

Description

Title of Invention: POLARIZING PLATE

Technical Field

[0001] The present invention relates to a polarizing plate.

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 (for example, Patent Literature 1). According to such method, a polarizing film having a small thickness is obtained. Accordingly, the method has been attracting attention because the method can contribute to, for example, the thinning of an image display apparatus.

[0003] The polarizing film can be used while being in a state of being laminated on the resin substrate (Patent Literature 2). However, in such embodiment, a crack may occur in the resultant polarizing plate, and hence an improvement in durability of the polarizing plate has been required.

Citation List

Patent Literature

[0004] [PTL 1] JP 2000-338329 A

[PTL 2] JP 4979833 B2

Summary of Invention

Technical Problem

[0005] The present invention has been made to solve the problem, and a primary object of the present invention is to provide a polarizing plate that can be used while being in a state in which a polarizing film is laminated on a resin substrate, the polarizing plate being improved in durability.

Solution to Problem

[0006] According to one embodiment of the present invention, there is provided a polarizing plate, including: a polyester-based resin substrate; and a polarizing film laminated on one side of the polyester-based resin substrate, the polarizing film having a thickness of 10 μm or less. In the polarizing plate according to the one embodiment of the present invention, a crystallization degree of the polyester-based resin substrate calculated by attenuated total reflection spectroscopy (ATR) is from 0.55 to 0.80, and a concentration of boric acid in the polarizing film is from 10 wt% to 20 wt%.

In one embodiment, the polyester-based resin includes polyethylene terephthalate or a copolymer thereof.

In one embodiment, the polarizing film is laminated on the

one side of the polyester-based resin substrate without an adhesion layer being interposed.

In one embodiment, the polarizing plate is free of a protective film on a side opposite to the side of the polarizing film on which the polyester-based resin substrate is laminated.

In one embodiment, the polarizing plate further includes an easy-adhesion layer between the polyester-based resin substrate and the polarizing film.

According to another embodiment of the present invention, there is provided a method of producing the polarizing plate. The production method includes: forming a polyvinyl alcohol-based resin film on a polyester-based resin substrate to produce a laminate; stretching the laminate; dyeing the polyvinyl alcohol-based resin film; and crystallizing the polyester-based resin substrate.

Advantageous Effects of Invention

[0007] According to the present invention, there can be obtained a polarizing plate obtained by stretching and dyeing a laminate in which a polyvinyl alcohol-based resin film is formed on a resin substrate, the polarizing plate having the following feature: the crystallization degree of the resin substrate and the concentration of boric acid in the polarizing film are adjusted within specific

ranges, and hence the polarizing plate can be used while being in a state in which the polarizing film is laminated on the resin substrate, and the polarizing plate is excellent in durability.

Brief Description of Drawings

[0008] FIG. **1(a)** and FIG. **1(b)** are each a schematic sectional view of a polarizing plate in one embodiment of the present invention.

Description of Embodiments

[0009] Embodiments of the present invention are described below. However, the present invention is not limited to these embodiments.

[0010] A. Polarizing Plate

A polarizing plate of the present invention includes a polyester-based resin substrate and a polarizing film laminated on one side of the polyester-based resin substrate, the polarizing film having a thickness of 10 μm or less. FIG. **1(a)** is a schematic sectional view of the polarizing plate in one embodiment of the present invention. A polarizing plate **10a** includes a polyester-based resin substrate **11** and a polarizing film **12** laminated on one surface of the polyester-based resin substrate **11** so as to be in close contact therewith (in other words, without an adhesion layer being interposed). FIG. **1(b)** is a schematic sectional view of the polarizing plate in another embodiment of the present invention. A polarizing plate **10b** further includes a protective film **13**. The

protective film **13** is arranged on a side opposite to the side of the polarizing film **12** on which the polyester-based resin substrate **11** is arranged. The protective film **13** may be laminated on the polarizing film **12** through intermediation of an adhesion layer, or may be laminated so as to be in close contact therewith (without the adhesion layer being interposed). In the polarizing plate **10a** or **10b**, the polyester-based resin substrate **11** can function as a protective film. In the present invention, the resin substrate to be used at the time of stretching and dyeing in a production process for the polarizing film can be used as a protective film without being peeled, and even in a construction including the resin substrate (protective film) only on one side of the polarizing film (construction illustrated in FIG. **1(a)**), the occurrence of a crack can be suppressed. The polarizing plate **10a** or **10b** may include an easy-adhesion layer (not shown) between the polyester-based resin substrate **11** and the polarizing film **12**.

[0011] In general, in a polarizing plate obtained by stretching and dyeing a laminate in which a polyvinyl alcohol (hereinafter sometimes referred to as "PVA")-based resin film is formed on a resin substrate, dimensional changes resulting from, for example, the relaxation of an orientation stress and the occurrence of a shrinkage stress occur in the resin substrate and the PVA-based resin film. At this time, the dimensional change amounts of both the substrate and the film differ from each other. Accordingly,

it is assumed that strain occurs at an interface therebetween, and the strain leads to the occurrence of a crack. In contrast, in the present invention, a polyester-based resin substrate having a crystallization degree within a specific range is used as the resin substrate, and the concentration of boric acid in the polarizing film is adjusted within a specific range. Thus, the dimensional change amount of the resin substrate and the dimensional change amount of the polarizing film are equilibrated with each other in each of both the absorption axis direction of the polarizing film and a direction perpendicular to the direction. Accordingly, strain hardly occurs at an interface between the resin substrate and the polarizing film, and the strain that has occurred is dispersed in both the directions. As a result, the occurrence of a crack can be suppressed. The term "perpendicular direction" as used herein includes a case in which an angle formed between two directions is $90^{\circ} \pm 5.0^{\circ}$, and the angle is preferably $90^{\circ} \pm 3.0^{\circ}$, more preferably $90^{\circ} \pm 1.0^{\circ}$. In addition, the term "parallel direction" as used herein includes a case in which an angle formed between two directions is $0^{\circ} \pm 5.0^{\circ}$, and the angle is preferably $0^{\circ} \pm 3.0^{\circ}$, more preferably $0^{\circ} \pm 1.0^{\circ}$.

[0012] A-1. Polarizing Film

The polarizing film is substantially a PVA-based resin film to which iodine is caused to adsorb and orient. The thickness of the polarizing film is 10 μm or less, preferably 7.5 μm or less,

more preferably 5 μm or less. Meanwhile, the thickness of the polarizing film is preferably 0.5 μm or more, more preferably 1.5 μm or more. When the thickness is excessively small, the optical characteristics of the polarizing film to be obtained may reduce. The polarizing film preferably shows absorption dichroism at any wavelength in the wavelength range of from 380 nm to 780 nm. The single layer transmittance of the polarizing film is preferably 40.0% or more, more preferably 41.0% or more, still more preferably 42.0% or more. The polarization degree of the polarizing film is preferably 99.8% or more, more preferably 99.9% or more, still more preferably 99.95% or more.

[0013] Any appropriate resin may be adopted as a PVA-based resin forming the PVA-based resin film. 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.

[0014] 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.

[0015] The polarizing film contains boric acid. The concentration of boric acid in the polarizing film is from 10 wt% to 20 wt%, preferably from 12 wt% to 19 wt%. When the boric acid concentration falls within the range, values for the dimensional change ratios of the polarizing film in the absorption axis direction and the direction perpendicular to the direction can be made close to those for the dimensional change ratios of the polyester-based resin substrate, and a difference between the dimensional change ratio of the polarizing film and the dimensional change ratio of the polyester-based resin substrate in the absorption axis direction can be prevented from becoming excessively larger than a difference between the dimensional change ratio of the polarizing film and the dimensional change ratio of the polyester-based resin substrate in the direction perpendicular to the absorption axis direction. The concentration of boric acid in the polarizing film may be adjusted by, for example, changing the concentration of boric acid in a stretching bath, an insolubilizing bath, a cross-linking bath, or

the like in a method of producing a polarizing plate to be described later, or changing the time period for which a laminate of the polyester-based resin substrate and the polarizing film is immersed in any such bath. The concentration (wt%) of boric acid in the polarizing film may be determined by using, for example, a boric acid amount index calculated from attenuated total reflection spectroscopy (ATR).

$$(\text{Boric acid amount index}) = (\text{intensity of boric acid peak at } 665 \text{ cm}^{-1}) / (\text{intensity of reference peak at } 2,941 \text{ cm}^{-1})$$

$$(\text{Boric acid concentration}) = (\text{boric acid amount index}) \times 5.54 + 4.1$$

Here, the values "5.54" and "4.1" are each a constant obtained by producing a calibration curve through the measurement of the fluorescent X-ray intensity of a sample having a known boric acid concentration.

[0016] A-2. Polyester-based Resin Substrate

As formation materials for the polyester-based resin substrate, there may be used, for example, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyethylene naphthalate (PEN), copolymerized PET (PET-G) containing isophthalic acid, an alicyclic dicarboxylic acid or an alicyclic diol containing, for example, a cyclohexane ring, and the like, and other polyesters, and copolymers

or blends thereof. Of those, PET or copolymerized PET is preferably used. Any such resin is amorphous and has excellent stretchability suitable for high-ratio stretching in an unstretched state, and can be crystallized by stretching and heating to impart heat resistance and dimensional stability to the substrate. Further, the resin can secure, in the unstretched state, such heat resistance that the PVA-based resin can be applied and dried.

[0017] The glass transition temperature (T_g) of the polyester-based 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 film. In consideration of the plasticization of the resin substrate by water and satisfactory performance of underwater stretching, the glass transition temperature is more preferably 120°C or less. In one embodiment, the glass transition temperature of the polyester-based resin substrate is preferably 60°C or more. The use of such polyester-based resin substrate can prevent an inconvenience, such as the deformation (e.g., the occurrence of unevenness, a sag, or a wrinkle) of the polyester-based 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 polyester-based 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.

[0018] In one embodiment, the water absorption ratio of the polyester-based resin substrate is preferably 0.2% or more, more preferably 0.3% or more. Such polyester-based resin substrate absorbs water, and the water can function like a plasticizer to plasticize the 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 polyester-based resin substrate is preferably 3.0% or less, more preferably 1.0% or less. The use of such polyester-based 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 polyester-based resin substrate at the time of the production of the laminate. In addition, the use can prevent the rupture of the substrate at the time of the underwater stretching and the peeling of the PVA-based resin film from the polyester-based resin substrate. The water absorption ratio is a value determined in conformity with JIS K 7209.

[0019] The thickness of the polyester-based resin substrate is preferably from 10 μm to 200 μm , more preferably from 20 μm to 150 μm .

[0020] The crystallization degree of the polyester-based resin substrate calculated by attenuated total reflection spectroscopy (ATR) is from 0.55 to 0.80, preferably from 0.58 to 0.80, more preferably from 0.60 to 0.75. When the crystallization degree of the polyester-based resin substrate falls within the range, the values for the dimensional change ratios of the polyester-based resin substrate in the absorption axis direction of the polarizing film and the direction perpendicular to the direction can be made close to those for the dimensional change ratios of the polarizing film, and the difference between the dimensional change ratio of the polarizing film and the dimensional change ratio of the polyester-based resin substrate in the absorption axis direction can be prevented from becoming excessively larger than the difference between the dimensional change ratio of the polarizing film and the dimensional change ratio of the polyester-based resin substrate in the direction perpendicular to the absorption axis direction. The crystallization degree of the polyester-based resin substrate may be adjusted by, for example, changing a heating temperature and/or a heating time at the time of its crystallization. The crystallization degree of the polyester-based resin substrate is calculated on the basis of the following equation.

(Crystallization degree)=(intensity of crystal peak at 1,340 cm^{-1})/(intensity of reference peak at 1,410 cm^{-1})

[0021] A-3. Protective Film

As formation materials for the protective film, there are given, for example, a (meth)acrylic resin, a cellulose-based resin, such as diacetyl cellulose or triacetyl cellulose, a cycloolefin-based resin, an olefin-based resin such as polypropylene, an ester-based resin, such as a polyethylene terephthalate-based resin, a polyamide-based resin, a polycarbonate-based resin, and copolymer resins thereof. The thickness of the protective film is preferably from 10 μm to 100 μm .

[0022] A-4. Easy-adhesion Layer

The easy-adhesion layer may be a layer formed substantially only of a composition for forming an easy-adhesion layer, or may be a layer or region in which the composition for forming an easy-adhesion layer and a formation material for the polarizing film are mixed with each other (including "compatible with each other"). The formation of the easy-adhesion layer can provide excellent adhesiveness between the resin substrate and the polarizing film. The thickness of the easy-adhesion layer is preferably set to from about 0.05 μm to about 1 μm . The easy-adhesion layer may be confirmed by, for example, observing a section of the

polarizing plate with a scanning electron microscope (SEM). The composition for forming an easy-adhesion layer is described in detail in the section B.

[0023] A-5. Adhesion Layer

The adhesion layer is formed of any appropriate adhesive or pressure-sensitive adhesive. A pressure-sensitive adhesive layer is typically formed of an acrylic pressure-sensitive adhesive. An adhesive layer is typically formed of a vinyl alcohol-based adhesive.

[0024] B. Method of producing Polarizing Plate

A method of producing a polarizing plate of the present invention typically includes: forming a PVA-based resin film on a polyester-based resin substrate to produce a laminate; stretching the laminate; dyeing the PVA-based resin film; and crystallizing the polyester-based resin substrate.

[0025] B-1. Production of Laminate

Any appropriate method may be adopted as a method of forming the PVA-based resin film on the polyester-based resin substrate. The PVA-based resin film is preferably formed by applying an application liquid containing a PVA-based resin onto the polyester-based resin substrate, and drying the liquid. In one embodiment, an easy-adhesion layer is formed by applying a composition for forming an easy-adhesion layer onto the

polyester-based resin substrate, and drying the composition, and the PVA-based resin film is formed on the easy-adhesion layer.

[0026] The formation material for the polyester-based resin substrate is as described above. The thickness of the polyester-based resin substrate (thickness before stretching to be described later) is preferably from 20 μm to 300 μm , more preferably from 50 μm to 200 μm . When the thickness is less than 20 μm , it may become difficult to form the PVA-based resin film. When the thickness is more than 300 μm , there is a risk in that in, for example, the underwater stretching, a long time period is required for the polyester-based resin substrate to absorb water, and an excessively large load is required for the stretching. The crystallization degree of the polyester-based resin substrate at the time of its use in the production of the laminate calculated by attenuated total reflection spectroscopy (ATR) may be, for example, from 0.20 to 0.50.

[0027] The application liquid is typically a solution in which the PVA-based resin is dissolved in a solvent. 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 solution 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 closely adhering to the polyester-based resin substrate.

[0028] 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 film to be obtained. In addition, the additive is, for example, an easy-adhesion component. The use of the easy-adhesion component can improve adhesiveness between the polyester-based resin substrate and the PVA-based resin film. As a result, an inconvenience, such as the peeling of the PVA-based resin film from the substrate, is suppressed, and hence dyeing and underwater stretching to be described later can be satisfactorily performed. For example, modified PVA, such as acetoacetyl-modified PVA, is used as the easy-adhesion component.

[0029] Any appropriate method may be adopted as a method of applying the application liquid. 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 (such as a comma coating method).

[0030] The temperature at which the application liquid is applied and dried is preferably 50°C or more.

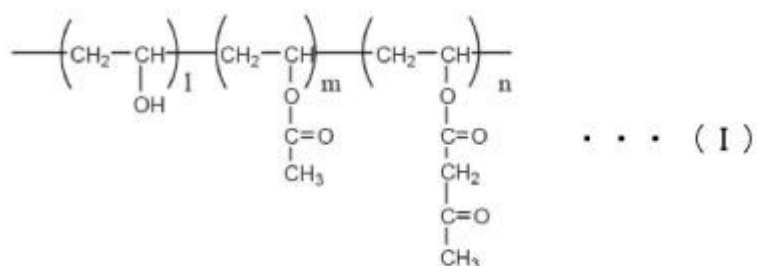
[0031] The thickness of the PVA-based resin film (thickness before stretching to be described later) is preferably from 3 μm to 20 μm .

[0032] Before the formation of the PVA-based resin film, the polyester-based resin substrate may be subjected to surface treatment (e.g., corona treatment), or a composition for forming an easy-adhesion layer may be applied onto the polyester-based resin substrate (coating treatment). The performance of any such treatment can improve adhesiveness between the polyester-based resin substrate and the PVA-based resin film. As a result, an inconvenience, such as the peeling of the PVA-based resin film from the substrate, is suppressed, and hence dyeing and stretching to be described later can be satisfactorily performed.

[0033] The composition for forming an easy-adhesion layer preferably contains a polyvinyl alcohol-based component. Any appropriate PVA-based resin may be used as the polyvinyl

alcohol-based component. Specific examples thereof include polyvinyl alcohol and modified polyvinyl alcohol. Examples of the modified polyvinyl alcohol include polyvinyl alcohols 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.

[0034]



[0035] In the formula (I), the ratio of n to l+m+n is preferably from 1% to 10%.

[0036] 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.

[0037] The composition for forming an easy-adhesion layer may further contain a polyolefin-based component, a polyester-based component, a polyacrylic component, or the like in accordance with, for example, purposes. It is preferred that the composition for forming an easy-adhesion layer further contain the polyolefin-based component.

[0038] Any appropriate polyolefin-based resin may be used as the polyolefin-based component. Examples of an olefin component serving as a main component of the polyolefin-based resin include olefin-based hydrocarbons each having 2 to 6 carbon atoms, such as ethylene, propylene, isobutylene, 1-butene, 1-pentene, and 1-hexene. Those olefin components may be used alone or in combination thereof. Of those, olefin-based hydrocarbons each having 2 to 4 carbon atoms, such as ethylene, propylene, isobutylene, and 1-butene are preferred, and ethylene is more preferably used.

[0039] The ratio of the olefin component to the monomer components forming the polyolefin-based resin is preferably from 50 wt% to 95 wt%.

[0040] 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 easy-adhesion layer can be satisfactorily formed. Examples of the monomer component having such functional group include unsaturated carboxylic acids and anhydrides thereof, and half esters and half amides of unsaturated dicarboxylic acids. Specific examples thereof include acrylic acid, methacrylic acid, maleic acid, maleic anhydride, itaconic acid, itaconic anhydride, fumaric acid, and crotonic acid.

[0041] The molecular weight of the polyolefin-based resin is, for example, from 5,000 to 80,000.

[0042] A compounding ratio (former:latter (solid content)) between the polyvinyl alcohol-based component and the polyolefin-based component in the composition for forming an easy-adhesion layer 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 force needed at the time of the peeling of the polarizing film 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 polarizing plate to be obtained may be impaired. Specifically, an inconvenience, such as the clouding of the applied

film at the time of the formation of the easy-adhesion layer, may occur to make it difficult to obtain a polarizing plate excellent in external appearance.

[0043] The composition for forming an easy-adhesion layer is preferably aqueous. The composition for forming an easy-adhesion 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 easy-adhesion layer is preferably from 1.0 wt% to 10 wt%.

[0044] Any appropriate method may be adopted as a method of applying the composition for forming an easy-adhesion layer. After the application of the composition for forming an easy-adhesion layer, the applied film may be dried. A drying temperature is, for example, 50°C or more.

[0045] B-2. Stretching

Any appropriate method may be adopted as a method of stretching the laminate. Specifically, the method may be fixed-end stretching (e.g., a method involving using a tenter stretching machine), or may be free-end stretching (e.g., a method involving passing the laminate between rolls having different peripheral speeds to uniaxially stretch the laminate). In addition, the method may be simultaneous biaxial stretching (e.g., a method involving using

a simultaneous biaxial stretching machine), or may be sequential biaxial stretching. 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, underwater stretching treatment is performed at least once, and the underwater stretching treatment and in-air stretching treatment are preferably combined. According to the underwater stretching, the stretching can be performed at a temperature lower than the glass transition temperature (typically about 80°C) of the polyester-based resin substrate or the PVA-based resin film, and hence the PVA-based resin film 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 a laminate having an elongate shape. Specifically, the laminate is conveyed in the lengthwise direction, and is stretched in the conveying

direction (MD). In another embodiment, the stretching is performed in the widthwise direction of the laminate having an elongate shape. Specifically, the laminate is conveyed in the lengthwise direction, and is stretched in a direction (TD) perpendicular to the conveying 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 polyester-based 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 polyester-based resin substrate, more preferably equal to or more than the glass transition temperature (T_g) of the polyester-based resin substrate + 10°C, particularly preferably equal to or more than $T_g + 15^\circ\text{C}$. 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 film 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 film is suppressed. Specifically, as described above, the glass transition temperature (T_g) of the polyester-based resin substrate is preferably 60°C or more in relation to the formation of the PVA-based resin film. 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 polyester-based 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 film 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 film, rigidity enabling the film to withstand a tension to be applied at the time of the stretching and water resistance preventing the film 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 film, and hence the film 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 film, 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 that the PVA-based resin film has been caused to adsorb. 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 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 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 by 0.2 than a separately determined value for the stretching ratio at which the laminate is ruptured.

[0055] B-3. Dyeing

 The dyeing of the PVA-based resin film is typically performed by causing the PVA-based resin film to adsorb iodine. A method for the adsorption is, for example, a method involving immersing the PVA-based resin film (laminate) in a dyeing liquid containing iodine, a method involving applying the dyeing liquid to the PVA-based resin film, or a method involving spraying the dyeing liquid on the PVA-based resin film. Of those, a method involving immersing the PVA-based resin film (laminate) in the dyeing liquid is preferred. This is

because iodine can satisfactorily adsorb to the PVA-based resin film (laminated).

[0056] 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. In order to increase the solubility of iodine in water, the aqueous solution of iodine is preferably compounded with an iodide. Specific examples of the iodide are as described above. 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. 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 film 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 film may be secured. In addition, the dyeing conditions (the concentrations, the liquid temperature, and the immersion time) may be set so that the polarization degree or single layer transmittance of the 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%.

[0057] The dyeing treatment may be performed at any appropriate timing. When the underwater stretching is performed, the treatment is preferably performed before the underwater stretching.

[0058] B-4. Crystallization

The crystallization of the polyester-based resin substrate is performed by, for example, heating the polyester-based resin substrate (substantially the laminate). The crystallization is preferably performed after the dyeing and stretching of the PVA-based resin film.

[0059] A heating temperature is typically a temperature more than the glass transition temperature (T_g) of the polyester-based resin substrate. The heating temperature is preferably 90°C or more, more preferably 100°C or more. In addition, the heating temperature is preferably 125°C or less, more preferably 120°C or less. When the heating is performed at such temperature, the crystallization degree of the polyester-based resin substrate can be set to a desired value. A heating time may be appropriately set in accordance with the heating temperature and the like. The heating time may be, for example, from 3 seconds to 2 minutes.

[0060] In the crystallization, the crystallization is preferably performed so that the haze value of the polyester-based resin substrate may be 2% or less.

[0061] B-5. Other Treatment

The PVA-based resin film (laminate) may be appropriately subjected to treatment for turning the film into a polarizing film except the stretching and the dyeing. Examples of the treatment for turning the film into the polarizing film include insolubilizing treatment, cross-linking treatment, washing treatment, and drying treatment. The number of times of each of those treatments, the order in which the treatments are performed, and the like are not particularly limited.

[0062] The insolubilizing treatment is typically performed by immersing the PVA-based resin film (laminate) in an aqueous solution of boric acid. The performance of the insolubilizing treatment can impart water resistance to the PVA-based resin film. 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 the insolubilizing bath (aqueous solution of boric acid) is preferably from 20°C to 50°C. The insolubilizing treatment is preferably performed before the underwater stretching and the dyeing treatment.

[0063] The cross-linking treatment is typically performed by immersing the PVA-based resin film (laminate) in an aqueous solution of boric acid. The performance of the cross-linking treatment can impart water resistance to the PVA-based resin film. The concentration of the aqueous solution of boric acid is preferably from 1 part by weight to 5 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 that the PVA-based resin film has been caused to adsorb. 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 the cross-linking bath (aqueous solution of boric acid) is preferably from 20°C to 60°C. The cross-linking treatment is preferably performed before the underwater stretching. In a preferred embodiment, the in-air stretching, the dyeing treatment, and the cross-linking treatment are performed in the stated order.

[0064] The washing treatment is typically performed by immersing the PVA-based resin film (laminate) in an aqueous solution of potassium iodide. A drying temperature in the drying treatment is preferably from 30°C to 100°C.

[0065] The polarizing plate of the present invention can be obtained by forming the polarizing film on the polyester-based resin substrate and crystallizing the polyester-based resin substrate as described above.

[0066] C. Application of Polarizing Plate

The polarizing plate of the present invention can 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 polyester-based resin substrate. According to such construction, an influence of a retardation that the polyester-based resin substrate may have on an image characteristic of the liquid crystal display apparatus to be obtained can be eliminated.

Examples

[0067] Now, the present invention is specifically described by way of Examples. However, the present invention is not limited by these Examples. Methods of measuring the respective characteristics are as described below. In addition, the terms "part(s)" and "%" in the following Examples and Comparative Examples represent "part(s) by weight" and "wt%," respectively.

<<Thickness>>

Measurement was performed with a digital micrometer

(manufactured by Anritsu Corporation, product name: "KC-351C").

<<Dimensional Change Ratio>>

A polarizing film and a resin substrate were peeled from a polarizing plate obtained in each of Examples and Comparative Examples by applying starting points to their end portions, heated from 30°C to 100°C at 10°C/min, and then held at 100°C for 60 minutes, followed by a measurement of their dimensional change ratios with a thermomechanical measuring apparatus (TMA). In Example 6 in which an easy-adhesion layer was sandwiched between a polarizing film and a resin substrate, a polarizing plate was produced in the same manner as in Example 6 except that the easy-adhesion layer was not formed, and the polarizing film and the resin substrate were isolated from the polarizing plate by the same procedure and subjected to the measurement to define the resultant values as the dimensional change ratios of the polarizing film and the resin substrate.

Dimensional change ratio (%) = (dimension after heat treatment - dimension before heat treatment) / dimension before heat treatment × 100

<<Crystallization Degree>>

The intensity of the crystal peak (1,340 cm⁻¹) of the polyester-based resin substrate obtained in each of Examples and Comparative Examples, and the intensity of the reference peak (1,410

cm⁻¹) thereof were measured with a Fourier transform infrared spectrophotometer (FT-IR) (manufactured by PerkinElmer, Inc., product name: "SPECTRUM2000") by attenuated total reflection spectroscopy (ATR). A crystallization degree was calculated from the resultant crystal peak intensity and reference peak intensity by using the following equation.

$$(\text{Crystallization degree}) = (\text{intensity of crystal peak at } 1,340 \text{ cm}^{-1}) / (\text{intensity of reference peak at } 1,410 \text{ cm}^{-1})$$

<<Glass Transition Temperature: Tg>>

Measurement was performed in conformity with JIS K 7121.

<<Boric Acid Concentration>>

The intensity of the boric acid peak (665 cm⁻¹) of the polarizing film obtained in each of Examples and Comparative Examples, and the intensity of the reference peak (2,941 cm⁻¹) thereof were measured with a Fourier transform infrared spectrophotometer (FT-IR) (manufactured by PerkinElmer, Inc., product name: "SPECTRUM2000") by attenuated total reflection spectroscopy (ATR) involving using polarized light as measurement light. A boric acid amount index was calculated from the resultant boric acid peak intensity and reference peak intensity by using the following equation. Further, a boric acid concentration was determined from the calculated boric acid amount index by using the following equation.

$$(\text{Boric acid amount index}) = (\text{intensity of boric acid peak at } 665 \text{ cm}^{-1}) / (\text{intensity of reference peak at } 2,941 \text{ cm}^{-1})$$

$$(\text{Boric acid concentration}) = (\text{boric acid amount index}) \times 5.54 + 4.1$$

<<Crack Evaluation>>

The polarizing plate obtained in each of Examples and Comparative Examples was heated in an oven at 100°C for 240 hours under a state in which the polarizing plate was bonded to a glass through intermediation of a pressure-sensitive adhesive so that its polyester-based resin substrate was positioned on a surface side. The presence or absence of a crack in the polarizing plate after the heating was confirmed, and the polarizing plate was evaluated in accordance with the following criteria.

Satisfactory: The occurrence of a crack is absent.

Unsatisfactory: The occurrence of a crack is present.

[0068] [Example 1]

An amorphous isophthalic acid-copolymerized polyethylene terephthalate (IPA-copolymerized PET) film of an elongate 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 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.

[0069] 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 1.8 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 (an aqueous solution of iodine obtained by compounding 100 parts by weight of water with 0.2 part by weight of iodine and 1.5 parts 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 3 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).

[0070] Next, the laminate was loaded into an oven at 100°C for 30 seconds to crystallize the resin substrate.

Thus, a polarizing plate in which a polarizing film having a thickness of 5 μm was laminated on the resin substrate was obtained.

[0071] [Example 2]

A polarizing plate was obtained in the same manner as in Example 1 except that the laminate was loaded into an oven at 110°C for 30 seconds to crystallize the resin substrate.

[0072] [Example 3]

A polarizing plate was obtained in the same manner as in Example 1 except that the laminate was loaded into an oven at 120°C for 30 seconds to crystallize the resin substrate.

[0073] [Example 4]

A polarizing plate was obtained in the same manner as in Example 1 except that: the compounding amount of boric acid in the stretching bath at the time of the underwater stretching was changed to 3.5 parts by weight; and the laminate was loaded into an oven at 110°C for 30 seconds to crystallize the resin substrate.

[0074] [Example 5]

A polarizing plate was obtained in the same manner as in Example 1 except that: the compounding amount of boric acid in the stretching bath at the time of the underwater stretching was changed to 2.5 parts by weight; and the laminate was loaded into an oven at 110°C

for 30 seconds to crystallize the resin substrate.

[0075] [Example 6]

An easy-adhesion layer was arranged on one surface of the resin substrate by the following method.

One surface of the resin substrate was subjected to 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 its thickness after drying became 2,000 nm, followed by drying at 60°C for 3 minutes. Thus, the easy-adhesion layer was formed. Here, a solid content compounding ratio between the acetoacetyl-modified PVA and the modified polyolefin resin in the mixed liquid was 30:70.

A polarizing plate was obtained in the same manner as in Example 1 except that: the surface of the easy-adhesion layer was subjected to corona treatment; and the PVA-based resin layer was formed on the corona-treated surface.

[0076] [Comparative Example 1]

A polarizing plate was obtained in the same manner as in Example 1 except that the laminate was loaded into an oven at 85°C for 30 seconds to crystallize the resin substrate.

[0077] [Comparative Example 2]

A polarizing plate was obtained in the same manner as in Example 1 except that: the compounding amount of boric acid in the stretching bath at the time of the underwater stretching was changed to 4.0 parts by weight; and the laminate was loaded into an oven at 110°C for 30 seconds to crystallize the resin substrate.

[0078] [Comparative Example 3]

A polarizing plate was obtained in the same manner as in Example 1 except that the laminate was loaded into an oven at 95°C for 30 seconds to crystallize the resin substrate.

[0079] Production conditions for the polarizing plates in Examples and Comparative Examples, and the respective characteristics of the resultant polarizing plates are shown in Table 1. In Table 1, the symbol "MD" represents the absorption axis direction of a polarizer, and the symbol "TD" represents a direction perpendicular to the absorption axis direction.

Table 1

	Stretching (MD)		Concentration of boric acid in bath	Concentration of boric acid in polarizing film	Crystallization		PET crystallization degree	MD dimensional change ratio (%)			TD dimensional change ratio (%)			Difference in TD - difference in MD	Crack evaluation
	In-air stretching	Underwater stretching			Heating temperature	Heating time		Polarizer	PET	Difference	Polarizer	PET	Difference		
Example 1	2.4 times	2.3 times	3.0%	16%	100°C	30 seconds	0.59	-3.5	-0.2	3.3	-2.5	1.0	3.5	0.2	Satisfactory
Example 2	2.4 times	2.3 times	3.0%	16%	110°C	30 seconds	0.64	-3.5	-0.6	2.9	-2.5	0.6	3.1	0.2	Satisfactory
Example 3	2.4 times	2.3 times	3.0%	16%	120°C	30 seconds	0.75	-3.5	1.0	4.5	-2.5	0.5	3.0	-1.5	Satisfactory
Example 4	2.4 times	2.3 times	3.5%	19%	110°C	30 seconds	0.64	-4.0	-0.6	3.4	-3.5	0.6	4.1	0.7	Satisfactory
Example 5	2.4 times	2.3 times	2.5%	12%	110°C	30 seconds	0.64	-2.5	-0.6	1.9	-1.8	0.6	2.4	0.5	Satisfactory
Example 6	2.4 times	2.3 times	3.0%	16%	100°C	30 seconds	0.59	-3.5	-0.2	3.3	-2.5	1.0	3.5	0.2	Satisfactory
Comparative Example 1	2.4 times	2.3 times	3.0%	16%	85°C	30 seconds	0.45	-3.5	-25.0	-21.5	-2.5	25.0	27.5	6.0	Unsatisfactory
Comparative Example 2	2.4 times	2.3 times	4.0%	22%	110°C	30 seconds	0.64	-4.5	-0.2	4.3	-4.1	1.0	5.1	0.8	Unsatisfactory
Comparative Example 3	2.4 times	2.3 times	3.0%	16%	95°C	30 seconds	0.53	-3.5	-1.5	2.0	-2.5	1.2	3.7	1.7	Unsatisfactory

[0080] As shown in Table 1, in each of the polarizing plates of Examples including a resin substrate having a specific crystallization degree and a polarizing film satisfying a specific boric acid concentration, the occurrence of a crack is suppressed. Meanwhile, it is understood that in each of the polarizing plates of Comparative Examples, a crack occurs, and hence the polarizing plates are inferior in durability to the polarizing plates of Examples. In addition, the polarizing plate of Example 6 was superior in adhesiveness between the resin substrate and the polarizing film (PVA-based resin layer) to the polarizing plates of the other Examples and Comparative Examples, and hence undesired peeling or floating of the polarizing film (PVA-based resin layer) or the resin substrate at the time of the production of the polarizing film or at the time of the processing (e.g., punching) of the polarizing plate was suitably prevented.

[0081] The reason why the occurrence of a crack was suppressed in each of the polarizing plates of Examples is assumed to be as described below. That is, in each of the polarizing plates of Examples, the difference (dimensional change ratio of resin substrate-dimensional change ratio of polarizing film) between the dimensional change ratio of the resin substrate and the dimensional change ratio of the polarizing film in the MD direction, and the difference (dimensional change ratio of resin substrate-dimensional change ratio of polarizing film) between the dimensional change

ratio of the resin substrate and the dimensional change ratio of the polarizing film in the TD direction are each 5% or less, and the difference (absolute value) between the dimensional change ratios in the TD direction is close to the difference (absolute value) between the dimensional change ratios in the MD direction (a difference between the absolute values is within $\pm 1.5\%$). The polarizing film is oriented in the stretching direction (MD), and hence its mechanical properties in the direction (TD) perpendicular to the stretching direction tend to be weak. Accordingly, it is assumed that when the difference (absolute value) between the dimensional change ratios in the TD direction was made close to the difference (absolute value) between the dimensional change ratios in the MD direction, strain was prevented from being biased in the TD direction, and hence the occurrence of a crack was suppressed.

Industrial Applicability

[0082] The polarizing plate of the present invention is suitably used in, for example, an image display apparatus.

Claims

[Claim 1] A polarizing plate, comprising:

a polyester-based resin substrate; and

a polarizing film laminated on one side of the polyester-based resin substrate, the polarizing film having a thickness of 10 μm or less,

wherein a crystallization degree of the polyester-based resin substrate calculated by attenuated total reflection spectroscopy is from 0.55 to 0.80, and

wherein a concentration of boric acid in the polarizing film is from 10 wt% to 20 wt%.

[Claim 2] The polarizing plate according to claim 1, wherein the polyester-based resin comprises polyethylene terephthalate or a copolymer thereof.

[Claim 3] The polarizing plate according to claim 1 or 2, wherein the polarizing film is laminated on the one side of the polyester-based resin substrate without an adhesion layer being interposed.

[Claim 4] The polarizing plate according to any one of claims 1 to 3, wherein the polarizing plate is free of a protective film on a side opposite to the side of the polarizing film on which the polyester-based resin substrate is laminated.

[Claim 5] The polarizing plate according to any one of claims 1 to 4, further comprising an easy-adhesion layer between the polyester-based resin substrate and the polarizing film.

[Claim 6] A method of producing the polarizing plate of any one of claims 1 to 5, comprising:

forming a polyvinyl alcohol-based resin film on a polyester-based resin substrate to produce a laminate;

stretching the laminate;

dyeing the polyvinyl alcohol-based resin film; and

crystallizing the polyester-based resin substrate.