Appendix 1

Case 1

[Claims]

Appendix 1

[Claim 1] A method of manufacturing a polarizing film by uniaxially stretching a polyvinylalcohol-based raw material film, wherein the polyvinylalcohol-based raw material film has a thickness in the range of 30 to 100 μm and the relationship between the complete dissolution temperature (X) in hot water and the equilibrium swelling degree (Y) thereof is defined by the following expressions:

$Y > -0.0667X + 6.73$ (I)

$X \geq 65$ (II)

wherein X is the complete dissolution temperature (°C) in hot water of a film piece with dimensions of 2 cm × 2 cm; and Y is the equilibrium swelling degree (weight fraction) when a film piece with dimensions of 10 cm × 10 cm is dipped in a constant-temperature water-bath of 20°C for 15 minutes for swelling and then is dried at 105°C for 2 hours, and is calculated from the expression of (film weight after dipping)/(film weight after drying); and

the polyvinylalcohol-based raw material film is uniaxially stretched to 1.2 to 2 times the original size thereof in a dyeing treatment process and further to 2 to 6 times the original size thereof in a boron-compound treatment process.

[Claim 2] The manufacturing method according to claim 1, wherein the polyvinylalcohol-based raw material film has a complete dissolution temperature in the range of 65 to 90°C.

[Claim 3] The manufacturing method according to claim 1, wherein the polyvinylalcohol-based raw material film has an average degree of polymerization of 2600 or more.

Appendix 1

Case 1

[Description]

Appendix 1

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to a method for manufacturing a polarizing film having excellent durability and polarization performance and manufacturing the film with excellent stability.

[0002]

[Description of the Related Art] Recently, liquid-crystal displays have been used in desktop electronic calculators, electronic clocks, word processors, and measuring gauges for automobiles and machinery, and thereby a demand for polarizing plates has been increased. Since measuring gauges and electric kitchen appliances are generally used under harsh circumstances, films are particularly required to have high durability and a high degree of polarization.

[0003] At present, typically known polarizing films are polyvinylalcohol-based films dyed with iodine or dyed with a dichromatic dye. These polarizing films are manufactured by forming a film from a polyvinylalcohol aqueous solution; uniaxially stretching the film and then dyeing the film, or dyeing the film and then uniaxially stretching the film; and preferably treating the film with a boron compound for providing durability to the film.

[0004] However, in the polyvinylalcohol-based polarizing film, a product dyed with iodine has excellent polarization performance, but the moisture resistance and the heat resistance are poor. Therefore, the degree of polarization is decreased by being exposed to a high-humidity atmosphere or a high-temperature atmosphere, namely, the durability is poor. On the other hand, a product dyed with a dichromatic dye has excellent durability, but the polarization performance is poor. Thus, polyvinylalcohol-based polarizing films have both merits and demerits. Consequently, such a film is actually obliged to be properly used depending on the performances necessary for satisfying end use requirements. Therefore, a polyvinylalcohol-based polarizing film having both excellent polarization performance and excellent durability is very useful and will have an expanded range of uses, if such a film can be developed.

[0005] Then, in order to solve the above-mentioned problems, the present applicant suggested a method for manufacturing a polarizing film by uniaxially stretching a polyvinylalcohol-based film in at least one of a dyeing process and a boron-compound treatment process. The raw material film is a PVA-based film having a thickness in the range of 30 to 100 μm and a complete dissolution temperature in hot water of 65 to 90°C (Japanese Unexamined Patent Application Publication No. 4-173125). This method can provide a polarizing film whose durability under high-moisture and high-temperature circumstances is improved and whose degree of polarization is not changed by the film being exposed to the atmosphere for a long period of time.

[0006]

[Problems to be Solved by the Invention] However, the present inventors have conducted further studies and have found that the polarizing film obtained by the method disclosed in Japanese Unexamined Patent Application Publication No. 4-173125 actually has excellent durability in high-temperature and high-humidity circumstances, but the polarization performance and the durability performance cannot be stably achieved only by defining the thickness and the complete dissolution temperature in hot water of a polyvinylalcohol-based raw material film. That is to say, unevenness in the degree of polarization is caused by slight fluctuations in manufacturing conditions, and therefore, careful process management is required.

[0007] Additionally, in the experiments regarding the method according to the above-mentioned patent application publication, a polarizing film is manufactured by being uniaxially stretching to 7.2 times the original size thereof finally. However, it is difficult to precisely control the stretching ratio in the manufacturing process. When the stretching ratio during the manufacturing process is higher than 7.2 times, problems such as breakage of the film and occurrence of fractures may be generated. From this point, the process management should be sufficiently careful. In other words, a raw material film is required to withstand excessive stretching force, which is hard to avoid, during the process of manufacturing a polarizing film, particularly, during the process of stretching the film. Consequently, it is desired to develop a method for manufacturing an excellent polarizing film having a high polarization performance and durability performance by using a film not susceptible to film breakage even if excessive stretching force is applied, namely, a film that can stand being highly stretched.

[0008]

[Means for Solving the Problems] Accordingly, the present inventors have conducted intensive studies in order to solve the above-mentioned problems, and, as a result, have found that the above-mentioned object can be achieved by the method below. Thus, the present invention has been accomplished. That is, in a method of manufacturing a polarizing film by uniaxially stretching a polyvinylalcohol-based raw material film, the polyvinylalcohol-based raw material film has a thickness in the range of 30 to 100 μm and the relationship between the complete dissolution temperature (X) in hot water and the equilibrium swelling degree (Y) thereof is defined by the following expressions:

$$Y > -0.0667X + 6.73 \qquad (I)$$

$$X \geq 65 \qquad (II)$$

wherein X is the complete dissolution temperature (°C) in hot water of a film piece with dimensions of 2 cm × 2 cm; and Y is the equilibrium swelling degree (weight fraction) when a film piece with dimensions of 10 cm × 10 cm is dipped in a constant-temperature water-bath of 20°C for 15 minutes for swelling and then is dried at 105°C for 2 hours and is calculated from the expression of (film weight after dipping)/(film weight after drying); and

the polyvinylalcohol-based raw material film is uniaxially stretched to 1.2 to 2 times the original size thereof in a dyeing treatment process and further to 2 to 6 times the original size thereof in a boron-compound treatment process.

[0009] The effects provided by the present invention can be achieved by using a polyvinylalcohol-based film having a particular thickness and a particular relationship between the complete dissolution temperature (X) and the equilibrium swelling degree (Y) thereof and preferably having a high degree of polymerization, as mentioned above. The complete dissolution temperature (X) in the present invention is defined as a temperature at which a film piece with dimensions of 2 cm × 2 cm is completely dissolved in 2000 ml of water. Firstly, the temperature of 2000 ml of water in a 2-liter beaker is increased to 30°C, and then the film piece is put into the water. The temperature of the water is increased at a rate of 3°C/min with stirring, and the temperature at which the film is completely dissolved is determined. The equilibrium swelling degree (Y) is calculated, when a film piece with dimensions of 10 cm × 10 cm is dipped in a constant-temperature water-bath of 20°C for 15 minutes for swelling and then is dried at 105°C for 2 hours, from the following expression:

Equilibrium swelling degree (weight fraction) = (film weight after dipping)/(film weight after drying).

Appendix 1

The present invention will now be specifically described.

[0010] The polarizing film according to the present invention is a uniaxially stretched polyvinylalcohol-based resin film. Polyvinylalcohol is generally manufactured by saponifying polyvinyl acetate prepared by polymerization of vinyl acetate. The present invention is not limited to this, and a small amount of a component which can be copolymerized with unsaturated carboxylic acid (including salts, esters, amides, and nitriles), olefins, vinylethers, unsaturated sulfonate, or vinyl acetate may be contained. The practical average degree of saponification of polyvinylalcohol is in the range of 85 to 100 mol%, preferably 98 to 100 mol%. The average degree of polymerization of 2600 or more, preferably, 3500 to 5000 is advantageous in order to achieve the effects of the present invention. When the average degree of polymerization is lower than 2600, significant effects are negligibly achieved.

[0011] The polyvinylalcohol is formed into a film by a known method. Generally, the film is formed by dissolving polyvinylalcohol in water, an organic solvent, or a solvent mixture of water and an organic solvent, and then casting the solution. The concentration of the solution is practically in the range of about 5 to 20 wt%. In addition, the formation of a film by introducing a polyvinylalcohol solution to a coagulation bath, a so-called gel film formation method, may be applied. The thickness of the raw material film is in the range of 30 to 100 μm, preferably 50 to 90 μm. When the thickness is 30 μm or less, the stretching cannot be performed. When the thickness is 100 μm or more, the accuracy in uniformity of the film thickness is inappropriately decreased.

[0012] Furthermore, the relationship between the complete dissolution temperature (X) in hot water and the equilibrium swelling degree (Y) of the film must be within the range defined by the following expression.

$Y > -0.0667X + 6.73$ (I)

$X \geq 65$ (II)

Such a specific film can be obtained by adjusting drying conditions for forming the polyvinylalcohol-based film or conditions for thermal treatment after the formation of the film. In any case, the uniaxial stretching can be performed only by using a film having such properties, and thereby the effects of the present invention, namely, improvement in the manufacturing stability and productivity of a polarizing film, can be achieved. The complete dissolution temperature in hot water is, as shown by the expression (II), 65°C or more, preferably 65 to 90°C, more preferably 71 to 80°C.

[0013] A film having a complete dissolution temperature of 65°C or less is partially dissolved or degraded during the stretching; thus, such a film is inapplicable. On the other hand, a film having a complete dissolution temperature of 90°C or more cannot be sufficiently stretched and readily causes problems during the stretching. In addition, even if the complete dissolution temperature is in the above-

Appendix 1

mentioned range, a film whose equilibrium swelling degree shown by the expression (I) is outside of the above-mentioned range causes a decrease in the polarization performance and durability performance of the polarizing film and further causes a decrease in the manufacturing stability. Thus, a targeted polarizing film cannot be readily obtained.

[0014] The polarizing film is manufactured by stretching and dyeing the above-mentioned raw material film, and treating the film with a boron compound. In the present invention, the uniaxial stretching is conducted in both processes of the dyeing and the boron-compound treatment.

[0015] Iodine dyeing of a film, namely, adsorption of a polarization element, is conducted by bringing a liquid containing the polarization element into contact with the film. Generally, an aqueous solution of iodine-potassium iodide is used. Preferably, the iodine content is in the range of 0.1 to 2 g/L, the potassium iodide content is in the range of 10 to 50 g/L, and the weight ratio of iodine to potassium iodide is in the range of 20 to 100. The dyeing time is practically in the range of about 30 to 500 seconds. The temperature of the treating bath is preferably in the range of 30 to 80°C. A small amount of an organic solvent having compatibility with water may be contained in addition to a water solvent. Dipping is a preferable method for bringing the film into contact with the liquid, but any method such as coating and spraying may be optionally used.

[0016] The dyed film is then treated with a boron compound, practically, with boric-acid or borax. The boron compound is used in the content range of about 0.5 to 2 mol/L and in the form of an aqueous solution or a solution mixture of water and an organic solvent. Practically, it is desirable that the solution contains a small amount of sodium iodide. The treatment is desirably conducted by dipping, but may be conducted by coating or spraying. The treatment temperature is preferably in the range of about 50 to 70°C, and the treatment time is preferably in the range of about 5 to 20 minutes.

[0017] In the present invention, as described above, the uniaxial stretching is conducted in both processes of dyeing and boron-compound treatment. Practically, the final stretching ratio is 2 to 8 times, preferably 3 to 6 times. The film is uniaxially stretched to 1.2 to 2 times the original size thereof, preferably 1.2 to 1.5 times the original size thereof in the dyeing process, and uniaxially stretched to 2 to 6 times the original size thereof, preferably 2 to 4 times the original size thereof in the boron-compound treatment. In order to stretch the film in such a range, roll stretching or tenter stretching is conducted. The former is usually employed. The roll stretching may be one-stage or multistage.

[0018] The thus resulting polarizing film is provided with a protective film on both surfaces or on one surface and then is dried to be used as a polarizing plate. The

Appendix 1

protective film has excellent optical transparency and mechanical strength. Examples of the protective film include known cellulose acetate-based films, acrylic-based films, polyester-based resin films, polyolefin-based resin films, polycarbonate-based films, polyetheretherketone-based films, and polysulfone-based films.

[0019]

[Operation] The present invention provides a method for manufacturing a polarizing film which has excellent durability and stability in the polarization performance. The method is highly excellent in manufacturing stability. The polarizing films obtained according to the method are used for liquid-crystal displays by utilizing such characteristics. In particular, the films are useful for displays in automobiles applications, measuring gauges used in various industries, and electric kitchen appliances.

[0020]

[Examples] The present invention will now be specifically described with reference to examples. The term "part" and "%" in the examples are weight bases as long as there is no particular indication. In addition, the degree of polarization is defined by the following expression:

[Mathematic expression 1]

$$\sqrt{\frac{H_{11}-H_{1}}{H_{11}+H_{1}}} \times 100\ (\%)$$

wherein H_{11} represents transmittance (%) measured by a spectrophotometer when two polarizing film samples overlap

Appendix 1

each other so that the polarization directions of the polarizing films are oriented in the same direction; and H_1 represents transmittance (%) measured when the two polarizing film samples overlap each other so that the polarization directions of the polarizing films are oriented in the directions orthogonal to each other. Furthermore, in the present invention, performances relating to polarization and durability are collectively evaluated as moisture and heat resistances.

[0021] Example 1

Polyvinylalcohol having an average degree of polymerization of 3800 and a degree of saponification of 99.5 mol% was dissolved in water to prepare an aqueous solution with a concentration of 8.0%. The solution was cast on polyethylene terephthalate and then was air-dried at 30°C for 24 hours to obtain a film having a thickness of 80 μm, a complete dissolution temperature (X) of 71.6°C, and an equilibrium swelling degree (Y) of 2.4 (the equilibrium swelling degree satisfies $Y > 1.95$ calculated from the expression (I) defined in the present invention). The film was cut so as to have a width of 10 cm and was fixed to a chuck. The film was dipped in an aqueous solution containing 0.2 g/L of iodine and 60 g/L of potassium iodide at 30°C for 240 seconds and, at the same time, was uniaxially stretched to 1.2 times the original size thereof. Then, the film was dipped in an aqueous solution containing 60 g/L of boric acid and 30 g/L of potassium iodide for 5 minutes for boric acid treatment and, at the same time, was uniaxially stretched to 6 times the original size thereof. Lastly, the film was dried at a room temperature for 24 hours.

[0022] The thus obtained polarizing film was evaluated for moisture and heat resistances by measuring a temperature of discoloration thereof in water, namely, a temperature at which the color of the polarizing film is completely faded when the polarizing film was dipped in a water and the temperature of the water was increased at a rate in the range of 2 to 3°C/min. A polarizing film having a temperature of discoloration in water of 60°C or more had excellent moisture and heat resistances and was recognized as being a highly durable polarizing film. In addition, in the above-mentioned process, no breakage and fractures of the film were observed even when the film was dyed and then was uniaxially stretched to 6.4 times the original size thereof during the boric-acid treatment.

[0023] Example 2

A polarizing film was manufactured as in Example 1 except that a raw material film prepared by using polyvinylalcohol having an average degree of polymerization of 2600 and a degree of saponification of 99.5 mol% was air-dried at 40°C for 24 hours and then was thermally treated at 90°C for 3 minutes so as to have a complete dissolution temperature (X) of 72°C and an equilibrium swelling degree (Y) of 2.2 (the equilibrium swelling degree satisfies $Y > 1.93$ calculated from the expression (I) defined in the present invention). The thus obtained polarizing film was evaluated for moisture and heat resistances as in Example 1. In addition, no breakage and fractures of the film were observed even when the film was uniaxially stretched to 6.4 times the original size thereof during the boric-acid treatment, as in Example 1.

[0024] Comparative Example 1

A polarizing film was manufactured as in Example 1 except that a raw material film prepared by using polyvinylalcohol was dried at 60°C for 24 hours so as to have a complete dissolution temperature (X) of 74.5°C and an equilibrium swelling degree (Y) of 1.6 (the equilibrium swelling degree is outside of the range of $Y > 1.76$ calculated from the expression (I) defined in the present invention). The thus obtained polarizing film was evaluated for moisture and heat resistances as in Example 1. In addition, the film was uniaxially stretched during the boric-acid treatment as in Example 1. The film was broken when the stretching ratio exceeded 6 times.

[0025] Comparative Example 2

A polarizing film was manufactured as in Example 2 except that a polyvinylalcohol raw material film was dried at 70°C for 24 hours and then was thermally treated at 100°C for 3 minutes so as to have a complete dissolution temperature (X) of 75.3°C and an equilibrium swelling degree (Y) of 1.6 (the equilibrium swelling degree is outside of the range of $Y >$

1.71 calculated from the expression (I) defined in the present invention). The thus obtained polarizing film was evaluated for moisture and heat resistances as in Example 1. In addition, the film was uniaxially stretched during the boric-acid treatment as in Example 1. The film was broken when the stretching ratio exceeded 6 times. Table 1 shows the results of Examples and Comparative Examples.

[0026]

[Table 1]

	Example 1	Example 2	Com. Example 1	Com. Example 2
Complete dissolution temperature (X) (°C)	71.6	72.0	74.5	75.3
Equilibrium swelling degree (Y)	2.4	2.2	1.6	1.6
Range of (Y) <calculated value>	Y > 1.95	Y > 1.93	Y > 1.76	Y > 1.71
Temperature of discoloration in water (°C)	63	62	52	54

[0027]

[Advantages] In the present invention, a polarizing film having excellent polarization performance and durability performance and polarizing-film manufacturing with highly excellent stability can be achieved by using a polyvinylalcohol-based film having a particular complete dissolution temperature and an equilibrium swelling degree as the raw material film and uniaxially stretching the film in at least the boron-compound treatment process.

Appendix 1

Case 1

[Experimental Evidence]

Appendix 1

1. Object

The grounds for deriving expressions (I) and (II) defined in Claim 1 of Japanese Patent No. 3327423 will be verified by clarifying that polarizing films having excellent polarization performance and durability performance can be obtained by using polyvinylalcohol-based films satisfying the following expressions (I) and (II). The polarization performance and durability performance of polarizing films manufactured using polyvinylalcohol-based films having various physical properties will be evaluated.

$Y > -0.0667X + 6.73$ (I)

$X \geq 65$ (II)

2. Date of experiment

From May 18, 1993 to August 25, 1993

3. Place of experiment

13-1, Muroyama 2-chome, Ibaraki-shi, Osaka

Functional-Materials Research Department, Central Research and Development, The Nippon Synthetic Chemical Industry Co., Ltd.

4. Experimenter

Chief: Shuichi KITAMURA

Functional-Materials Research Department, Central Research and Development, The Nippon Synthetic Chemical Industry Co., Ltd.

5. Experiments and results

Experiment 1

Polyvinylalcohol (hereinafter referred to as PVA) having an average degree of polymerization of 2600 and an average degree of saponification of 98.5 mol% was dissolved in water to prepare an aqueous solution of a concentration of 13 wt%. Then, the temperature of the resulting aqueous solution was adjusted to 35°C. The aqueous solution was cast on a polyethylene terephthalate film and was dried at 85°C for 10 minutes to prepare a PVA film having a thickness of 75 μm. The PVA film was thermally treated at 105°C for 2 minutes, and the complete dissolution temperature and equilibrium swelling degree thereof were measured by a method described below. The complete dissolution temperature (X) was 72°C and the equilibrium swelling degree (Y) was 2.3 (with regard to the expression (I), Y > 1.93).

The resulting film was cut so as to have a width of 10 cm and fixed to a chuck. The film was dipped in an aqueous solution containing 0.2 g/L of iodine and 60 g/L of potassium iodide at 30°C for 240 seconds and, at the same time, was uniaxially stretched to 1.2 times the original size thereof. Subsequently, the film was dipped in an aqueous solution containing 60 g/L of boric acid and 30 g/L of potassium iodide for 5 minutes for boric-acid treatment and, at the same time, was uniaxially stretched to 6 times the original size thereof. Then, the film was dried at room temperature for 24 hours to obtain a polarizing film. The resulting polarizing film was measured for temperature of discoloration in water as described below. In addition, no breakage or fracture of the film was observed even when the film was uniaxially stretched to 6.4 times the original size thereof in the boric-acid treatment process.

(1) Measurement of complete dissolution temperature

A 2-liter beaker is filled with 2000 mL of water, and the temperature of the water is increased to 30°C. A film piece with dimensions of 2 cm × 2 cm is put into the water. The temperature of the water is increased at a rate of 3°C/min with stirring, and the temperature at which the film is completely dissolved is measured.

(2) Measurement of equilibrium swelling degree

A film piece with dimensions of 10 cm × 10 cm is dipped in a constant-temperature water bath of 20°C for 15 minutes for swelling and then is dried at 105°C for 2 hours. The equilibrium swelling degree is calculated from the following expression.

Equilibrium swelling degree (weight fraction) = Film weight after dipping / Film weight after drying

(3) Measurement of temperature of discoloration in water

The polarizing film is dipped in water and the water temperature is increased at a rate in the range of 2 to 3°C/min, and the temperature at which the color of the polarizing film is completely faded is measured. If the temperature of discoloration in water is 60°C or more, it is recognized that the polarizing film has excellent moisture and heat resistances and has a high durability performance.

Experiment 2

PVA having an average degree of polymerization of 2600 and an average degree of saponification of 98.5 mol% was dissolved in water to prepare an aqueous solution of a concentration of 13 wt%. Then, the temperature of the resulting aqueous solution was adjusted to 35°C. The aqueous solution was cast on a polyethylene terephthalate film and was dried at 90°C for 10 minutes to prepare a PVA film having a thickness of 75 μm. This PVA film was thermally treated at 120°C for 1 minute, and the resulting film was confirmed to have a complete dissolution temperature (X) of 73°C and an equilibrium swelling degree (Y) of 2.2 (with regard to the expression (I), $Y > 1.86$).

A polarizing film was manufactured as in Example 1 by using the resulting film and was measured for temperature of discoloration in water. In addition, no breakage or fracture of the film was observed even when the film was uniaxially stretched to 6.4 times the original size thereof in the boric-acid treatment process.

Experiment 3

PVA having an average degree of polymerization of 2600 and an average degree of saponification of 98.5 mol% was dissolved in water to prepare an aqueous solution of a concentration of 18 wt%. Then, the temperature of the resulting aqueous solution was adjusted to 70°C. The aqueous solution was cast on a polyethylene terephthalate film and was dried at 95°C for 10 minutes to prepare a PVA film having a thickness of 75 μm. This PVA film was thermally treated at 130°C for 0.5 minutes, and the resulting film was confirmed to have a complete dissolution temperature (X) of 73°C and an equilibrium swelling degree (Y) of 2.0 (with regard to the expression (I), $Y > 1.86$).

A polarizing film was manufactured as in Example 1 by using the resulting film and was measured for temperature of discoloration in water. In addition, no breakage or fracture of the film was observed even when the film was uniaxially stretched to 6.4 times the original size thereof in the boric-acid treatment process.

Experiment 4

PVA having an average degree of polymerization of 2600 and an average degree of saponification of 98.5 mol% was dissolved in water to prepare an aqueous solution of a concentration of 20 wt%. Then, the temperature of the resulting aqueous solution was adjusted to 80°C. The aqueous solution was cast on an SUS plate whose surface had a mirror finish and the temperature thereof was adjusted to 95°C, and it was then dried for 2 minutes to prepare a PVA film having a thickness of 75 μm. This PVA film was thermally treated at 80°C for 1 minute, and the resulting film was confirmed to have a complete dissolution temperature (X) of 68°C and an equilibrium swelling degree (Y) of 2.3 (with regard to the expression (I), $Y > 2.19$).

A polarizing film was manufactured as in Example 1 by using the resulting film and was measured for temperature of discoloration in water. In addition, no breakage or fracture of the film was observed even when the film was uniaxially stretched to 6.4 times the original size thereof in the boric-acid treatment process.

Experiment 5

PVA having an average degree of polymerization of 2600 and an average degree of saponification of 98.5 mol% was dissolved in water to prepare an aqueous solution of a concentration of 20 wt%. Then, the temperature of the resulting aqueous solution was adjusted to 90°C. The aqueous solution was cast on an SUS plate whose surface had a mirror finish and the temperature thereof was adjusted to 102°C, and it was then dried for 2 minutes to prepare a PVA film having a thickness of 75 μm. This PVA film was thermally treated at 120°C for 2 minutes, and the resulting film was confirmed to have a complete dissolution temperature (X) of 75°C and an equilibrium swelling degree (Y) of 2.0 (with regard to the expression (I), $Y > 1.7$).

A polarizing film was manufactured as in Example 1 by using the resulting film and was measured for temperature of discoloration in water. In addition, no breakage or fracture of the film was observed even when the film was uniaxially stretched to 6.4 times the original size thereof in the boric-acid treatment process.

Experiment 6

PVA having an average degree of polymerization of 2600 and an average degree of saponification of 98.5 mol% was dissolved in water to prepare an aqueous solution of a concentration of 20 wt%. Then, the temperature of the resulting aqueous solution was adjusted to 80°C. The aqueous solution was cast on an SUS plate whose surface had a mirror finish and the temperature thereof was adjusted to 95°C, and it was then dried for 2 minutes to prepare a PVA film having a thickness of 75 μm. This PVA film was thermally treated at 130°C for 1 minute, and the resulting film was confirmed to have a complete dissolution temperature (X) of 75°C and an equilibrium swelling degree (Y) of 1.9 (with regard to the expression (I), $Y > 1.7$).

A polarizing film was manufactured as in Example 1 by using the resulting film and was measured for temperature of discoloration in water. In addition, no breakage or fracture of the film was observed even when the film was uniaxially stretched to 6.4 times the original size thereof in the boric-acid treatment process.

Experiment 7

Ten parts of glycerin were added to 100 parts of PVA having an average degree of polymerization of 2600 and an average degree of saponification of 98.5 mol%, and the mixture was dissolved in water to prepare an aqueous solution of a concentration of 20 wt%. Then, the temperature of the resulting aqueous solution was adjusted to 85°C. The aqueous solution was cast on an SUS plate whose surface had a mirror finish and the temperature thereof was adjusted to 90°C, and it was then dried for 2 minutes to prepare a PVA film having a thickness of 75 μm. This PVA film was thermally treated at 120°C for 2 minutes, and the resulting film was confirmed to have a complete dissolution temperature (X) of 73°C and an equilibrium swelling degree (Y) of 2.3 (with regard to the

Appendix 1

expression (I), Y > 1.86).

A polarizing film was manufactured as in Example 1 by using the resulting film and was measured for temperature of discoloration in water. In addition, no breakage or fracture of the film was observed even when the film was uniaxially stretched to 6.4 times the original size thereof in the boric-acid treatment process.

Experiment 8

A PVA film was prepared as in Example 4 except that the temperature for the thermal treatment was 95°C and the thermal treatment time was 2 minutes. The resulting film was confirmed to have a complete dissolution temperature (X) of 70°C and an equilibrium swelling degree (Y) of 2.2 (with regard to the expression (I), Y > 2.06).

A polarizing film was manufactured as in Example 1 by using the resulting film and was measured for temperature of discoloration in water. In addition, no breakage or fracture of the film was observed even when the film was uniaxially stretched to 6.4 times the original size thereof in the boric-acid treatment process.

Comparative Experiment 1

PVA having an average degree of polymerization of 3800 and an average degree of saponification of 99.5 mol% was dissolved in water to prepare an aqueous solution of a concentration of 8 wt%. The resulting aqueous solution was cast on a polyethylene terephthalate film and was dried at 90°C for 5 minutes to obtain a PVA film having a thickness of 80 μm. This PVA film was thermally treated at 150°C for 2 minutes, and the resulting film was confirmed to have a complete dissolution temperature (X) of 72°C and an equilibrium swelling degree (Y) of 1.7 (with regard to the expression (I), Y > 1.93).

A polarizing film was manufactured as in Example 1 by using the resulting film and was measured for temperature of discoloration in water. In addition, breakage and fracture of the film were observed when the film was uniaxially stretched to 6.4 times the original size thereof in the boric-acid treatment process.

Comparative Experiment 2

PVA having an average degree of polymerization of 3800 and an average degree of saponification of 98.5 mol% was dissolved in water to prepare an aqueous solution of a concentration of 10 wt%. Then, the temperature of the resulting aqueous solution was adjusted to 80°C. The aqueous solution was cast on an SUS plate whose surface had a mirror finish and the temperature thereof was adjusted to 97°C, and it was then dried for 2 minutes to prepare a PVA film having a thickness of 40 μm. This PVA film was thermally treated at 130°C for 0.5 minutes, and the resulting film was confirmed to have a complete dissolution temperature (X) of 69°C and an equilibrium swelling degree (Y) of 1.9 (with regard to the expression (I), $Y > 2.1$).

A polarizing film was manufactured as in Example 1 by using the resulting film and was measured for temperature of discoloration in water. However, since the film broke when uniaxially stretched to 5.1 times the original size thereof in the boric acid treatment process, the stretching ratio was modified to 5 times.

Table 1 shows the experimental conditions and experimental results of Experiments 1 to 8 and Comparative Experiments 1 and 2 of this report and also the experimental conditions and experimental results of Examples 1 and 2 and Comparative Examples 1 and 2 in the specification of Japanese Patent No. 3327423. FIG. 1 is a graph showing a relationship between the complete dissolution temperature (X) and the equilibrium swelling degree (Y) of films obtained in Experiments 1 to 8 and Comparative Experiments 1 and 2 of this report and Examples 1 and 2 and Comparative Examples 1 and 2 in the Patent specification. In FIG. 1, ○ denotes the results in Examples 1 and 2 in the Patent specification, ● denotes the results in Comparative Examples 1 and 2, □ denotes the results in Experiments 1 to 8, and ■ denotes the results in Comparative Experiments 1 and 2. In addition, the straight line in the graph is a straight line defined by the following expression.

$$Y > -0.0667X + 6.73$$

6. Consideration

With reference to Table 1 and FIG. 1, it is confirmed that a polarizing film having a high temperature of discoloration in water and excellent polarization performance and durability performance can be obtained by using a vinylalcohol-based film whose complete dissolution temperature (X) and equilibrium swelling degree (Y) satisfy the expressions (I) and (II).

7. Conclusion

The expressions (I) and (II) defined in Claim 1 of Japanese Patent No. 3327423 are derived from the evaluation results of polarization performance and durability performance of polarizing films manufactured by using polyvinylalcohol-based films having various physical properties.

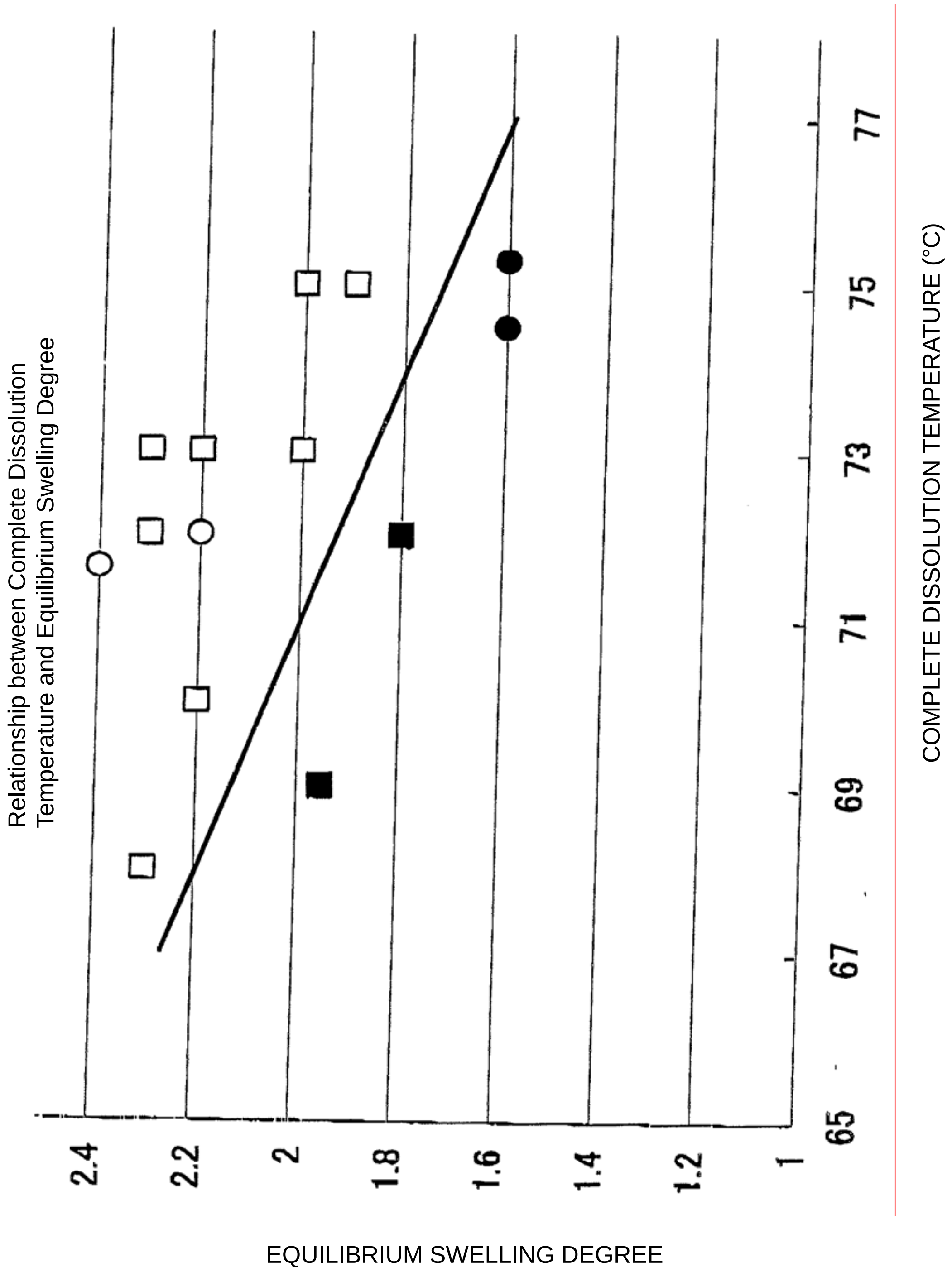
Appendix 1

Table 1

	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8	Patent Specification		Com. Exp. 1	Com. Exp. 2	Patent Specification	
									Example 1	Example 2			Com. Example 1	Com. Example 2
Deg. of Polymerization of PVA	2600	2600	2600	2600	2600	2600	2600	2600	3800	2600	3800	3800	3800	2600
Deg. of Saponification of PVA (mol%)	98.5	98.5	98.5	98.5	98.5	98.5	98.5	98.5	99.5	99.5	99.5	98.5	99.5	99.5
Elasticizer	0	0	0	0	0	0	10	0	0	0	0	0	0	0
Conc. of Solution (wt%)	13	13	18	20	20	20	20	20	8	8	8	10	8	8
Solution Temp. (°C)	35	35	70	80	90	80	85	80	-	-	-	80	-	-
Drying Temp. (°C)	85	90	95	95	102	95	90	95	30	40	90	97	60	70
Drying Time	10 min	10 min	10 min	2 min	2 min	2 min	2 min	2 min	24 h	24 h	5 min	2 min	24 h	24 h
Drying Backing Material	PET	PET	PET	SUS	SUS	SUS	SUS	SUS	PET	PET	PET	SUS	PET	PET
Heat Treatment Temp. (°C)	105	120	130	80	120	130	120	95	-	90	150	130	-	100
Heat Treatment Time	2 min	1 min	0.5 min	1 min	2 min	1 min	2 min	2 min	-	3 min	2 min	0.5 min	-	3 min
Film Thickness (μm)	75	75	75	75	75	75	75	75	80	80	80	40	80	80
Complete Dissolution Temp. (X) (°C)	72	73	73	68	75	75	73	70	71.6	72	72	69	74.5	75.3
Equilibrium Swelling Deg. (Y)	2.3	2.2	2.0	2.3	2.0	1.9	2.3	2.2	2.4	2.2	1.7	1.9	1.6	1.6
Expression (I)	Y > 1.93	Y > 1.86	Y > 1.86	Y > 2.19	Y > 1.7	Y > 1.7	Y > 1.86	Y > 2.06	Y > 1.95	Y > 1.93	Y > 1.93	Y > 2.1	Y > 1.76	Y > 1.71
Stretching Ratio	6	6	6	6	6	6	6	6	6	6	6	5	6	6
Breakage when Stretched to 6.4 times	No	No	No	No	No	No	No	No	No	No	Yes	Broken at 5.1 times	Yes	Yes
Temp. of Discolor. in water (°C)	63	62	62	63	61	61	63	62	63	62	52	49	52	54

Appendix 1

FIG. 1



Relationship between Complete Dissolution Temperature and Equilibrium Swelling Degree