E-AX) was added to 100 parts by weight (solid content basis) of an acrylate adhesive (Soken Chemistry, SK2094R). Next, the resultant mixture was further mixed with 1 part by weight of benzotriazole (Ciba, Tinuvin 1130) as a UV protecting agent and methyl ethyl ketone was added thereto to a solid content of 20% in the resultant solution, thereby preparing an adhesive composition.

[119] Preparation of Second Adhesive Composition

[120] First, 20 parts by weight of an isocyanate crosslinking agent (Kangnam Chemistry, Co. Ltd., CL 100) was added to 100 parts by weight (solid content basis) of a polyurethane resin (Kangnam Chemistry, Co. Ltd., Neoforce 338). Next, the resultant mixture was diluted with toluene as a solvent to provide a solution with a solid content of 10%.

[121] Fabrication of Protective Film

[122] As shown in Fig. 1, the second transparent plastic substrate having the first silicon oxide coating layer formed thereon and the third transparent plastic substrate having the second silicon oxide coating layer and acrylic resin coating layer formed thereon were combined using the second adhesive composition. Then, the resultant laminate was adhered to the first transparent plastic substrate provided with the anti-glare layer, using the first adhesive composition.

[123] More particularly, the second adhesive composition was coated onto the surface of the second transparent plastic substrate, on which the first silicon oxide coating layer was formed, and dried at 100°C for 2 minutes to form a second adhesive layer having a dry coating thickness of 3 ㎛. Then, the second silicon oxide coating layer of the third

transparent plastic substrate was adhered to the second adhesive layer.

[124] Then, the first adhesive composition was coated onto the surface of the second transparent plastic substrate, on which the first silicon oxide coating layer was not formed, and dried at 100°C for 3 minutes to form a first adhesive layer having a thickness of 50 ㎛. After that, the surface of the first transparent plastic substrate having no anti-glare layer was adhered to the first adhesive layer. The protective film obtained as described above was subjected to measurement of physical properties, and the results are shown in Table 1.

[125] Meanwhile, a third adhesive composition was applied to have a dry coating thickness of **30**㎛ onto the top of the acrylic resin coating layer of the prepared productive film and dried, followed by laminating a release film thereon to complete a protective film according to the present invention. The third adhesive composition used herein was prepared by mixing 1 part by weight of an epoxy based curing agent (Toyo Ink Co., BXX-5627), 0.01 parts by weight of a silane based coupling agent (Toyo Ink Co., BXX-320), 15 parts by weight of methylethylketone and 5 parts by weight of ethyl acetate, with 100 parts by weight of an acryl based two-component curable adhesive (Toyo Ink Co., EG6555). Workability, adhesiveness, total transmittance and shrinkage of the resultant protective film were assessed and results thereof are shown in Table 2.

[126] [Example 2]

[127] The procedures in Example 1 were repeated to fabricate a protective film, except that 3 parts by weight of an epoxy based curing agent was added to the third adhesive composition in Example 1.

[128] Physical properties of the fabricated protective film were measured and results thereof are shown in Tables 1 and 2.

[129] [Example 3]

[130] The procedures in Example 1 were repeated to fabricate a protective film, except that the acrylic resin coating layer was prepared to have a solid content of 1.2 wt.%.

[131] Physical properties of the fabricated protective film were measured and results thereof are shown in Tables 1 and 2.

[132] [Example 4]

[133] Fabrication of First Transparent Plastic Substrate Having Anti-Glare Coating Layer

[134] A polyethylene terephthalate film (HI IF available from Kolon) having a thickness of 188 ㎛ and a width of 1,000 mm was provided. Next, 5 parts by weight of silica beads (Shinetsu Chemical, X-52-854) were added to and mixed with 100 parts by weight of an acrylic urethane resin (DAI NIPPON PRINTING, UNIDIK 17-824-9) to prepare a composition for an anti-glare layer. The composition was applied to one surface of the polyethylene terephthalate film, dried at 100°C for 3 minutes, and irradiated immediately with UV rays using two ozone type high-pressure mercury lamps (80W/cm,

15 cm light collection type). As a result, an anti-glare layer having a thickness of 5 ㎛ was formed.

[135] Fabrication of Second Transparent Plastic Substrate Having First Silicon Oxide Coating Layer

[136] A SiOi.5 coating layer having a thickness of 500Å was provided onto a polyethylene terephthalate film (Kolon, FQOO) having a thickness of 12 ㎛ and a width of 1,000 mm through vacuum deposition.

[137] Fabrication of Third Transparent Plastic Substrate Having Second Silicon Oxide Deposition Layer and Acrylic Resin Coating Layer

[138] A SiOi.5 coating layer having a thickness of 500Å was provided onto a polyethylene terephthalate film (Kolon, FQOO) having a thickness of 12 ㎛ and a width of 1,000 mm via vacuum deposition.

[139] 12.5g of an acryl based binder (refractive index: 1.44, glass transition temperature: 48°C), O.lg of a silicon based wetting agent (TEGO Co., polyestersiloxane copolymer), 0.4g of colloidal silica particles having an average particle diameter of 200nm, 0.83g of a curing catalyst (ammonium thiocyanate based), 0.2g of an anti-oxidant (benzotriazol based), 80.97g of water and 5g of isopropyl alcohol were mixed together, thereby preparing an acrylic resin composition having a solid content of 5% and a viscosity of 30 cps.

[140] The prepared acrylic resin composition was applied to have a dry coating thickness of 80nm onto the top of the silicon oxide coating layer.

[141] Preparation of First Adhesive Composition

[142] First, 0.3 parts by weight of an isocyanate crosslinking agent (Soken Chemistry, E-AX) was added to 100 parts by weight (solid content basis) of an acrylate adhesive (Soken Chemistry, SK2094R). Next, the resultant mixture was further mixed with 1 part by weight of benzotriazole (Ciba, Tinuvin 1130) as a UV protecting agent and methyl ethyl ketone was added thereto to a solid content of 20% in the resultant solution, thereby preparing an adhesive composition.

[143] Preparation of Second Adhesive Composition

[144] First, 20 parts by weight of an isocyanate curing agent (Kangnam Chemistry, Co. Ltd., CL 100) was added to 100 parts by weight of the solid content of a polyurethane resin (Kangnam Chemistry, Co. Ltd., Neoforce 338). Next, the resultant mixture was diluted with toluene as a solvent to provide a solution with a solid content of 10%.

[145] Fabrication _of Protective _Film

[146] As shown in Fig. 2, the second transparent plastic substrate having the first silicon oxide coating layer formed thereon and the third transparent plastic substrate having the second silicon oxide coating layer and acrylic resin coating layer formed thereon were combined using the second adhesive composition. Then, the resultant laminate

was adhered to the first transparent plastic substrate provided with the anti-glare layer, using the first adhesive composition.

[147] More particularly, the second adhesive composition was coated onto the surface of the second transparent plastic substrate, on which the first silicon oxide coating layer was formed, and dried at 100°C for 2 minutes to form a second adhesive layer having a dry coating thickness of 3 ㎛. Then, the third transparent plastic substrate having the second silicon oxide coating layer was adhered to the second adhesive layer such that the surface of the third transparent plastic substrate faces the second adhesive layer.

[148] Then, the first adhesive composition was coated onto the surface of the second transparent plastic substrate, on which the first silicon oxide coating layer was not formed, and dried at 100°C for 3 minutes to form a first adhesive coating layer having a thickness of 50 ㎛. After that, the surface of the first transparent plastic substrate having no anti-glare layer was adhered to the first adhesive coating layer.

[149] Physical properties of the protective film obtained as described above were measured and results thereof are shown in Table 3.

[150] [Example 5]

[151] The procedures in Example 4 were repeated to fabricate a protective film, except that the acrylic resin coating layer was prepared to have a solid content of 1.2 wt.%.

[152] Physical properties of the fabricated protective film were measured and results thereof are shown in Table 3.

[153] [Example 6]

[154] The procedures in Example 4 were repeated to fabricate a protective film, except that the acrylic resin coating layer was prepared to have a solid content of 1.0 wt.%.

[155] Physical properties of the fabricated protective film were measured and results thereof are shown in Table 3.

[156] [Comparative Example 1]

[157] The procedures in Example 1 were repeated to fabricate a protective film, except that the third adhesive composition was applied onto the top of the third transparent plastic substrate without an acrylic resin coating layer, and 5 parts by weight of an epoxy based curing agent was added to the third adhesive composition.

[158] Physical properties of the fabricated protective film were measured and results thereof are shown in Tables 1 and 2.

[159] [Comparative Example 2]

[160] The procedures in Example 4 were repeated to fabricate a protective film, except that no acrylic resin coating layer was provided.

[161] Physical properties of the protective film were measured and results thereof are shown in Table 3.

[162]

[163] [TABLE 1]

[164]

	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1
Moisture permeability (g/m^2.day)	0.06	0.06	0.06	0.08
UV transmittance before QUV (max.%)	0.6	0.6	0.6	0.6
UV transmittance after QUV (max.%)	1.2	1.2	1.2	1.2
Appearance	No wrinkle	No wrinkle	No wrinkle	Wrinkle generation
Light transmittance (%)	89.5%	89.5%	90.5%	86.5%
Moisture vapor transmission rate (VTR) (g/m^2.day)	0.04g	0.04g	0.03g	0.08g
Total transmittance (%)	89.5%	89.5%	90.5%	86.5%
Haze (%)	10%	10%	8%	12%

[165] As shown in Table 1, the protective films according to the inventive examples have low moisture permeability, realizing excellent water vapor barrier property.

[166] Therefore, it can be seen that a protective film having the lamination order and thickness according to the present invention may have favorable water vapor barrier property and UV protectability, thus being effectively used as a protective film for e-books or in other applications.

[167] Compared to the protective film without an acrylic resin coating layer prepared in Comparative Example 1, it was found that the protective film of the present invention has improved total transmittance.

[168]

[169] [TABLE 2]

[170]

	Ex . 1	Ex. 2	Ex. 3	Comp . Ex . 1
Workability (Transcription rate, %)	0%	0%	0%	15%
Adhesion	5N/inch	5N/inch	5N/inch	5N/inch
Total transmittance (%)	89.5%	89.5%	90.5%	86.5%
shrinkage	1 .5mm	1 .5mm	1 .5mm	2mm

[171] As shown in Table 2, it was confirmed that, when the third adhesive composition of the present invention is applied, the protective film may have excellent adhesion to FPL surface, enhanced workability because of no transcription, and a desired total transmittance without influence of the third adhesive composition, and exhibit relatively low shrinkage of not more than 1.5mm.

[172]

[173] [TABLE 3]

[174]

	Ex . 4	Ex. 5	Ex. 6	Comp . Ex . 2
Moisture permeability (g/m^2.day)	0.06	0.06	0.06	0.08
UV transmittance before QUV (max.%)	0 .6	0.6	0 .6	0 .6
UV transmittance after QUV (max.%)	1 .2	1.2	1.2	1.2
Appearance	No wrinkle	No wrinkle	No wrinkle	Wrinkle generation
Light transmittance (%)	89.5%	90.5%	90%	86.5%
Moisture permeability (VTR) (g/m^2.day)	0 .Olg	0 .005g	0 .OOlg	0 .08g
Total transmittance (%)	89.5%	90.5%	90%	86.5%
Haze (%)	10%	8%	9%	12%

[175] As shown in Table 3, it was found that the protective films prepared in Examples 4 to 6 have considerably reduced moisture permeability, compared to those prepared in Examples 1 to 3. The reason for this fact is that, when a first oxide coating layer and a second oxide coating layer are combined using a polyurethane adhesive, inorganic oxide is influenced by a solvent portion in the adhesive residue. Further it was confirmed that excellent moisture permeability of 0.01g/m^2.day or lower may be realized by modifying a structure of the layer.

[176] Accordingly, it can be seen that the protective film having the lamination order and thickness according to the present invention may be suitably used as a protective film for e-books and in other applications.

[177] Moreover, compared to the protective film without an acrylic resin coating layer prepared in Comparative Example 2, it can be seen that the protective film of the present invention has improved total transmittance.

[178] While the present invention has been described with respect to the specific embodiments, it will be apparent to those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention as defined in the following claims.

[179]

Industrial Applicability

[180] As is apparent from the foregoing description, a protective film according to the present invention has low moisture permeability to minimize change in the e-ink over time, when the protective film is used as a protective film for e-books, and also has low UV transmittance to prevent ageing of a driving film.

[181] The protective film of the present invention may provide a protective film having a total transmittance of at least 89%.

[182] The present invention may provide a protective film by removing a release film, without an alternative adhesive coating process during post treatment, which has various advantages, for example; high adhesion to a substrate, enhanced workability, no transcription to the substrate, low shrinkage and no reduction in total transmittance of the protective film.

[183] The protective film disclosed herein may be applied not only to e-books but also to various fields, including household electronic appliances, cars, communication instruments, display devices, such as a PDA, or the like.

[184]

[185]

Claims

[Claim 1] A protective film, comprising:
an anti-glare coating layer, a first transparent plastic substrate, a first adhesive layer, a second transparent plastic substrate, a first silicon oxide (SiO_x, wherein x is 1.0-2.0) coating layer, a second adhesive layer, a second silicon oxide (SiO_x, wherein x is 1.0-2.0) coating layer, a third transparent plastic substrate, an acrylic resin coating layer, a third adhesive layer and a release film laminated in sequential order, wherein the protective film has a total (light) transmittance ranging from 89 to 91%, a moisture vapor transmission rate (MVTR) ranging from 0.02 to 0.06g/m^2.day, and a haze ranging from 6 to 10%.

[Claim 2] The protective film of claim 1, wherein the third adhesive layer is prepared by applying an adhesive composition, which includes; 1 to 3 parts by weight of an epoxy based curing agent, 0.01 to 1 parts by weight of a silane based coupling agent and 1 to 20 parts by weight of a solvent based on 100 parts by weight of an acryl based two-component curable adhesive, to have a dry coating thickness of 30 to **60㎛**.

[Claim 3] The protective film of claim 1, wherein the acrylic resin coating layer is prepared by applying an acrylic resin composition, which includes; 10 to 15 wt.% of an acryl binder resin having a refractive index of 1.4 to 1.5 and a glass transition temperature of -10 to 20°C, 0.01 to 1 wt.% of a wetting agent, 0.1 to 2 wt.% of particles, 0.1 to 3 wt.% of a curing catalyst, 0.01 to 1 wt.% of an anti-oxidant, 80 to 85 wt.% of water and 1 to 5 wt.% of an organic solvent, to have a dry coating thickness of 70 to 90nm.

[Claim 4] The protective film of claim 1, wherein the silicon oxide coating layer is formed to have a coating thickness of 300 to 1,000Å through vacuum deposition.

[Claim 5] The protective film of claim 1, wherein the anti-glare coating layer is formed to have a dry coating thickness of 3 to 5/**㎛**, using a composition prepared by adding silicone beads to an acrylic urethane resin.

[Claim 6] The protective film of claim 1, wherein the first adhesive layer is formed to have a dry coating thickness of 30 to 60**㎛** using an acryl adhesive composition containing a UV protecting agent, while the second adhesive layer is formed to have a dry coating thickness of 1 to 10/**㎛** using an urethane adhesive composition.

[Claim 7] The protective film of claim 6, wherein the first adhesive layer has a

light transmittance of 90% or higher, a haze of 1% or lower, and a shear storage modulus of 10^3 to 10^5 Pa.

[Claim 8] The protective film of claim 1, wherein the first transparent plastic substrate has a thickness of 50 to 250㎛, the second transparent plastic substrate has a thickness of 10 to 50㎛, and the third transparent plastic substrate has a thickness of 10 to **50**㎛.

[Claim 9] The protective film of claim 8, wherein the first transparent plastic substrate, second transparent plastic substrate or third transparent plastic substrate is formed using polyethylene terephthalate or polyethylene naphthalate having a light transmittance of 90% or higher.

[Claim 10] A protective film, comprising:
an anti-glare coating layer, a first transparent plastic substrate, a first adhesive layer, a second transparent plastic substrate, a first silicon oxide (SiO_x, wherein x is 1.0-2.0) coating layer, a second adhesive layer, a third transparent plastic substrate, a second silicon oxide (SiO_x, wherein x is 1.0-2.0) coating layer and an acrylic resin coating layer laminated in sequential order, wherein the protective film has a total transmittance ranging from 89 to 91%, an MVTR of 0.01g/m^2.day or lower, and a haze ranging from 6 to 10%.

[Claim 11] The protective film of claim 10, wherein the acrylic resin coating layer is prepared by applying an acrylic resin composition, which includes; 10 to 15 wt.% of an acryl binder resin having a refractive index of 1.4 to 1.5 and a glass transition temperature of -10 to 20°C, 0.01 to 1 wt.% of a wetting agent, 0.1 to 2 wt.% of particles, 0.1 to 3 wt.% of a curing catalyst, 0.01 to 1 wt.% of an anti-oxidant, 80 to 85 wt.% of water and 1 to 5 wt.% of an organic solvent, to have a dry coating thickness of 70 to 90nm.

[Claim 12] The protective film of claim 10, wherein the silicon oxide coating layer is formed to have a coating thickness of 300 to 1,000Å by vacuum deposition.

[Claim 13] The protective film of claim 10, wherein the anti-glare coating layer is formed to have a dry coating thickness of 3 to 5㎛, using a composition prepared by adding silicone beads to an acrylic urethane resin.

[Claim 14] The protective film of claim 10, wherein the first adhesive layer is formed to have a dry coating thickness of 30 to 60㎛ using an acryl adhesive composition containing a UV protecting agent, while the second adhesive layer is formed to have a dry coating thickness of 1 to 10㎛ using an urethane adhesive composition.

[Claim 15] The protective film of claim 10, wherein the first adhesive layer has a light transmittance of 90% or higher, a haze of 1% or lower, and a shear storage modulus of 10^3 to 10^5 Pa.

[Claim 16] The protective film of claim 10, wherein the first transparent plastic substrate has a thickness of 50 to 250/㎛, the second transparent plastic substrate has a thickness of 10 to 50/㎛, and the third transparent plastic substrate has a thickness of 10 to 50/㎛.

[Claim 17] The protective film of claim 16, wherein the first transparent plastic substrate, second transparent plastic substrate or third transparent plastic substrate is formed using polyethylene terephthalate or polyethylene naphthalate having a light transmittance of 90% or higher.

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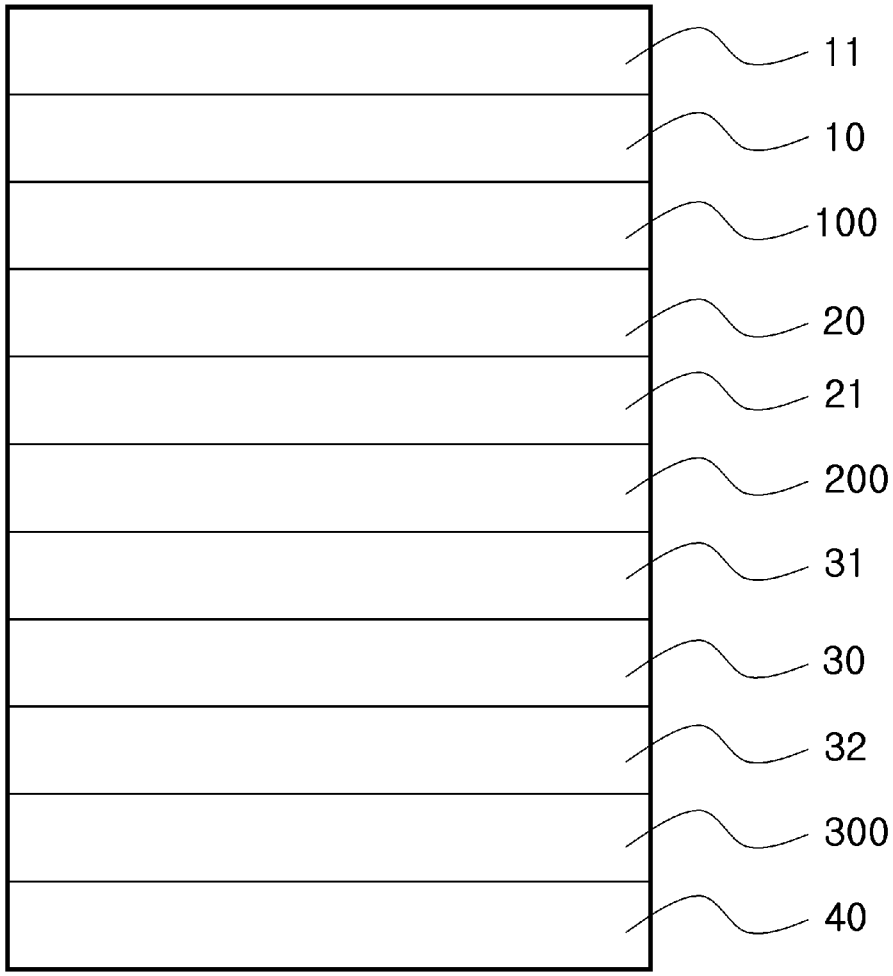
[Fig. 1]



[Fig. 2]

