

Description

Title of Invention: LAMINATE AND METHOD FOR PRODUCING LAMINATE

Technical Field

[0001] The present invention relates to a laminate including a polyvinyl alcohol-based resin layer.

Background Art

[0002] A method involving forming a polyvinyl alcohol-based resin layer on a resin substrate, and stretching and dyeing the laminate to provide a polarizing film has been proposed (e.g., Patent Literature 1). Such method has been attracting attention because a polarizing film having a small thickness is obtained by the method, and hence the method can contribute to, for example, the thinning of an image display apparatus.

[0003] The polarizing film may be used while being in a state of being laminated on the resin substrate. In such embodiment, the polyvinyl alcohol-based resin layer (polarizing film) and the resin substrate are required to have sufficient adhesiveness. Specifically, such conditions as described below are required. The polyvinyl alcohol-based resin layer does not peel from the resin substrate in the production of the polarizing film (e.g., in the stretching and conveyance of the laminate). The polarizing film and the resin substrate do not peel from each other at the time

of their reworking. The floating of the polarizing film or the resin substrate due to impact at the time of the processing (e.g., punching) of the laminate or during the use thereof does not occur.

[0004] The arrangement of an undercoat layer containing a polyvinyl alcohol-based material between the resin substrate and the polyvinyl alcohol-based resin layer has been proposed for improving the adhesiveness (Patent Literature 2). However, when the undercoat layer is arranged, there is a problem in that an excellent external appearance is hardly obtained.

Citation List

Patent Literature

[0005] [PTL 1] JP 2000-338329 A

[PTL 2] JP 4950357 B1

Summary of Invention

Technical Problem

[0006] The present invention has been made to solve the problems, and a primary object of the present invention is to provide a laminate bringing together excellent adhesiveness and an excellent external appearance.

Solution to Problem

[0007] According to one aspect of the present invention, there

is provided a laminate. The laminate according to the aspect of the present invention includes: a resin substrate; and a polyvinyl alcohol-based resin layer formed on one side of the resin substrate. A resin substrate side of the polyvinyl alcohol-based resin layer is an intermediate region in which a polyolefin-based component is present.

In one embodiment, the intermediate region contains a polyvinyl alcohol-based component and the polyolefin-based component.

In one embodiment, the polyvinyl alcohol-based component contains acetoacetyl-modified polyvinyl alcohol.

In one embodiment, a compounding ratio between the polyvinyl alcohol-based component and the polyolefin-based component is from 5:95 to 60:40.

In one embodiment, the intermediate region has a thickness of from 100 nm to 1,000 nm.

According to another aspect of the present invention, there is provided a method of producing a laminate. The method of producing a laminate includes the steps of: applying a composition for forming an undercoat layer containing a polyolefin-based component to one side of a resin substrate to form an undercoat layer; and applying

an application liquid containing a polyvinyl alcohol-based resin to a surface of the undercoat layer to form a polyvinyl alcohol-based resin-applied layer.

In one embodiment, the composition for forming an undercoat layer contains a polyvinyl alcohol-based component and the polyolefin-based component.

In one embodiment, the polyvinyl alcohol-based component contains acetoacetyl-modified polyvinyl alcohol.

In one embodiment, a solid content compounding ratio between the polyvinyl alcohol-based component and the polyolefin-based component is from 5:95 to 60:40.

In one embodiment, the undercoat layer has a thickness of from 500 nm to 3,000 nm.

According to yet another aspect of the present invention, there is provided a method of producing a polarizing plate. The method of producing a polarizing plate includes the step of stretching and dyeing a laminate obtained by the production method described above.

According to yet another aspect of the present invention, there

is provided a polarizing plate. The polarizing plate includes: a resin substrate; and a polyvinyl alcohol-based resin layer formed on one side of the resin substrate. A resin substrate side of the polyvinyl alcohol-based resin layer is an intermediate region in which a polyolefin-based component is present, and the polyvinyl alcohol-based resin layer includes a polarizing film having a dichroic substance adsorbed and aligned thereon.

In one embodiment, the intermediate region contains a polyvinyl alcohol-based component and the polyolefin-based component.

In one embodiment, the polyvinyl alcohol-based component contains acetoacetyl-modified polyvinyl alcohol.

In one embodiment, a compounding ratio between the polyvinyl alcohol-based component and the polyolefin-based component is from 5:95 to 60:40.

In one embodiment, the intermediate region has a thickness of from 100 nm to 1,000 nm.

Advantageous Effects of Invention

[0008] According to the present invention, the laminate bringing together excellent adhesiveness and an excellent external appearance can be obtained by allowing the resin substrate side

of the polyvinyl alcohol-based resin layer to be the intermediate region in which the polyolefin-based component is present.

Brief Description of Drawings

[0009] FIGS. **1** are SEM observation photographs of sections of laminates of Examples and Comparative Examples.

Description of Embodiments

[0010] Embodiments of the present invention are described below. However, the present invention is not limited to these embodiments.

[0011] A. Laminate

A laminate of the present invention includes a resin substrate and a polyvinyl alcohol-based resin (hereinafter referred to as "PVA-based resin") layer formed on one side of the resin substrate, and at least the resin substrate side of the PVA-based resin layer is an intermediate region in which a polyolefin-based component is present. In one embodiment, the intermediate region substantially corresponds to an undercoat layer to be described later, and the PVA-based resin layer includes the undercoat layer and a PVA-based resin-applied layer to be described later. In another embodiment, the PVA-based resin layer substantially forms a single layer, and the intermediate region is turned into, for example, a region in which the PVA-based resin-applied layer and the undercoat layer are compatibilized with each other. The PVA-based resin layer

may be turned into a polarizing film by various treatments, and thus, the laminate may be turned into a polarizing plate.

[0012] A-1. Resin Substrate

Any appropriate material may be adopted as a constituent material for the resin substrate. Examples thereof include: ester-based resins, such as a polyethylene terephthalate-based resin; olefin-based resins, such as a cycloolefin-based resin and polypropylene; (meth)acrylic resins; polyamide-based resins; and polycarbonate-based resins; and copolymer resins thereof. Of those, a polyethylene terephthalate-based resin is preferably used. Of such resins, an amorphous polyethylene terephthalate-based resin is preferably used. Specific examples of the amorphous polyethylene terephthalate-based resin include a copolymer further containing isophthalic acid as a dicarboxylic acid and a copolymer further containing cyclohexanedimethanol as a glycol.

[0013] The glass transition temperature (T_g) of the resin substrate is preferably 170°C or less. The use of such resin substrate can sufficiently secure the stretchability of the laminate while suppressing the crystallization of the PVA-based resin layer. In consideration of the plasticization of the resin substrate by water and satisfactory performance of the underwater stretching of the laminate, the glass transition temperature is more preferably 120°C or less. In one embodiment, the glass transition temperature

of the resin substrate is preferably 60°C or more. The use of such resin substrate can prevent an inconvenience, such as the deformation (e.g., the occurrence of unevenness, a sag, or a wrinkle) of the resin substrate at the time of the application and drying of an application liquid containing a PVA-based resin to be described later. In addition, the use enables the performance of the stretching of the laminate at a suitable temperature (e.g., from about 60°C to about 70°C). In another embodiment, the glass transition temperature may be lower than 60°C as long as the resin substrate does not deform at the time of the application and drying of the application liquid containing the PVA-based resin. The glass transition temperature (T_g) is a value determined in conformity with JIS K 7121.

[0014] In one embodiment, the water absorption ratio of the resin substrate is preferably 0.2% or more, more preferably 0.3% or more. Such resin substrate absorbs water, and the water can function like a plasticizer to plasticize the resin substrate. As a result, a stretching stress in the underwater stretching can be significantly reduced, and hence the laminate can be excellent in stretchability. Meanwhile, the water absorption ratio of the resin substrate is preferably 3.0% or less, more preferably 1.0% or less. The use of such resin substrate can prevent an inconvenience, such as the deterioration of the external appearance of the laminate to be obtained due to a remarkable reduction in dimensional stability

of the resin substrate at the time of the production. In addition, the use can prevent the rupture of the laminate and the peeling of the PVA-based resin layer from the resin substrate, at the time of the underwater stretching. The water absorption ratio is a value determined in conformity with JIS K 7209.

[0015] The thickness of the resin substrate is preferably from 20 μm to 300 μm , more preferably from 30 μm to 200 μm .

[0016] In advance, the surface of the resin substrate may be subjected to a surface modification treatment (e.g., a corona treatment), or an easy-adhesion layer may be formed thereon. Such treatment can further improve adhesiveness between the resin substrate and the PVA-based resin layer.

[0017] A-2. PVA-based Resin Layer

Any appropriate resin may be adopted as a PVA-based resin forming the PVA-based resin layer. Examples thereof include polyvinyl alcohol and an ethylene-vinyl alcohol copolymer. The polyvinyl alcohol is obtained by saponifying polyvinyl acetate. The ethylene-vinyl alcohol copolymer is obtained by saponifying an ethylene-vinyl acetate copolymer. The saponification degree of the PVA-based resin is typically from 85 mol% to 100 mol%, preferably from 95.0 mol% to 99.95 mol%, more preferably from 99.0 mol% to 99.93 mol%. The saponification degree may be determined in

conformity with JIS K 6726-1994. The use of a PVA-based resin having such saponification degree can provide a polarizing film excellent in durability. When the saponification degree is excessively high, the resin may gel.

[0018] The average polymerization degree of the PVA-based resin may be appropriately selected in accordance with purposes. The average polymerization degree is typically from 1,000 to 10,000, preferably from 1,200 to 4,500, more preferably from 1,500 to 4,300. The average polymerization degree may be determined in conformity with JIS K 6726-1994.

[0019] The thickness of the PVA-based resin layer is typically 20 μm or less, preferably 15 μm or less. When the PVA-based resin layer is turned into a polarizing film, its thickness is preferably 10 μm or less, more preferably 8 μm or less, still more preferably 7 μm or less, particularly preferably 6 μm or less. Meanwhile, the thickness of the PVA-based resin layer is preferably 1.0 μm or more, more preferably 2.0 μm or more.

[0020] In the case where the PVA-based resin layer is turned into a polarizing film, the PVA-based resin layer is substantially in a state of having adsorbed and aligned thereon a dichroic substance, and preferably shows absorption dichroism at any wavelength in the wavelength range of from 380 nm to 780 nm. In this case, the single

layer transmittance of the PVA-based resin layer is preferably 40.0% or more, more preferably 41.0% or more, still more preferably 42.0% or more, particularly preferably 43.0% or more. The polarization degree of the PVA-based resin layer is preferably 99.8% or more, more preferably 99.9% or more, still more preferably 99.95% or more.

[0021] As described above, the resin substrate side of the PVA-based resin layer is the intermediate region in which the polyolefin-based component is present. The formation of such region can achieve excellent adhesiveness and an excellent external appearance. The thickness of the intermediate region is, for example, from 100 nm to 1,000 nm. The intermediate region may be confirmed by, for example, observing a section of the laminate with a scanning electron microscope (SEM). In addition, the presence or absence of the polyolefin-based component may be confirmed by, for example, time-of-flight secondary ion mass spectrometry (TOF-SIMS) or infrared spectroscopy (IR). In one embodiment, the intermediate region contains a polyvinyl alcohol-based component and the polyolefin-based component. Details about the polyolefin-based component and the polyvinyl alcohol-based component are described later.

[0022] B. Production Method

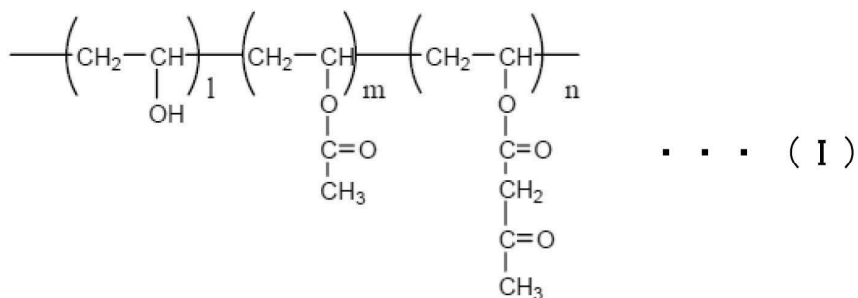
The laminate of the present invention may be produced by any appropriate method as long as the above-mentioned construction is

obtained. In one embodiment, the laminate is produced by a method including the steps of: applying a composition for forming an undercoat layer containing the polyolefin-based component to one side of the resin substrate to form an undercoat layer; and applying an application liquid containing a PVA-based resin to the surface of the undercoat layer to form a PVA-based resin-applied layer.

[0023] B-1. Formation of Undercoat Layer

The composition for forming an undercoat layer preferably contains a polyvinyl alcohol-based component and the polyolefin-based component. The adoption of such composition can provide a laminate bringing together excellent adhesiveness and an excellent external appearance. Any appropriate PVA-based resin may be used as the polyvinyl alcohol-based component. Specific examples thereof include polyvinyl alcohol and modified polyvinyl alcohol. The modified polyvinyl alcohol is, for example, polyvinyl alcohol modified with an acetoacetyl group, a carboxylic acid group, an acrylic group, and/or a urethane group. Of those, acetoacetyl-modified PVA is preferably used. A polymer having at least a repeating unit represented by the following general formula (I) is preferably used as the acetoacetyl-modified PVA.

[0024]



[0025] In the formula (I), the ratio of n to 1+m+n is preferably from 1% to 10%.

[0026] The average polymerization degree of the acetoacetyl-modified PVA is preferably from 1,000 to 10,000, more preferably from 1,200 to 5,000. The saponification degree of the acetoacetyl-modified PVA is preferably 97 mol% or more. The pH of a 4 wt% aqueous solution of the acetoacetyl-modified PVA is preferably from 3.5 to 5.5. The average polymerization degree and the saponification degree may be determined in conformity with JIS K 6726-1994.

[0027] Any appropriate polyolefin-based resin may be used as the polyolefin-based component. An olefin component serving as the main component of the polyolefin-based resin is, for example, an olefin-based hydrocarbon having 2 to 6 carbon atoms, such as ethylene, propylene, isobutylene, 1-butene, 1-pentene, or 1-hexene. Those components may be used alone or in combination thereof. Of those, an olefin-based hydrocarbon having 2 to 4 carbon atoms, such as

ethylene, propylene, isobutylene, or 1-butene, is preferably used, and ethylene is more preferably used.

[0028] The ratio of the olefin component to monomer components forming the polyolefin-based resin is preferably from 50 wt% to 95 wt%.

[0029] The polyolefin-based resin preferably has a carboxyl group and/or an anhydride group thereof. Such polyolefin-based resin can be dispersed in water, and hence the undercoat layer can be satisfactorily formed. A monomer component having such functional group is, for example, an unsaturated carboxylic acid, an anhydride thereof, or a half ester or a half amide of an unsaturated dicarboxylic acid. Specific examples thereof include acrylic acid, methacrylic acid, maleic acid, maleic anhydride, itaconic acid, itaconic anhydride, fumaric acid, and crotonic acid.

[0030] The polyolefin-based resin has a molecular weight of, for example, from 5,000 to 80,000.

[0031] In the composition for forming an undercoat layer, a compounding ratio (solid content) between the polyvinyl alcohol-based component and the polyolefin-based component is preferably from 5:95 to 60:40, more preferably from 20:80 to 50:50. When the amount of the polyvinyl alcohol-based component is

excessively large, the adhesiveness may not be sufficiently obtained. Specifically, there is a risk in that a peel strength needed at the time of the peeling of the PVA-based resin layer from the resin substrate reduces, and hence sufficient adhesiveness is not obtained. Meanwhile, when the amount of the polyvinyl alcohol-based component is excessively small, the external appearance of the laminate to be obtained may be impaired. Specifically, there is a risk in that an inconvenience, such as the cloudiness of an applied film, occurs at the time of the formation of the undercoat layer to be described later to make it difficult to obtain a laminate excellent in external appearance.

[0032] The composition for forming an undercoat layer is preferably aqueous. The composition for forming an undercoat layer may contain an organic solvent. Examples of the organic solvent include ethanol and isopropanol. The solid content concentration of the composition for forming an undercoat layer is preferably from 1.0 wt% to 10 wt%.

[0033] The composition for forming an undercoat layer may be compounded with an additive. The additive is, for example, a cross-linking agent. Examples of the cross-linking agent include: oxazoline; boric acid; a methylol compound, such as trimethylolmelamine; a carbodiimide; an isocyanate compound; and an epoxy compound. The compounding amount of the additive in the

composition for forming an undercoat layer may be appropriately set in accordance with purposes and the like. For example, the compounding amount of the cross-linking agent is preferably 10 parts by weight or less, more preferably from 0.01 part by weight to 10 parts by weight, still more preferably from 0.1 part by weight to 5 parts by weight with respect to 100 parts by weight of the total of the polyvinyl alcohol-based component and the polyolefin-based component.

[0034] Any appropriate method may be adopted as a method of applying the composition for forming an undercoat layer. Examples thereof include a roll coating method, a spin coating method, a wire bar coating method, a dip coating method, a die coating method, a curtain coating method, a spray coating method, and a knife coating method (e.g., a comma coating method).

[0035] The composition for forming an undercoat layer is applied so that the thickness of the undercoat layer to be obtained may be preferably from 500 nm to 3,000 nm, more preferably from 800 nm to 2,000 nm. When the thickness of the undercoat layer is excessively small, sufficient adhesiveness may not be obtained. Meanwhile, when the thickness of the undercoat layer is excessively large, there is a risk in that an inconvenience, such as the occurrence of cissing or the occurrence of unevenness in an applied film to be obtained, occurs at the time of the formation of the PVA-based

resin-applied layer to be described later to make it difficult to obtain a laminate excellent in external appearance.

[0036] After the application of the composition for forming an undercoat layer, the applied film may be dried. A drying temperature is, for example, 50°C or more.

[0037] B-2. Formation of PVA-based Resin-applied Layer

 The surface of the undercoat layer to which the application liquid containing the PVA-based resin is applied may be subjected to a surface modification treatment (e.g., a corona treatment) in advance. Such treatment can further improve the adhesiveness.

[0038] A solution in which the PVA-based resin is dissolved in a solvent is typically used as the application liquid containing the PVA-based resin. Examples of the solvent include water, dimethyl sulfoxide, dimethylformamide, dimethylacetamide, N-methylpyrrolidone, various glycols, polyhydric alcohols, such as trimethylolpropane, and amines, such as ethylenediamine and diethylenetriamine. Those solvents may be used alone or in combination thereof. Of those, water is preferred. The PVA-based resin concentration of the application liquid is preferably from 3 parts by weight to 20 parts by weight with respect to 100 parts by weight of the solvent. Such resin concentration enables the formation of a uniform applied film.

[0039] The application liquid may be compounded with an additive. Examples of the additive include a plasticizer and a surfactant. Examples of the plasticizer include polyhydric alcohols, such as ethylene glycol and glycerin. The surfactant is, for example, a nonionic surfactant. Any such additive may be used for the purpose of further improving the uniformity, dyeability, and stretchability of the PVA-based resin layer to be obtained. In addition, the additive is, for example, an easy-adhesion component. The use of the easy-adhesion component can further improve the adhesiveness. Modified PVA, such as acetoacetyl-modified PVA, is used as the easy-adhesion component.

[0040] The same method as the method of applying the composition for forming an undercoat layer may be adopted as a method of applying the application liquid. After the application, the applied film may be dried. A drying temperature is, for example, 50°C or more.

[0041] B-3. Production of Polarizing Film

As described above, the laminate may be subjected to various treatments. Specific examples of the various treatments include a dyeing treatment, a stretching treatment, an insolubilizing treatment, a cross-linking treatment, a washing treatment, and a drying treatment. Those treatments may be appropriately selected in accordance with purposes. In addition, the order in which the

treatments are performed, the timing at which any such treatment is performed, the number of times of any such treatment, and the like may be appropriately set. The respective treatments are described below.

[0042] (Dyeing Treatment)

The dyeing treatment is typically performed by dyeing the PVA-based resin layer with a dichroic substance. The treatment is preferably performed by causing the PVA-based resin layer to adsorb the dichroic substance. A method for the adsorption is, for example, a method involving immersing the PVA-based resin layer (laminate) in a dyeing liquid containing the dichroic substance, a method involving applying the dyeing liquid to the PVA-based resin layer, or a method involving spraying the dyeing liquid on the PVA-based resin layer. Of those, a method involving immersing the PVA-based resin layer in the dyeing liquid is preferred. This is because the dichroic substance can satisfactorily adsorb to the layer.

[0043] Examples of the dichroic substance include iodine and an organic dye. Those substances may be used alone or in combination thereof. The dichroic substance is preferably iodine. When iodine is used as the dichroic substance, the dyeing liquid is preferably an aqueous solution of iodine. The compounding amount of iodine is preferably from 0.1 part by weight to 0.5 part by weight with respect to 100 parts by weight of water. An iodide is preferably

compounded into the aqueous solution of iodine for improving the solubility of iodine in water. Examples of the iodide include potassium iodide, lithium iodide, sodium iodide, zinc iodide, aluminum iodide, lead iodide, copper iodide, barium iodide, calcium iodide, tin iodide, and titanium iodide. Of those, potassium iodide is preferred. The compounding amount of the iodide is preferably from 0.02 part by weight to 20 parts by weight, more preferably from 0.1 part by weight to 10 parts by weight with respect to 100 parts by weight of water.

[0044] The liquid temperature of the dyeing liquid at the time of the dyeing is preferably from 20°C to 50°C in order that the dissolution of the PVA-based resin may be suppressed. When the PVA-based resin layer is immersed in the dyeing liquid, an immersion time is preferably from 5 seconds to 5 minutes in order that the transmittance of the PVA-based resin layer may be secured. In addition, dyeing conditions (the concentration of the liquid, the liquid temperature, and the immersion time) may be set so that the polarization degree or single layer transmittance of a polarizing film to be finally obtained may fall within a predetermined range. In one embodiment, the immersion time is set so that the polarization degree of the polarizing film to be obtained may be 99.98% or more. In another embodiment, the immersion time is set so that the single layer transmittance of the polarizing film to be obtained may be from 40% to 44%.

[0045] (Stretching Treatment)

Any appropriate method may be adopted as a method of stretching the laminate. Specifically, fixed-end stretching (e.g., a method involving using a tenter stretching machine) may be adopted, or free-end stretching (e.g., a method involving passing the laminate between rolls having different peripheral speeds to uniaxially stretch the laminate) may be adopted. In addition, simultaneous biaxial stretching (e.g., a method involving using a simultaneous biaxial stretching machine) may be adopted, or sequential biaxial stretching may be adopted. The stretching of the laminate may be performed in one stage, or may be performed in a plurality of stages. When the stretching is performed in a plurality of stages, the stretching ratio (maximum stretching ratio) of the laminate to be described later is the product of stretching ratios at the respective stages.

[0046] The stretching treatment may be an underwater stretching mode involving stretching the laminate while immersing the laminate in a stretching bath, or may be an in-air stretching mode. In one embodiment, an underwater stretching treatment is performed at least once, and the underwater stretching treatment and an in-air stretching treatment are preferably combined. According to underwater stretching, the stretching can be performed at a temperature lower than the glass transition temperature (typically

about 80°C) of the resin substrate or the PVA-based resin layer, and hence the PVA-based resin layer can be stretched at a high ratio while its crystallization is suppressed. As a result, a polarizing film having excellent polarization characteristics can be produced.

[0047] Any appropriate direction may be selected as the stretching direction of the laminate. In one embodiment, the stretching is performed in the lengthwise direction of an elongated laminate. Specifically, the laminate is conveyed in its lengthwise direction, and is stretched in the conveyance direction (MD). In another embodiment, the stretching is performed in the widthwise direction of the elongated laminate. Specifically, the laminate is conveyed in its lengthwise direction, and is stretched in a direction (TD) perpendicular to the conveyance direction (MD).

[0048] The stretching temperature of the laminate may be set to any appropriate value in accordance with, for example, the formation material for the resin substrate and the stretching mode. When the in-air stretching mode is adopted, the stretching temperature is preferably equal to or more than the glass transition temperature (T_g) of the resin substrate, more preferably equal to or more than the glass transition temperature (T_g) of the resin substrate+10°C, particularly preferably equal to or more than T_g +15°C. Meanwhile, the stretching temperature of the laminate is preferably 170°C or less. When the stretching is performed at such

temperature, rapid progress of the crystallization of the PVA-based resin is suppressed, and hence an inconvenience due to the crystallization (e.g., the inhibition of the orientation of the PVA-based resin layer by the stretching) can be suppressed.

[0049] When the underwater stretching mode is adopted as the stretching mode, the liquid temperature of a stretching bath is preferably from 40°C to 85°C, more preferably from 50°C to 85°C. At such temperature, the stretching can be performed at a high ratio while the dissolution of the PVA-based resin layer is suppressed. Specifically, as described above, the glass transition temperature (T_g) of the resin substrate is preferably 60°C or more in relation to the formation of the PVA-based resin layer. In this case, when the stretching temperature is less than 40°C, there is a risk in that the stretching cannot be satisfactorily performed even in consideration of the plasticization of the resin substrate by water. Meanwhile, as the temperature of the stretching bath increases, there is a risk in that the solubility of the PVA-based resin layer is raised and hence excellent polarization characteristics cannot be obtained.

[0050] When the underwater stretching mode is adopted, the laminate is preferably stretched while being immersed in an aqueous solution of boric acid (boric acid underwater stretching). The use of the aqueous solution of boric acid as the stretching bath can

impart, to the PVA-based resin layer, rigidity enabling the layer to withstand a tension to be applied at the time of the stretching and water resistance preventing the layer from dissolving in water. Specifically, boric acid can produce a tetrahydroxyboric acid anion in the aqueous solution to cross-link with the PVA-based resin through a hydrogen bond. As a result, the rigidity and the water resistance are imparted to the PVA-based resin layer, and hence the layer can be satisfactorily stretched. Accordingly, a polarizing film having excellent polarization characteristics can be produced.

[0051] The aqueous solution of boric acid is preferably obtained by dissolving boric acid and/or a borate in water serving as a solvent. The concentration of boric acid is preferably from 1 part by weight to 10 parts by weight with respect to 100 parts by weight of water. The setting of the boric acid concentration to 1 part by weight or more can effectively suppress the dissolution of the PVA-based resin layer, and hence enables the production of a polarizing film having higher characteristics. In addition to boric acid or the borate, an aqueous solution obtained by dissolving, for example, a boron compound, such as borax, and glyoxal or glutaraldehyde in a solvent may also be used.

[0052] The stretching bath (aqueous solution of boric acid) is preferably compounded with an iodide. The compounding of the bath with the iodide can suppress the elution of iodine adsorbed

by the PVA-based resin layer. Specific examples of the iodide are as described above. The concentration of the iodide is preferably from 0.05 part by weight to 15 parts by weight, more preferably from 0.5 part by weight to 8 parts by weight with respect to 100 parts by weight of water.

[0053] The time period for which the laminate is immersed in the stretching bath is preferably from 15 seconds to 5 minutes. The underwater stretching treatment is preferably performed after the dyeing treatment.

[0054] The stretching ratio (maximum stretching ratio) of the laminate is preferably 4.0 times or more, more preferably 5.0 times or more with respect to the original length of the laminate. Such high stretching ratio can be achieved by adopting, for example, the underwater stretching mode (boric acid underwater stretching). The term "maximum stretching ratio" as used herein refers to a stretching ratio immediately before the rupture of the laminate, and refers to a value lower than a separately determined value for the stretching ratio at which the laminate is ruptured by 0.2.

[0055] (Insolubilizing Treatment)

 The insolubilizing treatment is typically performed by immersing the PVA-based resin layer in an aqueous solution of boric acid. Particularly when the underwater stretching mode is adopted,

the performance of the insolubilizing treatment can impart water resistance to the PVA-based resin layer. The concentration of the aqueous solution of boric acid is preferably from 1 part by weight to 4 parts by weight with respect to 100 parts by weight of water. The liquid temperature of an insolubilizing bath (aqueous solution of boric acid) is preferably from 20°C to 40°C. The insolubilizing treatment is preferably performed after the production of the laminate and before the dyeing treatment and the underwater stretching treatment.

[0056] (Cross-linking Treatment)

The cross-linking treatment is typically performed by immersing the PVA-based resin layer in an aqueous solution of boric acid. The performance of the cross-linking treatment can impart water resistance to the PVA-based resin layer. The concentration of the aqueous solution of boric acid is preferably from 1 part by weight to 4 parts by weight with respect to 100 parts by weight of water. In addition, when the cross-linking treatment is performed after the dyeing treatment, the solution is preferably further compounded with an iodide. The compounding of the solution with the iodide can suppress the elution of iodine adsorbed by the PVA-based resin layer. The compounding amount of the iodide is preferably from 1 part by weight to 5 parts by weight with respect to 100 parts by weight of water. Specific examples of the iodide are as described above. The liquid temperature of a cross-linking bath (aqueous

solution of boric acid) is preferably from 20°C to 50°C. The cross-linking treatment is preferably performed before the underwater stretching treatment. In a preferred embodiment, the dyeing treatment, the cross-linking treatment, and the underwater stretching treatment are performed in the stated order.

[0057] (Washing Treatment)

The washing treatment is typically performed by immersing the PVA-based resin layer in an aqueous solution of potassium iodide.

[0058] (Drying Treatment)

A drying temperature in the drying treatment is preferably from 30°C to 100°C.

[0059] B-4. Others

The polarizing plate may include a protective film arranged on a side opposite to the side on which the resin substrate of the polarizing film is arranged. As the formation material for the protective film, there are given, for example: (meth)acrylic resins; cellulose-based resins, such as diacetyl cellulose and triacetyl cellulose; olefin-based resins, such as a cycloolefin-based resin and polypropylene; ester-based resins, such as a polyethylene terephthalate-based resin; polyamide-based resins; and polycarbonate-based resins; and copolymer resins thereof. The protective film preferably has a thickness of from 10 μm to 100

μm. The protective film may be laminated on the polarizing film through the intermediation of an adhesion layer, or may be laminated on the polarizing film while being brought into close contact therewith (without through the intermediation of the adhesion layer). The adhesion layer is typically formed of an adhesive or a pressure-sensitive adhesive.

[0060] The polarizing plate may be mounted on, for example, a liquid crystal display apparatus. In this case, the polarizing plate is preferably mounted so that the polarizing film may be arranged on a side closer to a liquid crystal cell with respect to the resin substrate. Such construction can eliminate the influences of a retardation that the resin substrate may have on the image characteristics of the liquid crystal display apparatus to be obtained.

Examples

[0061] The present invention is specifically described below by way of Examples, but the present invention is not limited to these Examples. A method of measuring a thickness is as described below. In addition, in Examples and Comparative Examples described below, "part(s)" and "%" mean "part(s) by weight" and "wt%", respectively.

(Thickness)

Measurement was performed with a digital micrometer (manufactured by Anritsu Corporation, product name: "KC-351C").

[0062] [Example 1]

An amorphous isophthalic acid-copolymerized polyethylene terephthalate (IPA-copolymerized PET) film of an elongated shape (thickness: 100 μm) having a water absorption ratio of 0.75% and a T_g of 75°C was used as a resin substrate.

One surface of the resin substrate was subjected to a corona treatment, and a mixed liquid (solid content concentration: 4.0%) obtained by mixing a 4.0% aqueous solution of acetoacetyl-modified PVA (manufactured by The Nippon Synthetic Chemical Industry Co., Ltd., product name: "GOHSEFIMERZ-200," polymerization degree: 1,200, saponification degree: 99.0 mol% or more, acetoacetyl modification degree: 4.6%), a modified polyolefin resin aqueous dispersion (manufactured by Unitika Ltd., product name: "ARROWBASE SE1030N," solid content concentration: 22%), and pure water was applied to the corona-treated surface so that a thickness after its drying became 2,000 nm, followed by drying at 60°C for 3 minutes. Thus, an undercoat layer was formed. Here, a solid content compounding ratio between the acetoacetyl-modified PVA and the modified polyolefin in the mixed liquid was 30:70.

Next, a surface of the undercoat layer was subjected to a corona

treatment, and an aqueous solution containing polyvinyl alcohol (polymerization degree: 4,200, saponification degree: 99.2 mol%) and acetoacetyl-modified PVA (polymerization degree: 1,200, acetoacetyl modification degree: 4.6%, saponification degree: 99.0 mol% or more, manufactured by The Nippon Synthetic Chemical Industry Co., Ltd., product name: "GOHSEFIMER Z-200") at a ratio of 9:1 was applied to the corona-treated surface and dried at 25°C to form a PVA-based resin layer having a thickness of 11 μm . Thus, a laminate was produced.

[0063] The resultant laminate was subjected to free-end uniaxial stretching in an oven at 120°C between rolls having different peripheral speeds in a longitudinal direction (lengthwise direction) at 2.0 times (in-air auxiliary stretching).

Next, the laminate was immersed in an insolubilizing bath having a liquid temperature of 30°C (an aqueous solution of boric acid obtained by compounding 100 parts by weight of water with 4 parts by weight of boric acid) for 30 seconds (insolubilizing treatment).

Next, the laminate was immersed in a dyeing bath having a liquid temperature of 30°C while an iodine concentration and an immersion time were adjusted so that a polarizing plate to be obtained had a predetermined transmittance. In this example, the laminate was

immersed in an aqueous solution of iodine, which was obtained by compounding 100 parts by weight of water with 0.2 part by weight of iodine and 1.0 part by weight of potassium iodide, for 60 seconds (dyeing treatment).

Next, the laminate was immersed in a cross-linking bath having a liquid temperature of 30°C (an aqueous solution of boric acid obtained by compounding 100 parts by weight of water with 3 parts by weight of potassium iodide and 3 parts by weight of boric acid) for 30 seconds (cross-linking treatment).

After that, the laminate was subjected to uniaxial stretching between rolls having different peripheral speeds in a longitudinal direction (lengthwise direction) so that a total stretching ratio became 5.5 times while being immersed in an aqueous solution of boric acid having a liquid temperature of 70°C (an aqueous solution obtained by compounding 100 parts by weight of water with 4 parts by weight of boric acid and 5 parts by weight of potassium iodide) (underwater stretching).

After that, the laminate was immersed in a washing bath having a liquid temperature of 30°C (an aqueous solution obtained by compounding 100 parts by weight of water with 4 parts by weight of potassium iodide) (washing treatment).

Thus, a laminate (polarizing plate) in which a polarizing film having a thickness of 5 μm was formed on one side of the resin substrate having a thickness of 30 μm was obtained.

[0064] [Example 2]

A polarizing plate was obtained in the same manner as in Example 1 except that the mixed liquid was applied so that a thickness after its drying became 1,000 nm.

[0065] [Example 3]

A polarizing plate was obtained in the same manner as in Example 1 except that the mixed liquid was applied so that a thickness after its drying became 500 nm.

[0066] [Example 4]

A polarizing plate was obtained in the same manner as in Example 1 except that the solid content compounding ratio between the acetoacetyl-modified PVA and the modified polyolefin in the mixed liquid was set to 50:50.

[0067] [Example 5]

A polarizing plate was obtained in the same manner as in Example 1 except that a mixed liquid (solid content concentration: 4.0%) obtained by mixing a 4.0% aqueous solution of the acetoacetyl-modified PVA (GOHSEFIMER Z-200), a modified polyolefin

resin aqueous dispersion (manufactured by Unitika Ltd., product name: "ARROWBASE SD1030N," solid content concentration: 22%), and pure water was used at the time of the formation of the undercoat layer.

[0068] [Example 6]

A polarizing plate was obtained in the same manner as in Example 4 except that a mixed liquid (solid content concentration: 4.0%) obtained by mixing a 4.0% aqueous solution of the acetoacetyl-modified PVA (GOHSEFIMER Z-200), a modified polyolefin resin aqueous dispersion (manufactured by Unitika Ltd., product name: "ARROWBASE SE1035NJ2," solid content concentration: 22%), and pure water was used at the time of the formation of the undercoat layer.

[0069] [Example 7]

A polarizing plate was obtained in the same manner as in Example 1 except that a mixed liquid (solid content concentration: 4.0%) obtained by mixing a 4.0% aqueous solution of acetoacetyl-modified PVA (manufactured by The Nippon Synthetic Chemical Industry Co., Ltd., product name: "GOHSEFIMER Z-410," polymerization degree: 2,200, saponification degree: from 97.5% to 98.5%, acetoacetyl modification degree: 4.6%), a modified polyolefin resin aqueous dispersion (manufactured by Unitika Ltd., product name: "ARROWBASE SE1030N," solid content concentration: 22%), and pure water was used at the

time of the formation of the undercoat layer.

[0070] [Example 8]

A polarizing plate in which a polarizing film having a thickness of 6 μm was formed on one side of the resin substrate having a thickness of 37 μm was obtained in the same manner as in Example 1 except that: the stretching ratio of the in-air auxiliary stretching was set to 4.0 times; and the insolubilizing treatment and the underwater stretching were not performed.

[0071] [Comparative Example 1]

A polarizing plate was obtained in the same manner as in Example 1 except that the PVA-based resin-applied layer was directly formed on the resin substrate without the formation of any undercoat layer.

[0072] [Comparative Example 2]

A polarizing plate was obtained in the same manner as in Example 8 except that the PVA-based resin-applied layer was directly formed on the resin substrate without the formation of any undercoat layer.

[0073] [Comparative Example 3]

A polarizing plate was obtained in the same manner as in Example 3 except that a 4.0% aqueous solution of the acetoacetyl-modified PVA (GOHSEFIMER Z-200) was used at the time of the formation of the undercoat layer.

[0074] [Comparative Example 4]

A polarizing plate was obtained in the same manner as in Example 2 except that a 4.0% aqueous solution of the acetoacetyl-modified PVA (GOHSEFIMER Z-200) was used at the time of the formation of the undercoat layer.

[0075] [Comparative Example 5]

A polarizing plate was obtained in the same manner as in Example 1 except that a 4.0% aqueous solution of the acetoacetyl-modified PVA (GOHSEFIMER Z-200) was used at the time of the formation of the undercoat layer.

[0076] [Comparative Example 6]

A polarizing plate was obtained in the same manner as in Example 8 except that: a 4.0% aqueous solution of the acetoacetyl-modified PVA (GOHSEFIMER Z-200) was used at the time of the formation of the undercoat layer; and the aqueous solution was applied so that a thickness after its drying became 1,000 nm.

[0077] [Comparative Example 7]

A polarizing plate was obtained in the same manner as in Example 3 except that a polyester aqueous emulsion resin (manufactured by Unitika Ltd., product name: "ELITEL KT0507E6") was used at the time of the formation of the undercoat layer.

[0078] [Comparative Example 8]

A polarizing plate was obtained in the same manner as in Example 2 except that a polyester aqueous emulsion resin (manufactured by Unitika Ltd., product name: "ELITEL KT0507E6") was used at the time of the formation of the undercoat layer.

[0079] [Comparative Example 9]

A polarizing plate was obtained in the same manner as in Example 2 except that the modified polyolefin resin aqueous dispersion (ARROWBASE SB1035NJ2) was used at the time of the formation of the undercoat layer.

[0080] [Comparative Example 10]

A polarizing plate was obtained in the same manner as in Example 3 except that a mixed liquid obtained by mixing 10 g of a 4.0% aqueous solution of the acetoacetyl-modified PVA (GOHSEFIMER Z-200) and 62.5 g of the polyester aqueous emulsion resin (ELITEL KT0507E6) was used at the time of the formation of the undercoat layer. Here, a solid content compounding ratio between the acetoacetyl-modified PVA and the polyester in the mixed liquid was 50:50.

[0081] [Comparative Example 11]

A polarizing plate was obtained in the same manner as in Example 1 except that a mixed liquid obtained by mixing 10 g of a 4.0% aqueous

solution of the acetoacetyl-modified PVA (GOHSEFIMER Z-200) and 62.5 g of the polyester aqueous emulsion resin (ELITEL KT0507E6) was used at the time of the formation of the undercoat layer. Here, a solid content compounding ratio between the acetoacetyl-modified PVA and the polyester in the mixed liquid was 50:50.

[0082] (Evaluation)

The polarizing plates of Examples and Comparative Examples described above were subjected to the following evaluations. The results of the evaluations are summarized in Table 1. In addition, the results of the observation of sections of the laminates after the stretching in Example 1, Example 2, Example 8, Comparative Example 1, and Comparative Example 11 with a SEM (at a magnification of 6,500) are shown in FIGS. 1.

1. Adhesiveness

The adhesiveness of each of the polarizing plates was evaluated by measuring a PVA peel strength and a substrate peel strength. Methods of measuring the PVA peel strength and the substrate peel strength are as described below.

(PVA Peel Strength)

Each of the resultant polarizing plates was bonded to a glass plate by applying a pressure-sensitive adhesive to the resin substrate surface side of the polarizing plate, and a reinforcing

polyimide tape (manufactured by Nitto Denko Corporation, Polyimide Pressure-sensitive Adhesive Tape No. 360A) was bonded to the polarizing film surface thereof. Thus, a measurement sample was produced. A notch was made between the polarizing film and resin substrate of the measurement sample with a box cutter, and the polarizing film and the reinforcing polyimide tape were stood up together so as to form an angle of 90° relative to the resin substrate surface of the sample, followed by the measurement of a force (N/15 mm) needed at the time of the peeling of the polarizing film at a peel rate of 3,000 mm/min with a free-angle-type versatile peel analyzer "VPA-2" (manufactured by Kyowa Interface Science Co., Ltd.).

(Substrate Peel Strength)

Each of the resultant polarizing plates was bonded to a glass plate by applying a pressure-sensitive adhesive to the polarizing film surface side of the polarizing plate. Thus, a measurement sample was produced. A notch was made between the polarizing film and resin substrate of the measurement sample with a box cutter, and the resin substrate was stood up so as to form an angle of 90° relative to the polarizing film surface of the sample, followed by the measurement of a force (N/15 mm) needed at the time of the peeling of the resin substrate at a peel rate of 3,000 mm/min with the "VPA-2."

2. External Appearance

The external appearance of an applied film was visually observed at the time of each of the formation of the undercoat layer and the application of the polyvinyl alcohol solution.

[0083]

Table 1

	Undercoat layer				Thickness (nm)	Stretching ratio (times)		Adhesiveness (peel strength)		External appearance
	Component A	Component B	A:B	Thickness (nm)		In-air stretching	Underwater stretching	PVA (N/15 mm)	Substrate (N/15 mm)	
Example 1	PVA-based component Z-200	Polyolefin-based component ARROWBASE SE1030N	30:70	2,000		2.0	2.75	1.2	3.5	Satisfactory
Example 2	PVA-based component Z-200	Polyolefin-based component ARROWBASE SE1030N	30:70	1,000		2.0	2.75	0.8	3.0	Satisfactory
Example 3	PVA-based component Z-200	Polyolefin-based component ARROWBASE SE1030N	30:70	500		2.0	2.75	0.6	2.8	Satisfactory
Example 4	PVA-based component Z-200	Polyolefin-based component ARROWBASE SE1030N	50:50	2,000		2.0	2.75	1.1	3.6	Satisfactory
Example 5	PVA-based component Z-200	Polyolefin-based component ARROWBASE SE1030N	30:70	2,000		2.0	2.75	1.3	3.2	Satisfactory
Example 6	PVA-based component Z-200	Polyolefin-based component ARROWBASE SE1035NJ2	50:50	2,000		2.0	2.75	0.9	2.1	Satisfactory
Example 7	PVA-based component Z-410	Polyolefin-based component ARROWBASE SE1030N	30:70	2,000		2.0	2.75	1.3	3.4	Satisfactory
Example 8	PVA-based component Z-200	Polyolefin-based component ARROWBASE SE1030N	30:70	2,000		4.0	-	1.1	9.8	Satisfactory
Comparative Example 1	-	-	-	-		2.0	2.75	0.2	1.0	Satisfactory
Comparative Example 2	-	-	-	-		4.0	-	0.4	1.5	Satisfactory
Comparative Example 3	PVA-based component Z-200	-	100:0	500		2.0	2.75	0.2	7.0	Satisfactory
Comparative Example 4	PVA-based component Z-200	-	100:0	1,000		2.0	2.75	0.2	7.0	Cissing
Comparative Example 5	PVA-based component Z-200	-	100:0	2,000		2.0	2.75	0.2	7.0	Cissing
Comparative Example 6	PVA-based component Z-200	-	100:0	1,000		4.0	-	0.2	1.8	Cissing
Comparative Example 7	-	Polyester-based component ELITEL KT0507E6	0:100	500		2.0	2.75	0.8	0.4	Cloudiness
Comparative Example 8	-	Polyester-based component ELITEL KT0507E6	0:100	1,000		2.0	2.75	0.9	0.5	Cloudiness
Comparative Example 9	-	Polyolefin-based component ARROWBASE SE1035NJ2	0:100	1,000		2.0	2.75	3.6	1.8	Cloudiness
Comparative Example 10	PVA-based component Z-200	Polyester-based component ELITEL KT0507E6	50:50	500		2.0	2.75	1.5	0.8	Graininess
Comparative Example 11	PVA-based component Z-200	Polyester-based component ELITEL KT0507E6	50:50	2,000		2.0	2.75	2.5	2.5	Graininess

[0084] As shown in Table 1, the laminates of Examples are each excellent in adhesiveness and external appearance. Even when the laminates are each subjected to the underwater stretching, sufficient adhesiveness is retained. Meanwhile, in each of Comparative Examples 1 and 2 in which no undercoat layer is formed, sufficient adhesiveness is not obtained. In each of Comparative Examples 3 to 6 in which the undercoat layer is formed without the use of any polyolefin-based component, sufficient adhesiveness is not obtained. In addition, as the thickness of the undercoat layer is increased, cissing occurs at the time of the formation (at the time of the application) of the undercoat layer to a larger extent, and a portion in which the cissing occurs serves as air bubbles to reduce the external appearance of the laminate. In each of Comparative Examples 7 to 9 in which the undercoat layer is formed without the use of any polyvinyl alcohol-based component, the applied film becomes clouded at the time of the formation of the undercoat layer, and hence an excellent external appearance is not obtained. In each of Comparative Examples 10 and 11 in which the undercoat layer is formed by using the polyvinyl alcohol-based component and the polyester-based component, an agglomerate (graininess) occurs in the undercoat layer, and hence an excellent external appearance is not obtained.

Industrial Applicability

[0085] The laminate of the present invention is suitably used

in, for example, an image display apparatus. Specifically, the laminate is suitably used as, for example, the liquid crystal panel of a liquid crystal television, a liquid crystal display, a cellular phone, a digital camera, a video camera, a handheld game console, a car navigation system, a copying machine, a printer, a facsimile, a watch/clock, a microwave oven, or the like, or the antireflection plate of an organic EL device.

Claims

[Claim 1] A laminate, comprising:

a resin substrate; and

a polyvinyl alcohol-based resin layer formed on one side of the resin substrate,

wherein a resin substrate side of the polyvinyl alcohol-based resin layer is an intermediate region in which a polyolefin-based component is present.

[Claim 2] The laminate according to claim 1, wherein the intermediate region contains a polyvinyl alcohol-based component and the polyolefin-based component.

[Claim 3] The laminate according to claim 2, wherein the polyvinyl alcohol-based component contains acetoacetyl-modified polyvinyl alcohol.

[Claim 4] The laminate according to claim 2 or 3, wherein a compounding ratio between the polyvinyl alcohol-based component and the polyolefin-based component is from 5:95 to 60:40.

[Claim 5] The laminate according to any one of claims 1 to 4, wherein the intermediate region has a thickness of from 100 nm to 1,000 nm.

[Claim 6] A method of producing a laminate, comprising the steps of:

applying a composition for forming an undercoat layer containing a polyolefin-based component to one side of a resin substrate to form an undercoat layer; and

applying an application liquid containing a polyvinyl alcohol-based resin to a surface of the undercoat layer to form a polyvinyl alcohol-based resin-applied layer.

[Claim 7] The method of producing a laminate according to claim 6, wherein the composition for forming an undercoat layer contains a polyvinyl alcohol-based component and the polyolefin-based component.

[Claim 8] The method of producing a laminate according to claim 7, wherein the polyvinyl alcohol-based component contains acetoacetyl-modified polyvinyl alcohol.

[Claim 9] The method of producing a laminate according to claim 7 or 8, wherein a solid content compounding ratio between the polyvinyl alcohol-based component and the polyolefin-based component is from 5:95 to 60:40.

[Claim 10] The method of producing a laminate according to any one of claims 6 to 9, wherein the undercoat layer has a thickness of

from 500 nm to 3,000 nm.

[Claim 11] A method of producing a polarizing plate, comprising the step of stretching and dyeing a laminate obtained by the production method of any one of claims 6 to 10.

[Claim 12] A polarizing plate, comprising:

a resin substrate; and

a polyvinyl alcohol-based resin layer formed on one side of the resin substrate,

wherein a resin substrate side of the polyvinyl alcohol-based resin layer is an intermediate region in which a polyolefin-based component is present, and

wherein the polyvinyl alcohol-based resin layer comprises a polarizing film having a dichroic substance adsorbed and aligned thereon.

[Claim 13] The polarizing plate according to claim 12, wherein the intermediate region contains a polyvinyl alcohol-based component and the polyolefin-based component.

[Claim 14] The polarizing plate according to claim 13, wherein the polyvinyl alcohol-based component contains acetoacetyl-modified polyvinyl alcohol.

[Claim 15] The polarizing plate according to claim 13 or 14, wherein a compounding ratio between the polyvinyl alcohol-based component and the polyolefin-based component is from 5:95 to 60:40.

[Claim 16] The polarizing plate according to any one of claims 12 to 15, wherein the intermediate region has a thickness of from 100 nm to 1,000 nm.