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(54) Title: ALKALI SAPONIFICATION METHOD FOR CELLULOSE ACYLATE FILM, A SURFACE SAPONIFIED CELLULOSE ACYLATE FILM AND AN OPTICAL FILM UTILIZING THE SAME

(57) Abstract: The invention is to provide an alkali saponification method for uniformly and stably saponifying a cellulose acylate film, to provide a surface saponified cellulose acylate film adapted for an optical compensation sheet for a large-sized liquid crystal display apparatus without a display defect, and to provide a alkali saponified cellulose acylate film adapted for an optical compensation sheet with an appropriate adhesion between a transparent substrate and an orienting film. There is provided an alkali saponification method for cellulose acylate film characterized by alkali saponification of a cellulose acylate film with an alkali solution, particularly an alkali saponification method for achieving selective saponification by coating the alkali solution on one surface only of the film, and a cellulose acylate film processed by such alkali saponification method.

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DESCRIPTION

ALKALI SAPONIFICATION METHOD FOR CELLULOSE ACYLATE FILM, A SURFACE SAPONIFIED CELLULOSE ACYLATE FILM AND AN OPTICAL FILM UTILIZING THE SAME

TECHNICAL FIELD

The present invention relates to an alkali saponification method for a cellulose acylate film, a saponified cellulose acylate film and an optical film utilizing the same. In particular it relates to an optical film useful for an optical polarization, an optical diffusion, an optical compensation etc. for an image display apparatus.

The invention also relates to a replenishing method of a replenishing liquid in the production of an alkali saponified polymer film. More specifically it relates to a method of replenishing an alkali solution with a replenishing liquid, enabling to stably produce an alkali saponified polymer film even by a saponifying process of a polymer film surface with the alkali solution in a continuous manner.

BACKGROUND ART

In various displays equipped in a personal computer,

a television, a mobile phone or various instruments, visual information such as a character or a pattern is observed through a transparent protective substrate such as a glass or plastic plate on a surface. Also a liquid crystal display is employed in most of the displays in the equipment. A liquid crystal display apparatus is constituted of a liquid crystal cell, a polarizing plate, and an optical compensation sheet (phase difference plate). In a transmission liquid crystal display apparatus, two polarizing plates are mounted on both sides of the liquid crystal cell, and one or two optical compensation sheets are positioned between the liquid crystal cell and the polarizing plates. A reflective liquid crystal display apparatus is constituted by a reflecting plate, a liquid crystal cell, an optical compensation sheet, and a polarizing plate.

a liquid crystal cell is constituted of rod-shaped liquid crystal molecules, two substrates for sealing the same, and electrode layers for applying a voltage to the rod-shaped liquid crystal molecules, and, for the liquid crystal cell, there are proposed various display modes depending on a difference in an orientation of the rod-shaped liquid crystal molecules, such as TN (twisted nematic), IPS (in-plane switching), FLC (ferroelectric liquid crystal), OCB (optically compensatory bend), STN

(super twisted nematic), or VA (vertically aligned) for the transmission type, and HAN (hybrid aligned nematic) for the reflective type.

A polarizing plate is generally constituted of a polarizing film and two transparent protective films provided on both sides thereof. The polarizing film is generally obtained by impregnating polyvinyl alcohol with an aqueous solution of iodine or a dichroic dye and monoaxially stretching such film. A polarizing plate utilizing a cellulose acylate film is often employed as a polarizing plate for various image displays, because of excellent optical characteristics, a high transmittance and a polarization degree over a wide wavelength range and excellent brightness and contrast.

An optical compensation sheet is employed in various liquid crystal display apparatuses in order to eliminate a color in the image or expanding a viewing angle. As the optical compensation sheet, a stretched birefringent film has been used.

Instead of the optical compensation sheet formed by the stretched birefringent film, there is proposed an optical compensation sheet having an optical anisotropic layer formed by liquid crystalline molecules (particularly discotic liquid crystal molecules) on a transparent substrate. The optical anisotropic layer is formed by

orienting the liquid crystal molecules and fixing such oriented state.

Use of the liquid crystal molecules in the optical compensation sheet enables to realize optical characteristics which cannot be obtained in the prior stretched birefringent film.

Optical property of the optical compensation sheet is designed according to the optical property of the liquid crystal cell, more specifically according to a difference in the aforementioned display mode of the liquid crystal cell. By employing liquid crystal molecules, particular discotic liquid crystal molecules, in the optical compensation sheet, it is possible to create optical compensation sheets of various optical characteristics corresponding to various display modes of the liquid crystal cell.

The optical compensation sheet utilizing the discotic liquid crystal moelcules is proposed in forms corresponding to various display modes. For example an optical compensation sheet for a liquid crystal cell of TN mode is described in JP-A No. 6-214116, USP No. 5,583,679, USP No. 5,646,703 and GP No. 3911620A1. Also an optical compensation sheet for a liquid crystal cell of IPS mode or FLC mode is described in JP-A No. 10-54982. Also an optical compensation sheet for a liquid crystal cell of

OCB mode or HAN mode is described in USP No. 5,805,253 and WO96/37804. Also an optical compensation sheet for a liquid crystal cell of STN mode is described in JP-A No. 9-26572. Also an optical compensation sheet for a liquid crystal cell of VA mode is described in Japanese Patent No. 2866372.

By laminating an optical compensation sheet with a polarizing film to form an oval polarizing plate, the optical compensation sheet can also function as a transparent protective film of the polarizing plate. Such oval polarizing plate has a laminar structure formed by a transparent protective film, a polarizing film, a transparent substrate and an optical isotropic layer constituted of liquid crystal molecules, laminated in this order. The liquid crystal display apparatus is required to be thin and light-weight, and a deletion of one of the components by a co-use (transparent protective film of the polarizing plate and optical compensation sheet) allows to make the apparatus thinner and lighter in weight. Besides, a deletion of one of the components of the liquid crystal display apparatus eliminates one of adhering steps for the components, thereby advantageously reducing a possibility of causing a trouble in assembling the apparatus. An integral oval polarizing plate, utilizing the transparent substrate of the optical compensation sheet utilizing the

liquid crystal molecules and one of the protective films of the polarizing plate in common, is described for example in patent references JP-A No. 7-191217, JP-A No. 8-21996 and JP-A No. 8-94838.

A sheet-shaped material having an optical functionality such as a polarizing plate or an optical compensation sheet is called an optical film, and for a transparent substrate of such optical film, there is employed a cellulose acylate film having an excellent optical transmission, no optical orientation, excellent physical and mechanical properties, and a little dimensional change in response to a change in temperature and humidity.

On the cellulose acylate film constituting the transparent substrate, a polarizing film or an optical compensation layer is provided across an adhesive layer or an orienting layer (usually of polyvinyl alcohol), and, as a method for achieving adhesion with such adhesive layer or orienting film, there is known a method of immersing the cellulose acylate film in an aqueous alkali solution thereby saponifying and hydrophilizing a surface thereof (for example paragraph [0008] of JP-A No. 7-151914, paragraph [0033] of JP-A No. 8-94838, paragraph [0083] of JP-A No. 2001-16614 and paragraph [0042] of JP-A No. 2001-18813).

However, since such processing liquid is formed of an aqueous solution of an alkali agent only, it is difficult to uniformly saponify a surface of a hydrophobic film. Also since a saponifying bath process by immersion simultaneously saponifies both surface of the cellulose acylate film, there results a drawback of adhesion of the front and rear surfaces mutually adhere in case the film is rolled after coating a hydrophilic layer such as of polyvinyl alcohol on a surface. For saponifying a surface only in the saponifying bath process, there is a method of executing saponification after applying a waterproof process on an undesired surface, but such method is undesirable in productivity and environmental protection because of an additional cumbersome step and a generation of an unnecessary waste material.

On the other hand, there are proposed a method of immersion in an alkali saponifying solution formed by adding an organic solvent which does not dissolve nor swell the polymer film to an aqueous alkali solution (paragraph [0034] of JP-A No. 2002-82226), and a method of saponifying at least a surface of a film by coating an aqueous alkali solution or an alkali saponifying solution containing an organic solvent on a film surface (WO02/46809).

An inclusion of an organic solvent in an alkali

saponifying solution increases a saponifying reaction activity in comparison with an aqueous alkali solution. On the other hand, because of the increased reactive activity or depending on the kind or the content of the organic solvent, there may result a significant dissolution of an additive or a mixed substance contained in the film, or an adhesion of a concentrated alkali agent leading to a deterioration in the quality of the optical film, such as an increased haze, a defective adhesion, a defect caused by a foreign substance or a defect in the orientation.

On the other hand, it is desired to produce a web-shaped film in stable and continuous manner, in order to meet an increase in the production amount resulting from a recent increase in the image size of the image display apparatus and a rapid progress of mobile equipment, and a reduction in the production cost.

On the other hand, in case of executing the saponification process continuously in the aforementioned methods, since the alkali agent in the alkali solution is consumed by the saponification reaction, there result problems such as that the level of saponification changes in time or becomes uneven in case process conditions (for example a process temperature and a process time) are maintained constant. Also an absorption of carbon oxide

gas in the air by the alkali solution causes a consumption of the alkali agent by a neutralization reaction, thereby resulting in problems similar to those mentioned above.

Such deterioration of the alkali solution is usually coped with by replacing the alkali solution with a new solution in such a manner that a level of saponification becomes within a desired range.

However, when a process amount of the polymer film is large, the replacement of the alkali solution is required frequently to reduce the operation efficiency, and there is generated a large amount of alkaline waste liquid of which disposal constitutes another problem.

DISCLOSURE OF INVENTION

As explained in the foregoing, the known alkali saponification methods for the cellulose acylate film are unable to satisfactorily meet the requirement, and there is desired a method capable of producing a web-shaped film stably and with a satisfactory productivity. An object of the present invention is to provide an alkali saponifiation method capable of saponifying a cellulose acylate film stably and uniformly over the entire surface in a prompt alkali saponification process.

Another object of the present invention is to provide a surface saponified cellulose acylate film

enabling an easy manufacture of an optical sheet of a large area without a display defect in an image display apparatus.

Another object of the present invention is to provide a liquid crystal display apparatus equipped with an optical sheet employing a cellulose acylate film as a substrate and capable of a sharp image display.

Also an object of the present invention is to provide a method, in executing a saponification process of a polymer film in continuous manner, capable of achieving a saponification process in stable manner without problems such as a decrease in the work efficiency or disposal of waste liquid.

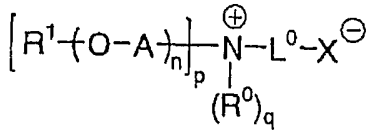
The aforementioned objectives of the invention are attained by an alkali saponification method, a surface saponified film and an optical film employing such film as described in following (1) to (23):

(1). A method of alkali-saponifying a cellulose acylate film with an alkali solution comprising an alkali agent, water, an organic solvent, a surfactant and a mutually solubilizing agent. (First embodiment)

(2). The method according to item (1), wherein said organic solvent has an inorganic/organic value (I/O value) of 0.5 or higher and a solubility parameter of 16 to 40 $[mJ/m^3]^{1/2}$.

(3). The method according to item (1) or (2),wherein said surfactant is at least one selected from the group consisting of a nonionic surfactant, an anionic surfactant, a cationic surfactant and an amphoteric surfactant.

(4). A method of alkali-saponifying a cellulose acylate film with an alkali solution comprising an alkali agent and a surfactant, wherein said surfactant is an amphoteric surfactant represented by a following general formula (I):



wherein A represents an alkylene group; L^0 represents a group connecting a nitrogen atom and X^-; X^- represents $-COO^-$, $-SO_3^-$ or $-PO_3H^-$; R^0 represents a hydrocarbon group; R^1 represents a hydrogen atom or a hydrocarbon group; n represents an integer of from 1 to 50; p and q each represents an integer of 1 or 2 and p + q = 3.) (Second embodiment)

(5). The method according to any of items (1) to (3), wherein said mutually solubilizing agent is at least one selected from polyol compounds having a solubility of 30 g or higher to 100 g of the mutually solubilizing agent at 25°C.

(6). The method according to item (4), wherein said alkali solution includes an alkali agent of 0.1 to 25 % by weight ,and water or a mixed solvent of water and a hydrophilic organic solvent.

(7). The method according to any of items (1) to (6), wherein said alkali solution has a concentration of the alkali agent of 0.1 to 25 % by weight, a surface tension of 45 mN/m or less, and a viscosity of 0.8 to 20 mPa·s.

(8). The method according to any of items (1) to (7), wherein said alkali solution includes at least one selected from hydrophilic compounds having a boiling point of 120°C or higher, and capable of dissolving water in an amount of 50 g or more in 100 g of the hydrophilic compound.

(9). The method according to any of items (1) to (8), wherein said alkali solution includes a defoaming agent.

(10). A method of alkali-saponifying a cellulose acylate film with an alkali solution comprising: a step of processing a cellulose acylate film with an alkali solution; and a step of washing off said alkali solution from the film with an alkali diluting liquid or a neutralizing liquid, wherein the alkali diluting liquid or the neutralizing liquid has a carbonate ion concentration

of 3500 mg/L or less. (Third embodiment)

(11). The method according to item (10), wherein the alkali diluting liquid or the neutralizing liquid has a polyvalent metal ion concentration of 500 mg/L or less and a chlorine ion concentration of 300 mg/L of less.

(12). The method according to item (10) or (11), wherein the alkali diluting liquid or the neutralizing liquid includes a surfactant.

(13). The method according to any of items (10) to (12), wherein a solvent of the alkali diluting liquid or the neutralizing liquid is water, or a mixture of water and an organic solvent.

(14). The method according to any of items (10) to (13), wherein the alkali diluting liquid or the neutralizing liquid includes a defoaming agent.

(15). The method according to any of claims (10) to (14), wherein the step of processing a cellulose acylate film with said alkali solution includes a step of coating the alkali solution to the cellulose acylate film.

(16). The method according to any of items (1) to (15), which includes a step of coating said alkali solution on the cellulose acylate film at the room temperature or higher and a step of washing off said alkali solution from said cellulose acylate film.

(17). A surface saponified cellulose acylate film

obtained by the method according to any of items (1) to (16).

(18). An optical film comprising the surface saponified cellulose acylate film according to item (17).

(19). A method of replenishing an alkali solution with a replenishing liquid in producing an alkali saponified polymer film by a continuous saponification process of a polymer film surface with said alkali solution, which comprises:

a step of measuring a saponifying ability of said alkali solution;

a step of determining a replenishing mode for the replenishing liquid in such a manner that the saponifying ability of the alkali solution after a replenishment with said replenishing liquid becomes within a predetermined range, based on said measured saponifying ability; and

a step of replenishing said alkali solution with said replenishing liquid in said determined replenishing mode. (Fourth embodiment)

(20). The method according to item (19), further comprising a step of measuring a process area per unit time of said polymer film, wherein said predetermined range is determined based on said measured process area per unit time.

(21). The method according to item (20), wherein

the saponifying ability of said alkali solution is measured by at least one selected from a group consisting of a pH measurement of the alkali solution, a measurement of an electrical conductivity of the alkali solution, a measurement of an electrical impedance of the alkali solution, a measurement of an electrode voltage between current-controlled electrodes, and a measurement of an electrode potential between current-controlled electrodes.

(22). A method of replenishing an alkali solution with a replenishing liquid in producing an alkali saponified polymer film by a continuous saponification process of a polymer film surface with said alkali solution, comprising:

a step of measuring a process area per unit time of said polymer film;

a step of calculating a consumption of the alkali solution per unit time from the measured process area per unit time, based on a pre-memorized amount of the alkali solution necessary for a saponification process per unit area of said polymer film;

a step of determining a replenishing mode for the replenishing liquid in such a manner that the saponifying ability of the alkali solution after a replenishment with said replenishing liquid becomes within a predetermined range, based on said calculated consumption per unit time;

and a step of replenishing said alkali solution with said replenishing liquid in said determined replenishing mode.

(23). The method according to item (22), wherein said saponifying process comprises a step of heating the polymer film in advance to 25°C or higher, a step of coating the polymer film with the alkali solution, a step of maintaining the polymer film at a temperature of 25°C or higher, and a step of washing off the alkali solution from the polymer film, in this order.

A surface saponified cellulose acylate film (17) obtained by alkali saponification with any of methods (1) to (16) can provide an optical compensation film by forming an orienting film thereon, then coating liquid crystal molecules on the orienting film, and fixing an orientation of the liquid crystal molecules thereby forming an optical anisotropic layer.

Also in a polarizing plate formed by a polarizing film and two transparent protective films positioned on both sides thereof, in which one of the transparent protective films is constituted of an optical compensation sheet having an orienting film and an optical anisotropic layer, formed by fixing an orientation of liquid crystal molecules, in this order on a cellulose acylate film, a surface saponified cellulose acylate film (17) obtained by

alkali saponification with any of methods (1) to (16) can be effectively employed as such cellulose acylate film.

Such cellulose acylate film can be used to prepare an optical film (18) excellent in an interlayer adhesion and a uniformity of display.

The alkali saponification method of the present invention, in a step of washing off an alkali saponification solution containing a concentrated alkali agent and an extracted material such as a material added to the film, maintains a carbonate ion concentration, a vopolyvalent ion concentration or a chlorine ion concentration in an alkali diluting liquid or an alkali neutralizing liquid within a predetermined range, thereby realizing an alkali saponification process not involving an increase in the haze of the film, a defective adhesion, a defect caused by a foreign substance or a defect in the orientation.

BEST MODE FOR CARRYING OUT THE INVENTION

[Polymer film]

The polymer film preferably has an optical transmission of 80 % or higher. It is preferable that the polymer film does not easily exhibit a birefringence by an external force.

The polymer includes a hydrolysable bond (bond

subjected to saponification) such as an ester bond or an amide bond. An ester bond is particularly preferred, and it is further preferred that the ester bond is present in a side chain. As a polymer including an ester bond in a side chain, a cellulose ester is preferred. In a cellulose ester, a cellulose acylate is most preferred, which is a substrate constituting an object of the present invention.

In the following, there will be given a detailed explanation on cellulose acylate. A raw material cellulose includes cotton linter and wood pulp, but the cellulose acylate prepared from either raw material can be employed and cellulose acylates obtained from both raw materials may be used in a mixture. The cellulose acylate, obtained from such cellulose and employed in the present invention have a substitution degree of cellulose to hydroxyl group satisfying all of f9ollowing relations (I) to (III):

relation (I): $2.6 \leq SA' + SB' \leq 3.0$

relation (II): $2.0 \leq SA' \leq 3.0$

relation (III): $0 \leq SB' \leq 0.8$

In the foregoing, SA' represents a substitution degree of acetyl groups substituting hydrogen atoms of hydroxyl groups of cellulose; and SB' represents a substitution degree of acetyl groups with 3 to 22 carbon atoms substituting hydrogen atoms of hydroxyl groups of

cellulose. SA represents an acetyl group substituting a hydrogen atom of a hydroxyl group of cellulose, and SB represents an acetyl group with 3 to 22 carbon atoms substituting a hydrogen atom of a hydroxyl group of cellulose.

A glucose unit having a β-1,4 bond, constituting cellulose, has free hydroxyl groups in 2-, 3- and 6-positions. Cellulose acylate is a polymer formed by esterifying all or a part of such hydroxyl groups with acyl groups. An acyl substitution degree means a proportion of esterification of cellulose in each of the 2-, 3- and 6-positions (for each position, a substitution degree 1 corresponds to an esterification of 100 %). In the invention, a sum of substitution degrees of SA and SB (SA' + SB') is more preferably 2.7 to 2.96, and particularly preferably 2.80 to 2.95. Also a substitution degree of SB (SB') is 0 to 0.8, particularly 0 to 0.6. Also it is preferable that 28 % or more of SB are substituents on the 6-position hydroxyl groups, more preferably 30 % or more are substituents on the 6-position hydroxyl groups, further preferably 31 % or more and particularly preferably 32 % or more are substituents on the 6-position hydroxyl groups. There is also preferred a cellulose acylate film in which a sum of the substitution degree of SA and SB in the 6-position of cellulose acylate

is 0.8 or more, further 0.85 or more and particularly 0.90 or more. Such cellulose acylate film allows to prepare a solution with a preferred solublity, and to prepare a satisfactory solution particularly in a non-chlorine organic solvent.

An acyl group (SB) with 3 to 22 carbon atoms in the cellulose acylate employed in the invention can be an aliphatic group or an aryl group and is not particularly limited. The cellulose acylate is for example an alkylcarbonyl ester, an alkenylcarbonyl ester, an aromatic carbonyl ester, an aromatic alkylcarbonyl ester etc. of cellulose, each of which may further have a substituent. Preferred examples of SB include a propionyl group, a butanoyl group, a heptanoyl group, a heptanoyl group, a hexanoyl group, an octanoyl group, a decanoyl group, a dodecanoyl group, a tridecanoyl group, a tetradecanoyl group, a hexadecanoyl group, an octadecanoyl group, an iso-butanoyl group, a t-butanoyl group, a cyclohexanecarbonyl group, an oleoyl group, a benzoyl group, a naphthylcarbonyl group and a cinnamoyl group. Among these, preferred examples of SB include a propionyl group, a butanoyl group, a dodecanoyl group, an octadecanoyl group, a t-butanoyl group, an oleoyl group, a benzoyl group, a naphthylcarbonyl group and a cinnamoyl group.

A basic principle of a method for synthesizing cellulose acylate is described in Migita et al., *Mokuzai Kagaku*, p180 - 190 (Kyoritsu Shuppan, 1968). A representative synthesizing method is a liquid phase acylation utilizing a carboxylic acid anhydride-acetic acid-sulfiric acid catalyst. Specific examples include methods described in JP-A Nos. 6-32801, 7-70702, 10-45804, 10-511728, and 2001-200901.

The cellulose acylate employed in the invention preferably has a polymerization degree (viscosity-averaged) of 200 to 700, particularly preferably 250 to 550. In order to satisfy a mechanical strength in a cellulose acylate film, a fiber or a molded article containing cellulose triacetate, there is generally required a polymerization degree of 200 or higher, as described in Hiroshi Sofue and Nobuhiko Migita, "Cellulose Handbook", Asakura Shobo (1958) or Hiroshi Marusawa and Kazuo Uda, "Plastic Material Text 17", Nikkan Kogyo Shimbun (1970).

The cellulose acylate film employed in the invention may include another compound in addition to cellulose acylate, according to a purpose or an application of use.

In case of employing a cellulose acylate film as an optical compensation sheet, a retardation in a film plane (Re retardation) and a retardation in a direction of

thickness (Rth retardation) are respectively defined by following formulas (I) and (II):

(I) $Re = |nx - ny| \times d$

(II) $Rth = ((nx + ny) /2 - nz) \times d$

In the formulas (I) and (II), nx represents a refractive index in a direction of a phase retarding axis in the film plane (direction where the refractive index becomes maximum); ny represents a refractive index in a direction of a phase advancing axis (direction where the refractive index becomes minimum); nz represents a refractive index in a direction of thickness of the film; and d indicates a film thickness in nm.

The cellulose acylate film preferably a Re retardation value from 1 to 200 nm, and a Rth retardation value from 70 to 400 nm. A specific value is determined by an extrapolation from a measurement result obtained with an incident measuring light inclined from a vertical direction to the film surface. The measurement can be executed with an ellipsometer (for example M-150, manufactured by Nippon Bunko Co.). For the measurement, there is employed a wavelength of 632.8 nm (He-Ne laser).

For adjusting the retardation of a cellulose acylate film, it is common to employ a method of applying an external force such as stretching, and a retardation increasing agent for increasing the optical anisotropy is

added in certain case. For regulating the retardation of a cellulose acylate film, it is preferred to employ an aromatic compound including at least two aromatic rings as the retardation increasing agent. The aromatic compound is preferably employed within a range of 0.01 to 20 parts by weight with respect to 100 parts by weight of cellulose acylate. It is also possible to use two or more aromatic compounds in combination. The aromatic ring of the aromatic compound includes an aromatic hetero ring in addition to an aromatic hydrocarbon ring. Examples includes compound described for example in EP-A No. 0911656A2, JP-A Nos. 2000-111914 and 2000-275434.

The cellulose acylate employed in the invention may further include various additives (for example a plasticizer, an ultraviolet absorber, an antideterioration agent, fine particles, a separation agent, an infrared absorber, an antistatic agent etc.) according to the purpose, which may be a solid substance or an oily substance. Also in case the cellulose acylate film is constituted of plural layers, kinds and amounts of the additives may be different in the layers. Materials detailedly described in Japan Institute of Invention and Innovation, Laid-open Technical Report (2001-1745, issued March 15, 2001, JIII), pages 16 - 22, can be advantageously employed. An amount of use of such

additive is not particularly limited as long as a function of each material can be exhibited, but is suitably employed preferably within a range from 0.001 to 20 weight% in the total cellulose acylate composition.

The cellulose acylate film of the invention is preferably prepared as a film by a solvent cast method.

A solvent to be employed can be a known solvent, preferably a solvent having a solubility parameter within a range of 17 to 22. Examples include a chlorinated product of a lower aliphatic hydrocarbon, a lower aliphatic alcohol, a ketone with 3 to 12 carbon atoms, an ester with 3 to 12 carbon atoms, an ether with 3 to 12 carbon atoms, an ester with 3 to 12 carbon atoms, an aliphatic hydrocarbon with 5 to 8 carbon atoms, and an aromatic hydrocarbon with 6 to 12 carbon atoms. Specific examples include compounds described in the aforementioned Laid-open Technical Report NO. 2001-1745, pages 12 - 16.

In particular it is preferable to employ, in a mixing ratio, an acetate ester in 20 to 90 weight%, a ketone in 5 to 60 weight% and an alcohol in 5 to 30 weight%, in consideration of solubility of cellulose acylate.

Also as a non-halgenated organic solvent system not containing a halogenated hydrocarbon, there can be employed a solvent system described for example in JP-A No.

2002-146043, paragraphs [0021] to [0025] and JP-A No. 2002-146045, paragraphs [0016] to [0021].

For preparing a cellulose acylate solution (dope) of the invention, a dissolving method thereof is not particularly restricted and can be a room-temperature dissolving method, a cooled dissolving method, a high-temperature dissolving method or a combination thereof. A method for preparing a cellulose acylate solution is described for example in JP-A Nos. 5-163301, 61-106628, 58-127737, 9-95544, 10-95854, 10-45950, 2000-53784, 11-322946, 11-322947, 2-276830, 2000-273239, 11-71463, 05-259511, 2000-273184, 11-323017 and 11-302388. The aforementioned dissolving methods for cellulose acylate in an organic solvent are also suitably applicable in the invention within the scope of the invention. The dope solution of cellulose acylate is usually subjected to a concentration and a filtration of the solution, as detailedly described in the aforementioned Laid-open Technical Report No. 2001-1745, page 25. In case of dissolution at a high temperature, the organic solvent is mostly employed at a boiling temperature thereof or higher, and is employed in a pressurized state in such case.

In the following, there will be explained a method of producing a film with a cellulose acylate solution. For producing a cellulose acylate film, there can be

employed a known solution cast film forming method and a solution cast film forming apparatus, called a drum method or a band method and employed for producing a cellulose triacetate film. Film forming steps will be explained in an example of the band method. A dope (cellulose acylate solution) prepared in a dissolving equipment (pot) is once stored in a storing pot and is subjected to an elimination of bubbles contained in the dope and to a final adjustment. The adjusted dope is fed, for example through a pressurized constant-rate gear pump capable of feeding a highly precise constant amount determined by a revolution, to a pressurized die, and is cast from lips (slit) of the pressurized die onto a running endless metal support member in a cast unit, and, in a peeling point on the metal support member after a substantially one cycle thereof, a semi-dried dope film (also called a web) is peeled from the metal support member. The obtained web is conveyed in a tenter, with both ends being supported by clips to maintain a width, further conveyed by rolls in a drying apparatus, and, after a drying, is wound in a predetermined length by a winder. A combination of the tenter and the rolls of the drying apparatus is variable depending on the purpose. These manufacturing steps (classified into casting (including co-casting), metal support member, drying, peeling, stretching etc.) are

described in detail in the aforementioned Laid-open Technical Report No. 2001-1745, pages 25 to 30. In the casting step, it is possible to cast a single layer of a cellulose acylate solution of one kind, or to co-cast two or more cellulose acylate solutions simultaneously or in succession.

The cellulose acylate film can be subjected to an adjustment of the retardation by a stretching process. A stretching factor is preferably 3 to 100 %.

The cellulose acylate film preferably has a thickness of 15 to 500 μm, more preferably 20 to 200 μm.

In a first embodiment of the invention, the surface saponified cellulose acylate film is saponified by an alkali solution comprising an alkali agent, water, an organic solvent, a surfactant and a mutually solubilizing agent.

In a second embodiment of the invention, the surface saponified cellulose acylate film is saponified by an alkali solution comprising an alkali agent and a surfactant.

In a third embodiment of the invention, an alkali solution can be prepared by dissolving an alkali in water or a mixture of water and an organic solvent. A preferred organic solvent is one, or two or more organic solvent selected from an alcohol with 8 or less carbon atoms, a

ketone with 6 or less carbon atoms, an ester with 6 or less carbon atoms and a polyhydric alcohol with 8 or less carbon atoms.

An alkali agent in the alkali solution of the invention can be an inorganic alkali agent or an organic alkali agent. A strong alkali is preferable in order to induce a saponification reaction at a low concentration. Preferable examples include an alkali metal hydroxide (such as NaOH, KOH or LiOH), an alkali earth metal hydroxide, sodium, potassium or ammonium tertiary phosphate, sodium, potassium or ammonium secondary phosphate, sodium, potassium or ammonium borate, ammonium hydroxide, an amine (such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropaynolamine, ethyleneimine, ethylenediamine, pyridine, DBU (1,8-diazabicyclo[5,4,0]-7-undecene, DBN (1,5-diazabicyclo[4,3,0]-5-nonene), tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropyammonium hydroxide, tetrabutylammonium hydroxide, triethylbutylammonium hydroxide, perfluorotributylamine, or triethylamine), and a free base of a complex salt (for example)$Pt(NH_3)_4)(OH)_4$,

more preferably an alkali metal hydroxide and most preferably NaOH or KOH. Such alkali agent may be employed singly or in a combination of two or more kinds.

A concentration of the alkali agent in the alkali solution is determined according a type of the alkali agent to be used, a reaction temperature and a reaction time. In order to complete the saponification reaction within a short time, it is preferable to prepare the solution at a high concentration. However, an excessively high concentration may deteriorate stability of the alkaline saponifying solution, resulting in a precipitation in a coating over a long time. The alkali saponifying solution preferably has a concentration of 0.1 to 25 weight%, more preferably 0.5 to 15 weight% and most preferably 1 to 10 weight%.

For a solvent of the alkali solution of the invention, there is employed water or a mixed solution of water and an organic solvent. There can be employed any organic solvent miscible with water.

Among such organic solvent, there is preferred an organic solvent having an inorganic/organic value (I/O value) of 0.5 or higher, and a solubility parameter of 16 to 40 $[mJ/m^3]^{1/2}$. An I.O value of 0.6 to 10 and a solubility parameter of 18 to 31 $[mJ/m^3]^{1/2}$ are more preferable. An I/O value stronger in the inorganic nature

than this range or a lower solubility parameter results in a decrease in the alkali saponifying speed, and an insufficient uniformity of the saponification degree over the entire surface. On the other hand, an I/O value stronger in the organic nature than this range or a higher solubility parameter provides a faster saponification speed but tends to cause a haze, thus being insufficient in the uniformity over the entire surface.

Examples of the organic solvent having the solubility parameter and the I/O value within the above-described ranges and advantageously employable in the invention include followings.

	solubility parameter $[mJ/m^3]^{1/2}$	I/O value
isopropanol	23.5	2.00
n-propanol	24.3	1.67
methyl cellosolve	23.3	2.00
2-butanol	22.1	1.25
ethanol	26.0	2.50
propylene glycol monomethyl ether	20.7	1.50
methanol	29.7	5.00

Also an organic solvent, particularly an organic solvent with the organic property and the solubility within the aforementioned ranges, combined with a mutually

solubilizing agent and a surfactant to be explained later allows to maintain a high saponifying speed and to improve the uniformity of the saponification degree over the entire surface.

An organic solvent having preferable characteristics can be those described for example in *Solvent Pocket Book New Edition*, edited by Society of Organic Synthetic Chemistry (Ohm Sha, 1994). (Also the inorganic property/organic property value (I/O value) of the organic solvent is described for example in *Yuki Gainen-zu*, Yukio Tanaka, Sankyo Shuppan, 1983, pages 1 - 31.

Specific examples includes a monohydric aliphatic alcohol (such as methanol, ethanol, propanol, butanol, pentanol or hexanol), an alicyclic alkanol (such as cyclohexanol, methylcyclohexanol, methoxycyclohexanol, cyclohexylmethanol, or cyclohexylpropanol), a phenylalkanol (benzyl alcohol, phenylethanol, phenylpropanol, phenoxyethanol, methoxybenzyl alcohol or benzyloxyethanol), a heterocyclic alkanol (such as furfuryl alcohol or tetrahydrofurfuryl alcohol), a monoether of a glycol (such as methyl cellosolve, ethyl cellosolve, propyl cellosolve, methoxymethoxyethanol, butyl cellosolve, hexyl cellosolve, methylcarbitol, ethylcarbitol, propylcarbitol, butylcarbitol, methoxytriglycol, ethoxytriglycol, propylene glycol

monomethyl ether, propylene glycol monoethyl ether, or propylene glycol monopropyl ether), a ketone (such as acetone, methyl ethyl ketone, or methyl isobutyl ketone), an ester (such as methyl acetate, ethyl acetate, or butyl acetate), an amide (such as N,N-dimethylformamide, dimethylformamide, N-methyl-2-pyrrolidone, or 1,3-dimethylimidazolidinone), a sulfoxide (such as dimethyl sulfoxide), and an ether (such as tetrahydrofuran, pyran, dioxane, trioxane, dimethyl cellosolve, diethyl cellosolve, dipropyl cellosolve, methyl ethyl cellosolve, dimethylcarbitol, diethylcarbitol or methylethyl carbitol). The organic solvent may be employed singly or in a mixture of two or more kinds.

In case of employing the organic solvent singly or in a mixture of two or more kinds, at least one of the organic solvents preferably has a large solubility in water. The organic solvent preferably has a solubility in water of 50 weight% or larger, and is more preferably arbitrarily miscible with water. Thus there can be prepared an alkali solution having a sufficient solubility for an alkali agent, a fatty acid salt by-produced in the saponification process and a carbonate salt generated by an absorption of carbon dioxide in the air.

A proportion of the organic solvent in the solvent is determined according to a kind of the solvent, a

miscibility (solubility) in water, a reaction temperature and a reaction time. For completing the saponification reaction within a short time, it is preferable to prepare the solution at a high concentration. However an excessively high solvent concentration may result in an extraction of a component (for example a plasticizer) in the acylate film or an excessive swelling of the film, and the solvent concentration has to be selected suitably.

A mixing ratio of water and the organic solvent can be selected suitably, but is preferably 3/97 to 85/15 in weight ratio, more preferably 5/95 to 60/40 and further preferably 15/85 to 40/60. Within such range, a uniform saponification process can be realized easily over the entire surface of the film without deteriorating the optical characteristics of the acylate film.

The organic solvent included in the alkali solution of the invention includes not only an organic solvent having function of decreasing haze and increasing uniformity and stability of saponification degree as the aforementioned objectives of the invention, but also an organic solvent having a function of an auxiliary dissolving agent for a surfactant, a mutually solubilizing agent and a defoaming agent to the alkali solution and capable of enhancing the effect of the invention by co-existance of such auxiliary dissolving agent. The organic

solvent having such function may be different from the organic solvent having the aforementioned preferred I/O value. A preferred organic solvent having the auxiliary dissolving function can be, for example, N-phenyl ethanolamine, N-phenyl diethanolamine, a fluorinated alcohol (for example $C_nF_{2n+1}(CH_2)_kOH$ (wherein n is an integer from 3 to 8 and k is an integer of 1 or 2) such as 1,2,2,3,3-heptafluoropropanol, hexafluorobutanediol or perfluorocyclohexanol). A content of the organic solvent employed as an auxiliary dissolving agent is preferably 0.1 to 5 % with respect to the total weight of the used liquid.

It is desirable to select an organic solvent with an appropriately low surface tension in order to facilitate coating of the alkali solution, and the alkali solution preferably has a surface tension of 45 mN/m or less, more preferably 20 to 40 mN/m and particularly preferably 20 to 35 mN/m.

Also such organic solvent can be advantageously employed in the alkali diluting liquid and the alkali neutralizing liquid. In such case, a mixing ratio of water and the organic solvent is preferably 50/50 to 100/0 in weight ratio, more preferably 70/30 to 97/3 and further preferably 80/20 to 95/5.

For an alkali agent of the alkali solution, the

aforementioned alkali agent can be employed.

An alkali coating amount necessary for the saponification reaction is given, as an index, by a total saponification site number obtained by multiplying a saponification reaction site number per unit area of the cellulose acylate film by a saponification depth necessary for realizing an adhesion with an orienting film. As the alkali is consumed and the reaction speed is lowered with a progress in the saponification reaction, it is preferably in practice to coat an amount equal to a several times of the theoretical alkali coating amount. Specifically, there is preferred an amount of 2 to 20 times of the theoretical alkali coating amount, more preferably 2 to 5 times.

A temperature of the alkali solution is preferably equal to a reaction temperature (= temperature of the cellulose acylate film). Depending on the type of the organic solvent used, the reaction temperature may exceed the boiling point of the alkali solution. For realizing a stable coating, there is preferred a temperature lower than the boiling point of the alkali solution, more preferably a temperature lower by 5°C than the boiling point of the alkali solution and most preferably a temperature lower by 10°C than the boiling point of the alkali solution.

In the alkali saponifying method of the invention, in order to achieve a stable coating operation according to a transporting speed, the alkali solution preferably has a viscosity of 0.8 to 20 mPa·s, more preferably 1 to 15 mPa·s. The alkali solution preferably has a surface tension explained in the foregoing, and, in such range, there can be sufficiently achieved a wetting property to the film surface, a holding property of the solution coated on the film surface and a removability of the alkali solution from the film surface after the saponification reaction.

Also in the alkali saponification method of the invention, the alkali solution preferably has a density of 0.65 to 1.05 g/cm^3, more preferably 0.70 to 1.00 g/cm^3, and most preferably 0.75 to 0.95 g/cm^3. A density less than 0.65 g/cm^3 results in an unevenness by an air pressure caused in transportation, thereby deteriorating uniformity of the process. Also a density exceeding 1.05 g/cm^3 causes a coating streak parallel to the transporting direction because of the liquid weight, thereby deteriorating uniformity of the process and leading to an unevenness in the thickness of the orienting film. Also in the alkali saponification method of the invention, in order to minimize a load in a rinsing step to be explained later, the alkali solution preferably has an electrical

conductivity of 1 to 100 mS/cm, more preferably 2 to 50 mS/cm and particularly preferably 3 to 20 mS/cm. An electrical conductivity less than 1 mS/cm tends to generate light spot failures (defects by foreign substances) because of remaining impurities, or an insufficient adhesion of the optical compensation layer.

As a liquid property of the alkali solution, an optical absorbance at a measuring wavelength of 400 nm is preferably less than 2.0. At the coating operation, a size of a liquid feeding system and a coater has to be so determined that the optical absorbance of the liquid does not increase by extraction of an additive in the cellulose acylate film. In case a liquid with a high optical absorbance is used, an additive of the cellulose acylate film, dissolved into the liquid, adheres to the cellulose acylate film thereby causing a light spot failure (defect by foreign substance). For controlling the optical absorbance of the alkali saponifying solution, there can be employed a method of adsorbing and eliminating the dissolved component with active charcoal. The active charcoal is only required to have a function of eliminating a colored component in the saponifying solution, and is not restricted in a shape or a material thereof. There may be employed a method of directly adding active charcoal in a bath of alkali saponifying

solution or a method of circulating the saponifying solution between a bath of the saponifying solution and a purifying apparatus filled with active charcoal.

In the fourth embodiment of the invention, components of the alkali solution and the replenishing liquid can be similar to those of the alkali solution described in the foregoing saponification method for the cellulose acylate film.

However, the replenishing liquid preferably has an alkali concentration equal to or higher than the alkali concentration of the alkali solution, more preferably 1.05 to 3 times of the alkali concentration of the alkali solution, and further preferably 1.1 to 2 times of the alkali concentration of the alkali solution. More specifically, it is preferably 0.52 weight% or higher, more preferably 0.55 weight% and further preferably 1.1 weight%. Also it is preferably 40 weight% or less, more preferably 30 weight% or less and further preferably 20 weight% or less.

[Surfactant]

The alkali solution employed in the invention includes a surfactant. An addition of the surfactant reduces the surface tension, thereby facilitating the coating, improves uniformity of the coated film thereby

preventing a non-wetting defect, also suppresses a haze which tends to occur in the presence of an organic solvent, and enables a uniform proceeding of the saponification reaction. Its effect becomes more conspicuous by a co-presence of a mutually solubilizing agent to be explained later. The surfactant to be employed is not particularly restricted, and can be an anionic surfactant, a cationic surfactant, an amphoteric surfactant, a nonionic surfactant or a fluorinated surfactant and the like.

In the following, the surfactants employable in the invention will be explained in succession.

(Anionic surfactant)

Preferred examples of the anionic surfactant include a fatty acid salt, an abietate salt, a hydroxyalkanesulfonate salt, an alkanesulfonate salt, a dialkylsulfosuccinate salt, an α-olefinsulfonate salt, a linear alkylbenzenesulfonate salt, a ramified alkylbenzenesulfonate salt, an alkylnaphthalenesulfonate salt, an alkylphenoxypolyoxyethylene propylsulfonate salt, a polyoxyethylene alkylsulfophenyl ether salt, an N-methyl-N-oleyltaurin sodium salt, N-alkylsulfosuccinate monoamide disodium salt, a petroleum sulfonate salt, a sulfonated tallow oil, a sulfuric acid ester of a fatty alkyl ester, an alkylsulfuric acid ester salt, a polyoxyethylene alkyl ether sulfuric acid ester salt, a

fatty acid monoglyceride sulfuric acid ester salt, a polyoxyethylene alkyl phenyl ether sulfuric acid ester salt, a polyoxyethylene styryl phenyl ether sulfuric acid ester salt, an alkylphosphoric acid ester salt, a polyoxyethylene alkyl phenyl ether phosphoric acid ester salt, a partially saponified product of a styrene/maleic anhydride copolymer, a partially saponified product of a olefin/maleic anhydride copolymer and a naphthalenesulfonic acid salt-formalin condensate.

(Cationic surfactant)

Examples of the cationic surfactant include an alkylamine salt, a quaternary ammonium salt such as tetrabutylammonium bromide, a polyoxyethylene alkylamine salt and a polyethylenepolyamine derivative.

(Amphoteric surfactant)

Examples of the amphoteric surfactant include a carboxybetain, an alkylaminocarboxylic acid, a sulfobetain, an aminosulfuric acid ester, and an imidazoline.

(Nonionic surfactant)

Examples of the nonionic surfactant include a polyoxyethylene alkyl ether, a polyoxyethylene alkylphenyl ether, a polyoxyethylene polystyrylphenyl ether, a polyoxypropylene alkyl ether, a fatty acid partial ester of glycerin, a fatty acid partial ester of sorbitan, a fatty acid partial ester of pentaerythritol, a fatty acid

ester of propylene glycol, a fatty acid partial ester of glucose, a fatty acid partial ester of polyoxyethylene sorbitan, a fatty acid partial ester of polyoxyethylene sorbitol, a fatty acid ester of polyethylene glycol, a fatty acid partial ester of polyglycerin, a polyoxyethylenated castor oil, a fatty acid partial ester of polyoxyethyleneglycerin, a fatty acid diethanolamide, an N,N-bis-2-hydroxyalkylamine, a polyoxyethylenealkylamine, a triethanolamine fatty acid ester and trialkylamine oxide.

Specific examples of these include polyethylene glycol, polyoxyethylene lauryl ether, polyoxyethylene nonyl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene behenyl ether, polyoxyethylene polyoxypropylene cetyl ether, polyoxyethylene polyoxypropylene behenyl ether, polyoxyethylene phenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene stearyl amine, polyoxyethyleneoleyl amine, polyoxyethylene stearyl amide, polyoxyethylene oleyl amide, polyoxyethylene castor oil, polyoxyethylene abietyl ether, polyoxyethylene nonyl ether, polyoxyethylene monolaurate, polyoxyethylene monosgtearate, polyoxyethylene glyceryl monoleate, polyoxyethylene glyceryl monostearate, polyoxyethylene propylene glycol monostearate, a

oxyethylene-oxypropylene block polymer, a distyrenated phenol-polyethylene oxide addition product, tribenzylphenol-polyethylene oxide addition product, glycerol monostearate, sorbitan monolaurate and polyoxyethylene sorbitan monolaurate. Such nonionic surface preferably has a weight-averaged molecular weight of 300 to 50,000, particularly preferably 500 to 5,000.

In the invention, among the aforementioned nonionic surfactants, a compound represented by a following general formula (2) is preferable:

General formula (2):

$$R^1-O(CH_2CHR^2O)_l-(CH_2CHR^3)_m-(CH_2CHR^4O)_n-R^5$$

wherein R^1 to R^5 each represents a hydrogen atom, an alkyl group with 1 to 18 carbon atoms, an alkenyl group, an alkinyl group, an aryl group, a carbonyl group, a carboxylate group, a sulfonyl group or a sulfonate group.

Specific examples of the alkyl group include a methyl group, an ethyl group and a hexyl group. Specific examples of the alkenyl group include a vinyl group and a propenyl group. Specific examples of the alkinyl group include an acetyl group and a propinyl group, and specific examples of the alkyl group include a phenyl group and a 4-hydroxyphenyl group.

Each of l, m and n represents an integer equal to or larger than 0. However, l, m and n do not become 0 at the

same time.

Specific examples of the compound represented by the general formula (2) include a monopolymer such as polyethylene glycol or polypropylene glycol, or a copolymer of ethylene glycol or propylene glycol. The copolymer has a proportion of 10/90 to 90/10 in consideration of solubility in the alkali solution. Also among the copolymers, a graft polymer or a block polymer is preferable in consideration of solubility in the alkali solution and of ease of the alkali saponification process.

(Fluorinated surfactant)

A fluorinated surfactant means a surfactant containing a perfluoroalkyl group within a molecule. Examples of such fluorinated surfactant include an anionic type such as a perfluoroalkylcarboxylate salt, a perfluoroalkylsulfonate salt, or a perfluoroalkylphosphate ester, an amphoteric type such as a perfluoroalkylbetain, a cationic type such as a perfluoroalkyl trimethyl ammonium salt, and a nonionic type such as a perfluoroalkylamine oxide, a perfluoroalkyl ethylene oxide addition product, an oligomer containing a perfluoroalkyl group and a hydrophilic group, an oligomer containing a perfluoroalkyl group and an oleophilic group, an oligomer containing a perfluoroalkyl group, a hydrophilic group and an oleophilic group, or an urethane containing a

perfluoroalkyl group and an oleophilic group.

Among the foregoing surfactants, a "polyoxyethylene" part may be replaced by a polyoxyalkylene such as polyoxymethylene, polyoxypropylene, or polyoxybutylene, and such compounds are also included in the surfactant. Such surfactant may be employed singly or in a combination of two or more kinds as long as the combined use does not affect the effect.

Among the aforementioned surfactants, in the invention, there is preferred the quaternary ammonium compound as the cationic surfactant, the polyethylene glycol derivatives and the polyethylene oxide derivatives such as the polyethylene oxide addition products as the nonionic surfactant, or the betain compound as the amphoteric surfactant.

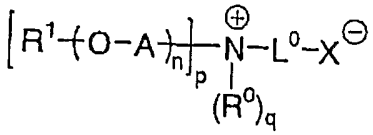
In the alkali solution, a combined use of a nonionic surfactant and an anionic surfactant, or a nonionic surfactant and a cationic surfactant is also preferable in enhancing the effect of the invention.

An addition amount of such surfactant to the alkali solution is preferably 0.001 to 20 weight%, more preferably 0.01 to 10 weight% and particularly preferably 0.03 to 3 weight%. An addition amount less than 0.001 weight% is difficult to obtain an effect of addition of the surfactant, and an addition amount exceeding 20

weight% tends to lower the saponifying property.

The alkali solution employed in the second embodiment of the invention includes an amphoteric surfactant represented by a following general formula (I). A specific surfactant in the invention is satisfactory in stability and solubility in the alkali solution and suppresses a separation of dissolved component from the alkali solution.

General formula (1):



wherein A represents an alkylene group; L^0 represents a group connecting a nitrogen atom and X^-; X^- represents $-COO^-$, $-SO_3^-$ or $-PO_3H^-$; R^0 represents a hydrocarbon group; R^1 represents a hydrogen atom or a hydrocarbon group; n represents an integer from 1 to 50; p and q each represents an integer of 1 or 2 and p + q = 3.

In the general formula (I), A preferably represents an alkylene group with 2 to 4 carbon atoms, such as $-(CH_2)_l-$ (l being an integer of 2 to 4), $-CH_2-C(CH_3)-$ or $-C(CH_3)-CH_2-$. R^1 preferably represents a hydrogen atom or an aliphatic group with 1 to 22 carbon atoms, more preferably a hydrogen atom or an aliphatic group with 1 to 12 carbon atoms. Examples of the aliphatic group includes

a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a benzyl group and a cyclohexylmethyl group.

R^0 preferably represents an aliphatic group with 1 to 22 carbon atoms. Specific examples are same as those of the aliphatic group of R^1.

Also for the aliphatic group of R^0, there is preferred a substituted aliphatic group represented by -$[L^1-NHCO-R^2]$.

L^1 represents an alkylene group, which may be substituted, with 1 to 5 total carbon atoms, and R^2 represents an alkyl group with 1 to 20 carbon atoms.

A $[R^1-(O-A)n]$ group bonded to a nitrogen atom is formed from a polyoxyalkylene chain, and is formed by an addition reaction of at least an epoxy compound selected from ethylene oxide, propylene oxide and butylenes oxide.

A number n, representing a number of repeating units of an oxyalkylene chain, is preferably an integer from 2 to 20, more preferably an integer from 5 to 15.

Also the [-(O-A)n-] chain may be a substituent formed by a single addition of alkylene oxide, or a substituent formed by additions of different alkylene oxides. An oxyalkylene chain formed by additions of two or more kinds may have a random bonding type or a block

bonding type, but preferably is a block bonding type.

An addition amount of such amphoteric surfactant to the alkali solution is preferably 0.001 to 20 weight%, more preferably 0.01 to 10 weight% and particularly preferably 0.03 to 3 weight%. An addition amount less than 0.001 weight% is difficult to obtain an effect of addition of the surfactant, and an addition amount exceeding 20 weight% tends to lower the saponifying property.

(Other surfactants)

In the alkali solution to be employed in the invention, there may be employed another surfactant together with the aforementioned specific amphoteric surfactant. There can be employed a nonionic surfactant, an anionic surfactant, a cationic surfactant, or a fluorinated surfactant as explained in the foregoing.

The alkali solution employed in the first embodiment of the invention includes a mutually solubilizing agent. In the invention, a mutually solubilizing agent is at least one selected from hydrophilic compounds having a solubility of water of 30 g or higher to 100 g of the mutually solubilizing agent at 25°C. The solubility of water is preferably 50 g/100g or higher, more preferably 100 g/100 g or higher. Also in case the mutually solubilizing agent in the invention is a liquid compound,

it preferably has a boiling point of 100°C or higher, more preferably 120°C or higher.

In an apparatus having an alkali process bath of the invention, the mutually solubilizing agent prevents a drying and suppresses a solidification of the alkali solution adhering to a wall surface, thereby allowing to stably maintain the solution. It also suppresses that a coated thin film is dried to generate a precipitation of a solid substance, in a period from a coating of the alkali solution on the film surface to a saponification terminating process after a retention for a predetermined time, whereby the solid substance becomes difficult to wash off in a rinsing step. It further prevents a phase separation of water and an organic solvent constituting the solvent. In particular, a co-presence of the surfactant, the organic solvent and the aforementioned mutually solubilizing agent, reduces a haze in the processed film and provides a uniform saponification degree over the entire surface in a stable manner even in case of a long and continuous saponification process.

The mutually solubilizing agent to be employed in the invention can be any material meeting the aforementioned conditions. Preferable examples of the mutually solubilizing agent include a polyol compound, and a water-soluble polymer including a repeating unit having

a hydroxyl group and/or an amide group, such as a sugar.

A polyol compound can be a low-molecular compound, an oligomer compound or a polymer compound. Examples of an aliphatic polyol include an alkanediol with 2 to 8 carbon atoms (such as ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, glycerin monomethyl ether, glycerin monoethyl ether, cyclohexanediol, cyclohexanedimethanol, diethylene glycol or dipropylene glycol), and an alkane with 3 to 18 carbon atoms including 3 or more hydroxy groups (such as glycerin, trimethylol ethane, trimethylol propane, trimethylol butane, hexanetriol, pentaerythritol, diglycerin, dipentaerythritol or inositol). A polyalkyleneoxypolyol may be formed by a mutual bonding of same alkylenediol or of different alkylenediols, but a polyalkylenepolyol formed by a mutual bonding of same alkylenediol is more preferable. In any case, a number of bondings is preferably 3 to 100, more preferably 3 to 50. Specific examples include polyethylene glycol, polypropylene glycol and poly(oxyethylene-oxypropylene).

Examples of a sugar include water-soluble compounds described for example in *Tennen Kobunshi*, edited by The Society of Polymer Science, Japan, Polymer Experimentology Editing committee (Kyoritsu Shuppan, 1984), chapter 2, and *Kindai Kogyo Kagaku 22, Tennenbutsu Kogyo Kagaku II*,

edited by Ryohei Oda et al. (Asakura Shoten, 1967). There is preferred a sugar free from a liberated aldehyde or ketone group and not having a reducing property. It is classified into glucose, sucrose, a trehalose-type oligosaccharide in which reducing groups are mutually bonded, a glycosidefoamed by bonding a reducing group of a sugar and a non-sugar, and a sugar alcohol formed by a hydrogenation reduction of a sugar, all of which can be advantageously employed in the invention. The trahalose-type oligosaccharide includes saccharose and trehalose, and the glycoside includes for example an alkyl glycoside, a phenol glycoside and a mustard oil glycoside. Also the sugar alcohol includes D/L-arabit, ribit, xylit, D/L-sorbit, D/L-mannit, D/L-igit, D/L-talit, dulcit and arodulcit. Also there can be advantageously employed multibit obtained by hydrogenation of disaccharides, and a reduced substance (reduced maltose) formed by hydrogenation of oligosaccharide. Among these, a non-reducing sugar preferable in the invention is a sugar alcohol or saccharose, and particularly D-sorbit, saccharose and reduced maltose are preferable in having a buffer function in an appropriate pH range and is inexpensive. Such non-reducing sugar can be employed singly or in a combination of two or more kinds.

Examples of the water-soluble polymer including a

repeating unit having a hydroxy group and/or an amide group includes a natural gum (such as gum Arabic, guar gum or tragacanth gum), polyvinyl alcohol, polyvinylpyrrolidone, a dihydroxypropyl acrylate polymer, an addition reaction product of a cellulose or a chitosan with ethylene oxide or propylene oxide, alkylenepolyol, polyalkyleneoxypolyol and sugar alcohol.

Among these alkylenepolyol, polyalkyleneoxypolyol and sugar alcohol are preferable. Specific examples include ethylene glycol, propylene glycol, butylenes glycol, diethylene glycol, di(n-propylene glycol), di(i-propylene glycol), polyethylene glycol (with a bonding number of 3 to 20), polypropylene glycol (with a bonding number of 3 to 10), glycerin and diglycerin.

A content of such mutually solubilizing agent in the alkali solution is preferably 0.5 to 35 weight%, more preferably 1 to 25 weight%.

In the alkali solution of the invention, it is further preferable to add a defoaming agent. This additive can be contained in the alkali solution preferably in an amount of 0.001 to 5 weight%, particularly preferably 0.005 to 3 weight%.

Within such range, an adhesion of small bubbles on the film surface can be eliminated and the saponification by an alkali treatment can proceed uniformly without an

unevenness.

Examples of the defoaming agent include an oil such as castor oil or linseed oil; a fatty acid such as stearic acid or oleic acid, a fatty acid ester such as natural wax; an alcohol such as polyoxyalkylene monohydric alcohol; an ether such as di-t-amylphenoxyethanol, heptyl cellosolve, nonyl cellosolve, or 3-heptylcarbitol; a phasphate ester such as tributyl phosphate or tris8butoxyethyl) phosphate; an amine such as diamylamine; an amide such as polyalkyleneamide or acylatepolyamide; a metal soap such as aluminum stearate, calcium stearate, potassium oleate or a calcium salt of wool oleic acid; a sulfate ester such as sodium laurylsulfate ester; a silicone oil such as dimethylpolysiloxane, methylphenylpolysiloxane, methylhydrogenpolysiloxane, fluoropolysiloxane or a copolymer of dimethylpolysiloxane and polyalkylene oxide; and a silicone such as a solution-type, emulsion-type or paste-type silicone oil.

The alkali solution to be employed in the invention preferably includes further an antimold agent and/or an antibacterial agent. The antimold agent and the antibacterial agent to be employed in the invention can be of any type as long as they do not detrimentally affect the alkali saponification, and specific examples include a thiazolylbenzimidazole compound, an isothiazolone compound,

a chlorophenol compound, a bromophenol compound, thiocyanic acid or a thiocyanate compound, an acid azide compound, a diazine or triazine compound, a thiourea compound, an alkylguanidine compound, a quaternary ammonium salt, an organic tin or zinc compound, a cyclohexylphenol compound, an imidazole and benzimidazole compound, a sulfamide compound, an active halogenated compound such as chlorinated sodium isocyanurate, a chalating agent, a sulfite compound, an antibiotic represented by penicillin. There can also be employed antibacterial agents described in L. E. West, "Wagter Quality Criteria", Photo. Sci. and Eng., Vol.9, No. 6 (1965), antimold agents described in JP-A Nos. 57-8542, 58-105145, 59-126533, 55-111942, and 57-157244, and chemical substances described in Hiroshi Horiguchi, "Antibacterial-antimold Chemistry" (Sankyo Shuppan, 1982), *Bokin-Bokun Gijutu Handbook*, Antibacterial-Antimold Society of Japan (Giho-do, 1986). Specific examples are shown in the following, but such examples are not exhaustive.

An addition amount of the antimold agent and/or antibacterial agent is preferably 0.01 to 50 g/L in the alkali solution, more preferably 0.05 to 20 g/L.

In the alkali solution employed in the invention, another additive may be used in combination. For example

there can be employed an alkali solution stabilizer (antiaging agent). In the invention, an additive to the alkali solution is not limited to such naterials.

Water to be employed in the alkali solution is preferably based on a city water regulation of Japan (Law No. 177 of 1957) and a ministerial ordinance based thereon (Ordinance No. 56 of the Ministry of Health of August 31, 1978), a hot spring regulation of Japan (Law No. 125 of July 10, 1948 and Appendix thereof) and a WHO city water standard defining influences on elements and minerals in a mixed state in water. Also in order to attain the effect of the invention more securely, a calcium concentration as a concentration calcium carbonate is preferably within a range of 0.001 to 200 mg/L, further preferably 0.01 to 150 mg/L and particularly preferably 0.05 to 10 mg/L. Within such range, it is possible to suppress generation of an insoluble substance in the solution.

The alkali solution constituted of the aforementioned components preferably has a surface tension of 45 mN/m or less (25°C), and a viscosity of 0.8 to 20 mPa·s (25°C). Preferably, the surface tension is 20 to 40 mN/m (25°C), and the viscosity is 1 to 15 Pa·s (25°C). In such range, there can be sufficiently achieved a wetting property to the film surface, a holding property of the solution coated on the film surface and a removal of the

alkali solution from the film surface after the saponification reaction.

In the first and second embodiments of the invention, a surface treatment of a cellulose acylate film employing the aforementioned alkali solution can be executed by any known method, such as a dipping method, a spraying method or a coating method.

In case of saponifying a surface only of the film uniformly without an unevenness, a coating method is particularly preferable. For coating, there can be employed a known coating method as will be explained later.

A saponification process is preferably executed at a process temperature not exceeding 120°C, which does not cause a defoamation of the processed film or a denaturing of a process liquid. The temperature is further preferably within a range from 10 to 100°C, particularly preferably 20 to 80°C.

Also in case of process with a coating method, the alkali saponification process is preferably executed by a step of saponifying a cellulose acylate film with the alkali solution at a surface temperature equal to or higher than 10°C, a step of maintaining the cellulose acylate film at a temperature at least equal to 10°C, and a step of washing off the alkali solution from the cellulose acylate film.

The process of saponifying the cellulose acylate film with the alkali solution at a predetermined surface temperature may employ a step of adjusting the film to a predetermined temperature before coating, a step of adjusting the alkali solution to a predetermined temperature, or a step of a combination thereof. It is preferably combined with a step of adjusting to a predetermined temperature before coating.

In a step of temperature adjustment of the cellulose acylate film in advance to 20°C or higher, there can be advantageously employed a collision by an air flow of a predetermined temperature, a contact heat conduction by a heating roll, a microwave induction heating, or a radiation heating by an infrared heater. In particular, a contact heat conduction by a heating roller is preferable because it has a high heat conduction efficiency and can be executed with a small installation area and it enables a rapid temperature increase of the film temperature at the start of the transportation. There can be utilized an ordinary double-jacketed roller or an electromagnetic induction roll (manufactured by Tokuden Co.).

In the step of saponifying the cellulose acylate film with the alkali solution, it is preferable to restrict a variation in the coating amount to 30 % or less in a transversal direction and a longitudinal direction of

the film.

As the coating method, there can be advantageously employed, for example, a die coater (extrusion coater or slide coater), a roll coater (forward roll coater, reverse roll coater or gravure coater), a rod coater (utilizing a rod wound with a fine metal wire), or a blade coater. The coating method is described in various references (for example Modern Coating and Drying Technology, Edward Cohen and Edgar B. Gutoff, Edits, VCH Publishers, Inc., 1992). A coating amount of the alkali solution is desirably made as small as possible, in consideration of a waste disposal at a removal by rinsing afterwards. There is particularly preferred a rod coater, a die coater, a gravure coater or a blade coater, which can be operated stably even at a low coating amount.

It is also preferable to employ a continuous coating method.

An alkali coating amount necessary for the saponification reaction is given, as an index, by a total saponification site number obtained by multiplying a saponification reaction site number per unit area of the cellulose acylate film by a saponification depth necessary for realizing an adhesion with an orienting film. As the alkali is consumed and the reaction speed is lowered with a progress in the saponification reaction, it is

preferably in practice to coat an amount equal to a several times of the theoretical alkali coating amount. Specifically, there is preferred an amount of 2 to 20 times of the theoretical alkali coating amount, more preferably 2 to 5 times.

A temperature of the alkali solution is preferably equal to a reaction temperature (= film temperature).

After coating of the alkali solution, the cellulose acylate film is maintained at a temperature at least equal to 10°C until the termination of the saponification reaction. The temperature is preferably 15°C or higher.

Heating means is selected in consideration of a fact that a surface of the cellulose acylate film is wet with the alkali solution. For example, there can be preferably employed a hot air blowing to a surface opposite to the coated surface, a contact heat conduction by a heating roll, a microwave induction heating, or a radiation heating by an infrared heater. An infrared heater is preferable since it can achieve heating in a non-contact manner and without involving an air flow, thereby minimizing an influence to the surface coated with the alkali solution. As the infrared heater, there can be utilized a far-infrared ceramic heater of electric, gas, oil or steam type. An infrared heater of oil or steam type utilizing oil or steam as a heating medium is

preferable for explosion-proof property in an environment where an organic solvent is present. A temperature of the cellulose acylate film may be same as or different from the heated temperature before the alkali solution processing. Also the temperature may be changed continuously or stepwise during the saponification reaction. For detecting the film temperature, there can be utilized a commercially available non-contact infrared thermometer, and a feedback control may be applied to the heating means in order to control the temperature within the aforementioned range.

In the invention, it is particularly preferable to execute the saponification process while the cellulose acylate film is transported. A transporting speed of the film is determined by a combination of the composition of the alkali solution and the coating method. It is generally preferably 10 to 500 m/min., more preferably 20 to 300 m/min. Physical properties (specific gravity, viscosity and surface tension), coating method and coating conditions are determined according to the transporting speed, in order to achieve a stable coating operation.

For terminating the saponification reaction of the cellulose acylate film and the alkali solution, three methods are available. First is a method of diluting the coated alkali solution to reduce the alkali concentration

thereby lowering a reaction rate. Second is a method of lowering the temperature of the cellulose acylate film coated with the alkali solution thereby lowering a reaction rate, and third is a method of neutralization with an acidic liquid.

For diluting the coated alkali solution, there can be employed a method of coating a diluting liquid, a method of spraying a diluting liquid, or a method of immersing the cellulose acylate film in a container containing a diluting liquid. Among these, a method of coating a diluting liquid and a method of spraying is preferable in an operation under continuous transportation of the cellulose acylate film. The method of coating a diluting liquid is most preferable as it can be executed with a minimum necessary amount of the diluting liquid.

Coating of the diluting liquid is preferably executed by a continuous coating method capable of re-applying the diluting liquid onto the cellulose acylate film on which the alkali solution is already coated. The coating method can be similar to those described for the aforementioned saponification process. In order to promptly mix the alkali solution and the diluting liquid thereby reducing the alkali concentration, there is preferred a roll coater or a rod coater in which a flow is not uniform in a small area (also called a coating bead)

where the coating liquid is coated, in comparison with a die coater in which such flow becomes a laminar flow.

The diluting liquid has to be a liquid capable of dissolving the alkali agent in the alkali solution, since it has an objective of lowering the alkali concentration without dissolving or swelling the cellulose acylate film. Therefore, it employs, as a solvent, water or a mixture of an organic solvent and water. The organic solvent may be employed singly or in a combination of two or more kinds, and can be employed in an arbitrary manner with such a proportion in the diluting liquid as not to dissolve or swell the cellulose acylate film.

A coating amount of the diluting liquid is determined according to the concentration of the alkali solution. In case of a die coater which has a laminar flow in the coating bead, the coating amount is such that the original alkali concentration is diluted 1.5 to 10 times, more preferably 2 to 5 times. In a roll coater or a rod coater, because of an uneven flow in the coating bead, the alkali solution and the diluting liquid are mixed and a mixed solution is re-applied. Therefore, since it is not possible to specify a dilution rate from the coating amount of the diluting solvent, there is executed a measurement of the alkali concentration after the coating of the diluting solvent. Also in a roll

coater or a rod coater, it is preferable that the original alkali concentration is diluted 1.5 to 10 times, more preferably 2 to 5 times.

In order to promptly terminate the saponification reaction by alkali, an acid may also be employed. In order to achieve neutralization with a small amount, a strong acid is preferable. Also in consideration of ease of rinsing, it is preferable to select an acid of which salt formed after neutralization with alkali has a high solubility in water. Hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, chromic acid and methanesulfonic acid are particularly preferable.

For neutralizing the coated alkali solution with the acid, there can be employed a method of coating an acid solution, a method of spraying an acid solution, or a method of immersing the cellulose acylate film in a container containing an acid solution. Among these, a method of coating an acid solution and a method of spraying are preferable in an operation under continuous transportation of the cellulose acylate film. The method of coating an acid solution is most preferable as it can be executed with a minimum necessary amount of the acid solution.

Coating of the acid solution is preferably executed by a continuous coating method capable of re-applying the

acid solution onto the cellulose acylate film on which the alkali solution is already coated. The coating method can be similar to those described for the aforementioned saponification process. In order to promptly mix the alkali solution and the acid solution thereby neutralizing the alkali, there is preferred a roll coater or a rod coater.

A coating amount of the acid solution is determined according to the kind of the alkali and the concentration of the alkali solution. In case of a die coater which has a laminar flow in the coating bead, a coating amount of the acid is preferably 0.1 to 5 times of the original alkali coating amount, more preferably 0.5 to 2 times. In a roll coater or a rod coater, because of an uneven flow in the coating bead, the alkali solution and the diluting liquid are mixed and a mixed solution is re-applied. Therefore, since it is not possible to specify a neutralization rate from the coating amount of the acid solution, it is necessary to measure the alkali concentration after the coating of the acid solution. Also in a roll coater or a rod coater, it is preferable to determine the coating amount of the acid solution so as to obtain a pH value of 4 to 9 after the coating of the acid solution, more preferably a pH value of 6 to 8.

It is also possible to terminate the saponification

reaction by lowering the temperature of the cellulose acylate film. The saponification reaction is substantially terminated by a sufficient temperature decrease from a state maintained at the room temperature or higher for accelerating the reaction. Cooling means is selected in consideration of a fact that a surface of the cellulose acylate film is wet. For example, there can be preferably employed a cold air blowing to a surface opposite to the coated surface, or a contact heat conduction by a cooling roll. A film temperature after the cooling is preferably 0 to 60°C, more preferably 5 to 50°C and most preferably 10 to 30°C. The film temperature is preferably measured with a non-contact infrared thermometer. It is also possible to regulate the cooling temperature by a feedback control on the cooling means based on the measured temperature. Temperature reducing means may be used in combination with the diluting method with the diluting liquid or the neutralizing method explained above.

A rinsing step is executed in order to completely eliminate the alkali solution. It is also executed, in case of employing neutralizing means, to completely eliminate a composition such as a salt generated by neutralization. A remnant of a composition of the alkali solution or a salt generated by neutralization not only

causes the saponification reaction to proceed but also affects a coated film formation of an orienting film and liquid crystal molecules to be coated later and an orientation of the liquid crystal molecules.

Rinsing can be executed by a method of coating water, a method of spraying water, or a method of immersing the polymer film in a container containing water.

A water spraying method can be executed by a method utilizing a coating head (for example a fountain coater or a frog mouth coater), or a method utilizing a spray nozzle utilized in air humidifying, painting or automatic tank washing. The coating method is described in "All of Coating", Masayoshi Araki, Kako Gijutsu Kenkyu-kai (1999). It is possible to arrange conical- or fan-shaped spray nozzles along a transversal direction of the film in such a manner that a water flow collides with an entire width of the film. It is also possible to employ a commercially available spray nozzle (for example manufactured by Ikeuchi Co. or Spraying Systems Inc.).

A higher spraying speed of water provides a larger random flow mixing. However, a high speed may affect the transporting stability of the cellulose acylate film under continuous transportation. A collision speed of spraying is preferably 50 to 1000 cm/sec, more preferably 100 to 700 cm/sec.

Though dependent on an alkali concentration, a by-product and a solvent in the employed alkaline coating liquid, rinsing water is employed in such an amount of obtaining a dilution of at least 100 to 1,000 times, preferably 500 to 10,000 times and further preferably 1,000 to 100,000 times.

For a given amount of water for rinsing, there is preferred a batch-type rinsing method of applying water in several divided portions, rather than applying the entire amount at a time. More specifically, the water is divided into certain portions which are supplied to plural rinsing means provided in tandem along the transporting direction of the film. Between rinsing means and next rinsing means, there is provided a suitable time (distance) thereby promoting a dilution of the alkaline coating liquid by diffusion. More preferably, the transported polymer film is made to incline whereby the water on the film flows along the film surface thereby achieving a mixing dilution by a flow in addition to the diffusion. In a most preferable method, water squeezing means is provided between the rinsing means thereby further improving the efficiency of rinsing and dilution. Specific examples of the water squeezing means include a blade employed in a blade coater, an air knife employed in an air knife coater, a rod employed in a rod coater, and a roll employed in a

roll coater.

A larger number of the rinsing means in a tandem arrangement is more advantageous. However, in consideration of an installation space and a facility cost, there are usually employed 2 to 10 stages, preferably 2 to 5 stages.

A thickness of a water film after the water squeezing means is preferably as small as possible, but a minimum water film thickness is limited by the type of the water squeezing means to be employed. In a method of contacting a physically solid member such as a blade, a rod or a roll with the film, it is necessary to leave a finite water film as a lubricating fluid since, even in case the solid member is constituted of an elastic member of a low hardness such as rubber, there may result a scratch on the film surface or an abrasion of the elastic member. Usually there is left a water film of several micrometers or more, preferably 10 μm or more, as a lubricating fluid.

As water squeezing means capable of reducing the water film thickness extremely, an air knife is preferable. The water film thickness may be made close to zero, by employing sufficient air amount and air pressure. However, an air blowing amount has a certain preferable range since an excessively high air blow amount may cause a flapping

or a skewing of the cellulose acylate film, thus affecting the transporting stability thereof. Such range is dependent also on the thickness of the original water film on the cellulose acylate film and the transporting speed of the film, but there is usually employed an air speed of 10 to 500 m/sec, preferably 20 to 300 m/sec and more preferably 30 to 200 m/sec. Also for achieving uniform elimination of the water film, an air blow aperture of the air knife or an air supply method thereto is so regulated that the air speed in the transversal direction of the cellulose acylate film has a distribution normally within 10 %, preferably within 5 %. A gap between a surface of the transported cellulose acylate film and the air blowing aperture of the air knife has an appropriate range since a smaller gap provides a higher water squeezing ability but results in a higher possibility of causing a scratch by a contact with the cellulose acylate film. Therefore, the air knife is installed usually with a gap of 10 μm to 10 cm, preferably 100 μm to 5 cm and further preferably 500 μm to 1 cm. Also a backup roll is preferably provided at a side opposite to the rinsed surface of the film, so as to be opposed to the air knife, thereby stabilizing the gap setting and relaxing influences on the film such as a flapping, a crease or a defoamation.

For the rinsing water, purified water is preferably

employed. The purified water to be employed in the invention means water having a specific resistivity of at least 1 MΩ or higher, with metal ions such as sodium, potassium, magnesium or calcium less than 1 mg/L and anions such as of chlorine or nitric acid less than 0.1 mg/L. The purified water can be easily obtained by a reverse osmosis film, an ion exchange resin, a distillation or a combination thereof.

A higher temperature of the rinsing water provides a higher rinsing ability. However, in a method of spraying water onto the transported cellulose acylate film, the water has a large contact area with the air and evaporates more at a higher temperature, thereby increasing the humidity in the environment and resulting in a danger of dewing. Therefore, a temperature of the rinsing water is usually set within a range of 5 to 90°C, preferably 25 to 80°C and more preferably 25 to 60°C.

In case a component of the alkaline coating liquid or a product of the saponification reaction is not easily soluble in water, a solvent washing step for eliminating a water-insoluble component may be added before or after the rinsing step. The solvent washing step may utilize the rinsing method or the water squeezing means, and a solvent similar to that described for the diluting liquid.

A drying step may be executed after the rinsing step.

The drying step is usually unnecessary because the water film can be sufficiently eliminated by the water squeezing means such as an air knife, but a heat drying may be executed in order to adjust the cellulose acylate film to a desirable water content before being wound in a roll. On the other hand, it is also possible to execute a humidity adjustment with an air flow having a selected humidity.

[Alkali-saponifying process]

A surface treating process in the third embodiment of the invention comprises a step of processing a cellulose acylate film with an alkali solution and a step of washing off the alkali solution from the film, and is preferably executed by a step of saponifying a cellulose acylate film with an alkali solution at a surface temperature equal to or higher than the room temperature, a step of maintaining the cellulose acylate film at a temperature equal to or higher than the room temperature, and a step of washing off the alkali solution from the cellulose acylate film.

The step of processing the cellulose acylate film with the alkali solution can be executed by any known method, such as a dipping method, a spraying method or a coating method. Particularly in case of saponifying a

surface only of the film uniformly without an unevenness, a coating method is preferable. For coating, there can be employed a known coating method as will be explained later.

The step of washing off the alkali solution from the film is, after the film is maintained at a temperature equal to or higher than the room temperature to promote the saponification reaction, to dilute or neutralize the alkali solution containing a concentrated alkali agent and an extracted substance such as an additive of the film thereby decelerating or terminating the saponification reaction and to wash it off with a large amount of rinsing liquid. In this step, a diluting or neutralizing step for the alkali solution is extremely important in order not to deposit a concentrated alkali agent or an extracted substance such as an additive of the film onto the film surface, and a precipitate deposition on the film surface can be effectively prevented by maintaining a carbonate ion concentration in an alkali diluting liquid and an alkali neutralizing liquid at 3500 mg/L or less. It is more preferably 1000 mg/L or less and particularly preferably 100 mg/L or less. A carbonate ion concentration equal to or less than 3500 mg/L allows to decrease defects by foreign substances or defects in orientation, in case of coating an orienting film on the saponified cellulose acylate film and, after a rubbing

treatment, forming an optical anisotropic layer with liquid crystal molecules.

An alkali solution of a high concentration tends to absorb CO_2 in the environmental atmosphere, thereby resulting in a decrease in pH and generation of a precipitate. In order to suppress the absorption of CO_2 in the environmental atmosphere, it is more preferable that a coater for the alkali solution is given a semi-closed structure or is covered with dry air, an inert gas or a saturated vapor of the organic solvent of the alkali saponifying solution.

Also in the alkali diluting liquid and the alkali neutralizing liquid, by maintaining chloride ions and polyvalent metal ions such as calcium ions or magnesium ions respectively at 300 mg/L or less and 500 mg/L or less, it is rendered possible not to deposit a concentrated alkali agent or an extracted substance such as an additive of the film onto the film surface, thereby decreasing a defective adhesion to the optical anisotropic layer, in case of coating an orienting film on the saponified cellulose acylate film and, after a rubbing treatment, forming an optical anisotropic layer with liquid crystal molecules.

For the alkali diluting liquid or the alkali neutralizing liquid, a liquid constituted of water or

water and an organic solvent is preferably employed as will be explained later, and the water to be employed is preferably purified water. For the purified water, a calcium concentration in the liquid is preferably 0.001 to 100 mg/L, more preferably 0.001 to 50 mg/L and particularly preferably 0.001 to 10 mg/L. A magnesium concentration is preferably 0.001 to 50 mg/L, more preferably 0.001 to 30 mg/L and particularly preferably 0.001 to 10 mg/L. Polyvalent metal ions other than calcium and magnesium, such as Be, Sr, Ba, Al, Sn, Pb, Ti, Cr, Mn, Fe, Co, Ni, Cu(II), Co or Zn are preferably absent. A concentration of the polyvalent metal ions is preferably 0.001 to 150 mg/L. On the other hand, the alkali saponifying solution is preferably free from anions such as chloride ions or carbonate ions. A concentration of chloride ions is preferably 0.001 to 100 mg/L, more preferably 0.001 to 50 mg/L and particularly preferably 0.001 to 10 mg/L. Also carbonate ions are preferably absent. A concentration of carbonate ions is preferably 0.001 to 500 mg/L, more preferably 0.001 to 100 mg/L and particularly preferably 0.001 to 20 mg/L. For each of these ion species, the concentration is preferably as low as possible, and the lower limit of 0.001 mg/L means it is equal to or less than a measurable limit. Generation of an insoluble substance in the solution can be suppressed

in these concentration ranges.

The alkali saponification method for the cellulose acylate film is preferably executed by a step of heating a cellulose acylate film in advance to the room temperature or higher, a step of coating an alkali solution on the cellulose acylate film, a step of maintaining the cellulose acylate film at the room temperature or higher, and a step of washing off the alkali solution from the cellulose acylate film, and it is preferable to execute these steps and other steps while the cellulose acylate film is transported.

The saponification process of the cellulose acylate film with the alkali solution at a surface temperature equal to or higher than the room temperature may employ a step of adjusting the film to a temperature equal to or higher than the room temperature before coating, a step of pre-heating the alkali solution, or a step of a combination thereof. It is preferably combined with a step of pre-heating to a temperature equal to or higher than the room temperature before coating.

In a step of heating in advance the cellulose acylate film to the room temperature or higher, there can be advantageously employed a direct heating by a collision (blowing) of an hot air flow, a contact heat conduction by a heating roll, a microwave induction heating, or a

radiation heating by an infrared heater. In particular, a contact heat conduction by a heating roller is preferable because it has a high heat conduction efficiency and can be executed with a small installation area and it enables a rapid temperature increase of the film temperature at the start of the transportation. There can be utilized an ordinary double-jacketed roller or an electromagnetic induction roll (manufactured by Tokuden Co.).

In a step of coating the alkali saponifying solution on the cellulose acylate film, there can be advantageously employed, for example, a die coater (extrusion coater or slide coater), a roll coater (forward roll coater, reverse roll coater or gravure coater), or a rod coater (utilizing a rod wound with a fine metal wire). The coating method is described in various references (for example Modern Coating and Drying Technology, Edward Cohen and Edgar B. Gutoff, Edits, VCH Publishers, Inc., 1992). A coating amount of the alkali solution is desirably made as small as possible, in consideration of a waste disposal at a removal by rinsing afterwards, and is preferably 1 to 100 cc/cm^3, more preferably 1 to 50 cc/cm^3. There is particularly preferred a rod coater, a gravure coater or a blade coater, which can be operated stably even at a low coating amount.

The alkali solution is preferably coated on a lower

surface of the cellulose acylate film, in order that, after the saponification process of the cellulose acylate film by the coating of the alkali solution, the alkali solution can be easily washed off from the cellulose acylate film.

It is preferable to restrict a variation in the coating amount to 30 % or less in a transversal direction and a longitudinal direction of the film. A continuous coating method can also be employed.

In the alkali saponification method of the invention, after the coating of the alkali solution, the cellulose acylate film is maintained at a temperature equal to or higher than the room temperature. In the invention, the room temperature means 20°C.

Heating means is selected in consideration of a fact that a surface of the cellulose acylate film is wet with the alkali solution. For example, there can be preferably employed a hot air collision (blowing) to a surface opposite to the coated surface, a contact heat conduction by a heating roll, a microwave induction heating, or a radiation heating by an infrared heater. An infrared heater is preferable since it can achieve heating in a non-contact manner and without involving an air flow, thereby minimizing an influence to the surface coated with the alkali solution. As the infrared heater, there can be

utilized a far-infrared ceramic heater of electric, gas, oil or steam type. A commercially available infrared heater (for example manufactured by Noritake Co., Ltd.) may be employed. An infrared heater of oil or steam type utilizing oil or steam as a heating medium is preferable for explosion-proof property in an environment where an organic solvent is present. A temperature of the cellulose acylate film may be same as or different from the heated temperature before the alkali solution coating. Also the temperature may be changed continuously or stepwise during the saponification reaction. A film temperature is 20 to 150°C, preferably 25 to 100°C and further preferably 35 to 80°C. For detecting the film temperature, there can be utilized a commercially available non-contact infrared thermometer, and a feedback control may be applied to the heating means in order to control the temperature within the aforementioned range.

A maintaining time at the aforementioned temperature range from the coating of the alkali solution to the washing-off thereof is variable depending on a transportation speed to be explained later, but is preferably 1 second to 5 minutes, more preferably 2 to 100 seconds and particularly preferably 3 to 50 seconds.

The alkali saponification process is preferably executed by the process steps while a cellulose acylate

film is transported, and a transporting speed of the cellulose acylate film is determined by a combination of the composition of the alkali solution and the coating method. It is generally preferably 10 to 500 m/min, more preferably 20 to 300 m/min.

Also, prior to the step of heating the cellulose acylate film in advance to the room temperature or higher or the step of coating the alkali solution on the cellulose acylate film, there may be executed a charge eliminating process, a dust eliminating process or a wet process in order to eliminate dusts and to obtain a more uniform wetting property of a film surface. These can be executed by commonly known methods, and a charge eliminating method can be a method described in JP-A No. 62-131500, and a dust eliminating method can be a method described in JP-A No. 2-43157.

For decelerating or terminating the saponification reaction of the cellulose acylate film and the alkali solution after the film temperature is maintained at the room temperature or higher to promote the saponification reaction, mainly three methods are available. First is a method of diluting the coated alkali solution to reduce the alkali concentration thereby lowering a reaction rate. Second is a method of lowering the temperature of the cellulose acylate film coated with the alkali solution

thereby lowering a reaction rate, and third is a method of neutralization with an acidic liquid.

A method of utilizing an alkali diluting liquid and a method of utilizing an alkali neutralizing liquid are, as already explained in the foregoing, also a part of the step of washing off the alkali solution from the film.

For diluting the coated alkali solution, there can be employed a method of coating a diluting liquid, a method of spraying a diluting liquid, or a method of immersing the cellulose acylate film in a container containing a diluting liquid. A method of coating a diluting liquid and a method of spraying are preferable in an operation under continuous transportation of the cellulose acylate film. The method of coating a diluting liquid is most preferable as it can be executed with a minimum necessary amount of the diluting liquid.

Coating of the diluting liquid is preferably executed by a continuous coating method capable of re-applying the diluting liquid onto the cellulose acylate film on which the alkali solution is already coated. For the coating, there can be advantageously employed, for example, a die coater (extrusion coater or slide coater), a roll coater (forward roll coater, reverse roll coater or gravure coater), or a rod coater (utilizing a rod wound with a fine metal wire). The coating method is described

in various references (for example Modern Coating and Drying Technology, Edward Cohen and Edgar B. Gutoff, Edits, VCH Publishers, Inc., 1992). In order to promptly mix the alkali solution and the diluting liquid thereby reducing the alkali concentration, there is preferred a roll coater or a rod coater in which a flow is not uniform in a small area (also called a coating bead) where the coating liquid is coated, in comparison with a die coater in which such flow becomes a laminar flow.

The alkali diluting liquid or the neutralizing liquid has to be a liquid capable of dissolving the alkali agent in the alkali solution, since it has an objective of lowering the alkali concentration and of not depositing, onto the film, an extracted substance such as an additive in the film. Therefore, it is preferable to employ, as a solvent, water or a mixture of an organic solvent and water, and two or more organic solvents may be employed in a mixture. An organic solvent employed in the alkali solution to be explained later can be employed preferentially. A preferred solvent is water.

Also in order not to deposit, on the film, an extracted substance such as an additive in the film, the alkali diluting liquid or the neutralizing liquid preferably includes a surfactant. The surfactant is not particularly restricted, but a surfactant employed in the

alkali solution to be explained later can be advantageously employed. Also the alkali diluting liquid or the neutralizing liquid preferably includes a defoaming agent to be explained later, in order to avoid deposition of small bubbles onto the film surface and to achieve rinsing of the alkali solution and the alkali diluting liquid uniformly without unevenness.

A coating amount of the diluting liquid is determined according to the concentration of the alkali solution. In case of a die coater which has a laminar flow in the coating bead, the coating amount is such that the original alkali concentration is diluted 1.5 to 10 times, more preferably 2 to 5 times. In a roll coater or a rod coater, because of an uneven flow in the coating bead, the alkali solution and the diluting liquid are mixed and a mixed solution is re-applied. Therefore, since it is not possible to specify a dilution rate from the coating amount of the diluting solvent, it is necessary to measure the alkali concentration after the coating of the diluting solvent. Also in a roll coater or a rod coater, it is preferable that the original alkali concentration is diluted 1.5 to 10 times, more preferably 2 to 5 times.

In order to promptly terminate the saponification reaction by alkali, an acid may also be employed. In

order to achieve neutralization with a small amount, a strong acid is preferable. Also in consideration of ease of rinsing, it is preferable to select an acid of which salt formed after neutralization with alkali has a high solubility in water. Hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, chromic acid and methanesulfonic acid are particularly preferable.

In case the alkali solution has a high concentration of carbonate ions or chloride ions, a precipitate may be generated by a rapid neutralization reaction, and, in such case, it is preferable to add a weak acid of a buffering property to the alkali neutralizing liquid. Such weak acid can be a sugar such as sorbit, saccharose, glucose, galactose, arabinose, xylose, fructose, ribose, mannose, or L-ascorbic acid, an alcohol, an aldehyde, a compound having a phenolic hydroxyl group, an oxime or a nucleic acid-related substance, as described in Ionization Constants of Organic Acids in Aqueous Solution, Pergamon Press.

For neutralizing the coated alkali solution with the acid, there can be employed a method of coating an acid solution (alkali neutralizing liquid), a method of spraying an acid solution, or a method of immersing the cellulose acylate film in a container containing an acid solution. Among these, a method of coating an acid

solution and a method of spraying are preferable in an operation under continuous transportation of the cellulose acylate film. The method of coating an acid solution is most preferable as it can be executed with a minimum necessary amount of the acid solution.

Coating of the alkali neutralizing liquid is preferably executed by a continuous coating method capable of re-applying the acid solution onto the cellulose acylate film on which the alkali solution is already coated. For the coating, there can be advantageously employed, for example, a die coater (extrusion coater or slide coater), a roll coater (forward roll coater, reverse roll coater or gravure coater), or a rod coater (utilizing a rod wound with a fine metal wire). The coating method is described in various references (for example Modern Coating and Drying Technology, Edward Cohen and Edgar B. Gutoff, Edits, VCH Publishers, Inc., 1992). In order to promptly mix the alkali solution and the neutralizing liquid thereby reducing the alkali concentration, there is preferred a roll coater or a rod coater in which a flow is not uniform in a small area (also called a coating bead) where the coating liquid is coated, in comparison with a die coater in which such flow becomes a laminar flow.

A coating amount of the alkali neutralizing liquid is determined according to the kind of the alkali and the

concentration of the alkali solution. In case of a die coater which has a laminar flow in the coating bead, a coating amount of the neutralizing liquid is preferably 0.1 to 5 times of the original alkali coating amount, more preferably 0.5 to 2 times. In a roll coater or a rod coater, because of an uneven flow in the coating bead, the alkali solution and the diluting liquid are mixed and a mixed solution is re-applied. Therefore, since it is not possible to specify a neutralization rate from the coating amount of the acid solution, it is necessary to measure the alkali concentration after the coating of the neutralizing liquid. Also in a roll coater or a rod coater, it is preferable to determine the coating amount of the acid solution so as to obtain a pH value of 4 to 9 after the coating of the acid solution, more preferably a pH value of 6 to 8.

The alkali neutralizing liquid has to be a solvent capable of dissolving the alkali agent in the alkali solution, since it has an objective of lowering the alkali concentration and of not depositing an extracted substance such as an additive in the film onto the film. Therefore, it is preferable to employ, as a solvent, water or a mixture of an organic solvent and water, and two or more organic solvents may be employed in a mixture. An organic solvent employed in the alkali solution to be explained

later can be employed advantageously. A preferred solvent is water.

Also in order not to deposit, on the film, an extracted substance such as an additive in the film, the alkali neutralizing liquid preferably includes a surfactant. The surfactant is not particularly restricted, but a surfactant employed in the alkali solution to be explained later can be advantageously employed. Also the alkali neutralizing liquid preferably includes a buffer agent, in order to improve a rinsing efficiency.

It is also possible to terminate the saponification reaction by lowering the temperature of the cellulose acylate film. The saponification reaction is substantially terminated by a sufficient temperature decrease from a state maintained at the room temperature or higher for accelerating the reaction. Means of lowering the temperature of the cellulose acylate film is determined in consideration of a fact that a surface of the cellulose acylate film is wet. For example, there can be preferably employed a cold air collision to a surface opposite to the coated surface, or a contact heat conduction by a cooling roll. A film temperature after the cooling is preferably 5 to 60°C, more preferably 10 to 50°C and most preferably 15 to 30°C. The film temperature is preferably measured with a non-contact infrared

thermometer. It is also possible to regulate the cooling temperature by a feedback control on the cooling means based on the measured temperature.

[Rinsing step]

A rinsing step is executed in order to eliminate the alkali solution, the alkali diluting liquid or the alkali neutralizing liquid. A remnant of an alkali agent, an acid, a salt, or an extracted substance such as an additive in the film not only causes the saponification reaction to proceed but also affects a coated film formation of an orienting film and liquid crystal molecules to be coated later and an orientation of the liquid crystal molecules.

Rinsing can be executed by a method of coating water, a method of spraying rinsing water, or a method of immersing the cellulose acylate film in a container containing rinsing water. A method of coating rinsing water and a method of spraying are preferable in an operation under continuous transportation of the cellulose acylate film. The method of spraying rinsing water is particularly preferable since a random flow mixing of the rinsing water on the cellulose acylate film and the alkaline coating liquid can be obtained in a jet flow.

A water spraying method can be executed by a method

utilizing a coating head (for example a fountain coater or a frog mouth coater), or a method utilizing a spray nozzle utilized in air humidifying, painting or automatic tank washing. The coating method is described in "All of Coating", Masayoshi Araki, Kako Gijutsu Kenkyu-kai (1999). It is possible to arrange conical- or fan-shaped spray nozzles along a transversal direction of the film in such a manner that a water flow collides with an entire width of the film. It is also possible to employ a commercially available spray nozzle (for example manufactured by Ikeuchi Co. or Spraying Systems Inc.).

A higher spraying speed of water provides a larger random flow mixing. However, a high speed may affect the transporting stability of the cellulose acylate film under continuous transportation. A collision speed of spraying is preferably 50 to 1000 cm/sec, more preferably 100 to 700 cm/sec and most preferably 100 to 500 cm/sec.

A fluctuation in a water spraying amount per unit time is preferably controlled to less than 30 % both in the longitudinal direction and the transversal direction of the transported cellulose acylate film. However, in both ends of the transversal direction of the cellulose acylate film, there often occurs a large coating amount in the alkali saponifying solution and the acid solution used for neutralization. In order to secure rinsing in a

portion with a larger coating amount, it is also possible to increase the water spraying amount on both ends in the transversal direction. In case of employing a coating head, a clearance of a water emitting slit is made wider so as to increase the flow amount on both ends. Also in order to locally supply a water film on both ends, a coater of a small width may be provided separately. The coater of the small width may be provided in plural units. Also in case of employing a spray nozzle, a nozzle may be provided for locally spraying water on both ends.

For a given amount of water for rinsing, there is preferred a batch-type rinsing method of applying water in several divided portions, rather than applying the entire amount at a time. More specifically, the water is divided into certain portions which are supplied to plural rinsing means provided in tandem along the transporting direction of the film. Between rinsing means and next rinsing means, there is provided a suitable time (distance) thereby promoting a dilution of the alkaline coating liquid by diffusion. More preferably, the transported polymer film is made to incline whereby the water on the film flows along the film surface thereby achieving a mixing dilution by a flow in addition to the diffusion. In a most preferable method, water squeezing means is provided between the rinsing means, for eliminating the water film

on the cellulose acylate film, thereby further improving the efficiency of rinsing and dilution. Specific examples of the water squeezing means include a blade employed in a blade coater, an air knife employed in an air knife coater, a rod employed in a rod coater, and a roll employed in a roll coater.

A larger number of the rinsing means in a tandem arrangement is more advantageous. However, in consideration of an installation space and a facility cost, there are usually employed 2 to 10 stages, preferably 2 to 5 stages.

A thickness of a water film after the water squeezing means is preferably as small as possible, but a minimum water film thickness is limited by the type of the water squeezing means to be employed. In a method of contacting a physically solid member such as a blade, a rod or a roll with the film, it is necessary to leave a finite water film as a lubricating fluid since, even in case the solid member is constituted of an elastic member of a low hardness such as rubber, there may result a scratch on the film surface or an abrasion of the elastic member. Usually there is left a water film of several micrometers or more, preferably 10 μm or more, as a lubricating fluid.

As water squeezing means capable of reducing the

water film thickness extremely, an air knife is preferable. The water film thickness may be made close to zero, by employing sufficient air amount and air pressure. However, an air blowing amount has a certain preferable range since an excessively high air blow amount may cause a flapping or a skewing of the cellulose acylate film, thus affecting the transporting stability thereof. Such range is dependent also on the thickness of the original water film on the cellulose acylate film and the transporting speed of the film, but there is usually employed an air speed of 10 to 500 m/sec, preferably 20 to 300 m/sec and more preferably 30 to 200 m/sec. Also for achieving uniform elimination of the water film, an air blow aperture of the air knife or an air supply method thereto is so regulated that the air speed in the transversal direction of the cellulose acylate film has a distribution normally within 10 %, preferably within 5 %. A gap between a surface of the transported cellulose acylate film and the air blowing aperture of the air knife has an appropriate range since a smaller gap provides a higher water squeezing ability but results in a higher possibility of causing a scratch by a contact with the cellulose acylate film. Therefore, the air knife is installed usually with a gap of 10 μm to 10 cm, preferably 100 μm to 5 cm and further preferably 500 μm to 1 cm. Also a backup roll is preferably provided at

a side opposite to the rinsed surface of the film, so as to be opposed to the air knife, thereby stabilizing the gap setting and relaxing influences on the film such as a flapping, a crease or a defoamation.

For the rinsing water, purified water is preferably employed. The purified water to be employed in the invention means water having a specific resistivity of at least 1 MΩ or higher, with metal ions such as sodium, potassium, magnesium or calcium less than 1 mg/L and anions such as of chlorine or nitric acid less than 0.1 mg/L. The purified water can be easily obtained by a reverse osmosis film, an ion exchange resin, a distillation or a combination thereof.

A higher temperature of the rinsing water provides a higher rinsing ability. However, in a method of spraying water onto the transported cellulose acylate film, the water has a large contact area with the air and evaporates more at a higher temperature, thereby increasing the humidity in the environment and resulting in a danger of dewing. Therefore, a temperature of the rinsing water is usually set within a range of 5 to 90°C, preferably 20 to 80°C and more preferably 25 to 60°C.

In case a component of the alkali solution or a product of the saponification reaction is not easily soluble in water, a solvent washing step for eliminating a

water-insoluble component may be added before or after the rinsing step. The solvent washing step may utilize the rinsing method or the water squeezing means, and a solvent similar to that described for the alkali solution to be explained later, or *Solvent Pocket Book New Edition* (Ohm-sha, 1994).

A drying step may be executed after the rinsing step. The drying step is usually unnecessary because the water film can be sufficiently eliminated by the water squeezing means such as an air knife, but a heat drying may be executed in order to adjust the cellulose acylate film to a desirable water content before being wound in a roll. On the other hand, it is also possible to execute a humidity adjustment with an air flow having a selected humidity. A drying air has a temperature preferably of 30 to 200°C, more preferably 40 to 150°C and particularly preferably 50 to 120°C.

In the alkali process of the invention, a coating of a functional layer may be executed in continuation to the aforementioned saponification step. A saponification process by coating on a surface, followed by a coating of a functional layer thereon, allows to prevent sticking between the surface of the functional layer and an opposite surface of the film when the film is rolled after the functional layer is provided.

[Replenishing method of replenishing liquid]

A first embodiment of a replenishing method for a replenishing liquid of the invention is, in producing an alkali saponified polymer film by a continuous saponification process of a polymer film surface with an alkali solution, a method of replenishing the alkali solution with a replenishing liquid, which comprises:

a step of measuring a saponifying ability of the alkali solution;

a step of determining a replenishing mode for the replenishing liquid in such a manner that the saponifying ability of the alkali solution after a replenishment with the replenishing liquid becomes within a predetermined range, based on the measured saponifying ability; and

a step of replenishing the alkali solution with the replenishing liquid in thus determined replenishing mode.

In the first embodiment of the replenishing method for a replenishing liquid of the invention, there is at first executed a step of measuring a saponifying ability of the alkali solution.

In general, a "saponifying ability" of an alkali solution in a saponification process is generally dependent on a concentration of hydroxide ions (OH^-) in the alkali solution. In the invention, therefore, the

concentration of the hydroxide ions is measured directly or indirectly as an index of the saponifying ability.

Means for measuring the saponifying ability of the alkali solution is not particularly restricted, and is preferably at least one selected from a group of a pH measurement of the alkali solution, a measurement of an electrical conductivity of the alkali solution, a measurement of an electrical impedance of the alkali solution, a measurement of an electrode voltage between current-controlled electrodes, and a measurement of an electrode potential between current-controlled electrodes. This is because such means can be executed in a measuring apparatus that can be easily and inexpensively prepared and can provide an exact measured value.

The means for measuring the saponifying ability of the alkali solution may be provided in the alkali solution. Such means may be provided in two or more positions, and the saponifying ability may be measured from the respective data.

A pH measurement of the alkali solution can be executed with a commercially available pH sensor such as a glass electrode pH sensor or a semiconductor pH sensor. Among these, a semiconductor pH sensor is preferable.

The semiconductor pH sensor is provided with a measuring electrode, a comparison electrode and a

temperature compensating electrode, and the measuring electrode employs an ISFET (ion sensitive field effect transistor), responsive to hydrogen ions. The ISFET has features of being formed by a durable solid-state silicon chip and providing an excellent responsiveness. Also the semiconductor pH sensor is not eroded even in a pH measurement under constant immersion in the alkali solution of a high alkalinity, and can exactly measure the pH of the alkali solution over a prolonged period.

A semiconductor pH sensor advantageously employable in the invention can be, for example, LQH21 (manufactured by Honeywell Inc., and distributed by Yamatake Co., which a distributor in Japan), 0010-15C manufactured by Horiba Seisakusho Co., and 1001 pH System (manufactured by Centron Inc., and distributed by Japan Machinery Co, which is a distributor in Japan).

An electrical conductivity measurement of the alkali solution can be executed with a commercially available electroconducto meter. More specifically, it can be of an electrode type or an electromagnetic induction type. A preferred electroconductometer is equipped with a temperature compensation circuit (for example ±2 %/°C). A sensor of the electroconductometer may be provided in a position immersible in the alkali solution at the measurement, for example in an alkali solution circulating

system of a saponifying apparatus. In particular, there is preferred a position in a tank of the alkali solution or in a circulating pipe.

An electrical impedance measurement of the alkali solution can be executed with an electrical impedance measuring apparatus such as an AC impedance meter, an AC bridge meter or another impedance meter.

Optimum conditions of a measurement current, an oscillating frequency etc. of the electrical impedance measuring apparatus vary according to a composition etc. of the alkali solution. In general, the measuring current is preferably at a relatively low level in order to protect the apparatus and to prevent electrolysis of the alkali solution. An oscillation frequency is preferably from several hundred Hz to several hundred kHz, in consideration of a relation with an electrostatic capacitance component in the alkali solution.

An electrical impedance of the alkali solution containing an electrolyte is dependent on the temperature of the solution. More specifically, an increase in the temperature of the solution decreases the electrical impedance. Consequently, there is preferred an electrical impedance measuring apparatus provided with a temperature sensor and a temperature compensating circuit.

A sensor of the electrical impedance measuring

apparatus may be provided in a position immersible in the alkali solution at the measurement, for example in an alkali solution circulating system of a saponifying apparatus. In particular, there is preferred a position in a tank of the alkali solution or in a circulating pipe.

A measurement of an electrode voltage and/or an electrode potential between current-controlled electrodes can be executed by installing current-controlled electrodes in the alkali solution in a tank therefor and measuring an electrode voltage and/or an electrode potential between the electrodes.

The measurement of an electrode voltage and/or an electrode potential between the current-controlled electrodes can prevent an abnormal electrode reaction, since a current flows only within a controlled range. It is therefore possible to prevent a deterioration in measuring means for the electrode voltage and/or the electrode potential, a deterioration of the alkali solution and a stain, resulting from an abnormal electrode reaction.

A current in the electrodes is preferably a constant current. This is because of an easy current control and a high stability, and the current is preferably about 5 to 100 mA.

It is also preferable to measure an electrode

voltage and/or an electrode potential by controlling the current in the electrodes by a current scanning method. For the current scanning method, there can be employed a known method such as a single sweeping method or a multiple sweeping method. In such operation, it is preferred to provide means for simultaneously measurement the temperature of the alkali solution and to apply a temperature correction to the measurement of the electrode voltage and/or the electrode potential.

Electrodes employed for the measurement of the electrode voltage and/or the electrode potential between the current-controlled electrodes are preferably of a conductive material resistant to alkali. Preferred examples include titanium, a SUS material (for example SUS316 or SUS316L), platinum, a platinum-covered titanium electrode, a titanium electrode covered with an oxide of platinum group, and a carbon electrode.

An electrode structure is not particularly limited and can be a cylindrical shape, a rod shape, a mesh, a ring shape, or a disk shape. Also the electrode can be a fixed electrode or a movable electrode such as a rotating electrode.

An electrode voltage measurement can be executed with a commercially available voltmeter. Also an electrode potential measurement can be executed with a

commercially available potentiometer.

A pulse-shaped current waveform is preferable in the current control, as it enhances an effect of preventing a stain on the electrode by an electrolytic effect and a stain by a precipitate etc.

As a pulsed method, there can be employed a known method such as a constant-current single pulse method or a constant-current double pulse method. A pulsed waveform can be, for example, a ramp wave, a stepped wave, a triangular wave, a rectangular wave, a trapezoidal wave, a sawtooth wave or a sinusoidal wave.

An inversion of a current polarity in the current control enhances an effect of preventing a stain on the electrode by an electrolytic effect and a stain by a precipitate etc. A polarity inversion time is preferably 1 to 1000 ms, and a polarity inversion ratio is preferably about -:+ = 1:1 to 1:10.

Then, based on the measured saponifying ability, there is executed a step of determining a replenishing mode for the replenishing liquid in such a manner that the saponifying ability of the alkali solution after a replenishment with the replenishing liquid becomes within a predetermined range.

An increased deterioration of the saponifying ability results in drawbacks of an excessively low

saponification level on the polymer film surface or an unevenness in the saponification level. It is therefore necessary to maintain a level of deterioration of the saponifying ability always within a range not causing the aforementioned drawbacks.

For this purpose, in case the measured saponifying ability is for example lower than a predetermined value, there is determined a level of increase of the saponifying ability based on the level of the measured saponifying ability, and a necessary replenishing mode of the replenishing liquid is determined. The replenishing mode of the replenishing liquid is constituted of a composition of the replenishing liquid, a replenishing amount, a replenishing interval etc.

For example, in case the measured saponifying ability indicates a large level of deterioration, there is executed an increase in the alkali concentration of the replenishing liquid, an increase in the replenishing amount of the replenishing liquid, a decrease in the replenishing interval of the replenishing liquid, or a combination thereof. Also in case of a small level of deterioration, there is executed a decrease in the alkali concentration of the replenishing liquid, a decrease in the replenishing amount of the replenishing liquid, an increase in the replenishing interval of the replenishing

liquid, or a combination thereof.

In the following, there will be given a specific explanation according to the means used for measuring the saponifying ability of the alkali solution.

In case of employing a pH measurement of the alkali solution as the means of measuring the saponifying ability of the alkali solution, the pH value of the alkali solution is measured, then, when the measured pH value becomes lower than a predetermined value, a level of increase in the saponifying ability is determined based on the measured pH value, and a corresponding replenishing mode of the replenishing liquid is determined.

In case of employing a measurement of the electrical conductivity of the alkali solution, the electrical conductivity of the alkali solution is measured, then, when the measured electrical conductivity becomes lower than a predetermined value, a level of increase in the saponifying ability is determined based on the measured electrical conductivity, and a corresponding replenishing mode of the replenishing liquid is determined.

In case of employing a measurement of the electrical impedance of the alkali solution, the electrical impedance of the alkali solution is measured, then, when the measured electrical impedance becomes lower than a predetermined value, a level of increase in the

saponifying ability is determined based on the measured electrical impedance, and a corresponding replenishing mode of the replenishing liquid is determined.

The aforementioned predetermined value is selected lower than an electrical impedance of the alkali solution before use (hereinafter called "first impedance value") and higher than an electrical impedance when the alkali solution is so deteriorated as to start to generate a saponification unevenness on the polymer film surface (hereinafter called "second impedance value"). The predetermined value is preferably set at about a center value between the first impedance value and the second impedance value.

Also the replenishing mode of the replenishing liquid is preferably a replenishing mode required to bring the alkali solution to the first impedance value.

A value of the replenishing mode can be determined by a simple simulation test, once compositions of the alkali solution and the replenishing liquid, and a charge amount of the alkali solution into an alkali solution tank are determined.

In case of employing a measurement of the electrode voltage and/or the electrode potential between the current-controlled electrodes, the electrode voltage and/or the electrode potential between the current-

controlled electrodes is measured, then, when the electrode voltage and/or the electrode potential thus measured is not within a predetermined reference range, a level of increase in the saponifying ability is determined based on the measured the electrode voltage and/or electrode potential and a corresponding replenishing mode of the replenishing liquid is determined.

In the method of the invention, it is also one of preferable embodiments to execute a step of measuring a process area of the polymer film per unit time, and to determine the aforementioned predetermined range based on the measured process area of the polymer film per unit time. Specifically, it is preferable, in case the process area of the polymer film per unit time is large, to decrease a level of deterioration of the predetermined value, and, in case the process area of the polymer film per unit time is small, to increase a level of deterioration of the predetermined value.

More specifically, for example in case of employing a measurement of the electrical conductivity of the alkali solution as the means of measuring the saponifying ability of the alkali solution, an electrical conductivity predetermined as a reference whether or not to conduct a replenishment is selected high or low respectively in case the process area of the polymer film per unit time is

large or small.

A similar method can apply also to a case where a pH measurement etc. is employed as the means of measuring the saponifying ability of the alkali solution.

The measurement of the process area of the polymer film per unit time will be explained in a following second embodiment of the invention.

Then there is executed a step of replenishing the alkali solution with the replenishing liquid in the determined replenishing mode as explained above.

The replenishing method with the replenishing liquid is not particularly restricted and can be executed by a known method.

For example, in case a replenishing amount is changed in the replenishing mode, automatic measuring means such as an automatic measuring pump can be employed.

A second embodiment of the invention is a replenishing method for a replenishing liquid, in producing an alkali saponified polymer film by a continuous saponification process of a polymer film surface with an alkali solution, the method including:

a step of measuring a process area of the polymer film per unit time;

a step of calculating a consumption of the alkali solution per unit time from the measured process area per

unit time, based on a pre-memorized amount of the alkali solution necessary for a saponification process of the polymer film per unit area;

a step of determining a replenishing mode for the replenishing liquid in such a manner that the saponifying ability of the alkali solution after a replenishment with the replenishing liquid becomes within a predetermined range, based on the calculated consumption per unit time; and

a step of replenishing the alkali solution with the replenishing liquid in thus determined replenishing mode.

In the second embodiment of the replenishing method for a replenishing liquid of the invention, there is at first executed a step of measuring a process area of the polymer film per unit time.

A process area of the polymer film per unit time can be measured by a known method. For example there can be employed a method of positioning a plurality of optical sensors at a constant interval and perpendicularly to a surface of the continuously transported polymer film, then causing a polymer film width detecting circuit to detect a width of the polymer film based on reflected lights from the polymer film and causing a polymer film area integrating circuit to calculate the process area of the polymer film per unit time, by processing a detected

information and a transporting speed.

Then there is executed a step of calculating a consumption of the alkali solution per unit time from the measured process area per unit time, based on a pre-memorized amount of the alkali solution necessary for a saponification process of the polymer film per unit area.

An amount of the alkali solution necessary for a saponification process of the polymer film per unit area is a theoretical alkali consumption amount to be explained later. The theoretical alkali consumption amount is multiplied by the process area per unit time measured in the preceding step to calculate a consumption of the alkali solution per unit time.

Then there is executed a step of determining a replenishing mode for the replenishing liquid in such a manner that the saponifying ability of the alkali solution after a replenishment with the replenishing liquid becomes within a predetermined range, based on the calculated consumption per unit time.

Specifically, a saponifying ability at the measurement of the consumption of the alkali solution per unit time is calculated from an amount and an alkali concentration of the alkali solution prior to the saponification process, and a consumption of the alkali solution. Thereafter, as in the first embodiment of the

invention, a level of increase in the saponifying ability is determined based on the calculated saponifying ability, and a replenishing mode of the replenishing liquid required therefor is determined.

Thereafter, a step of replenishing the alkali solution with the replenishing liquid in thus determined replenishing mode. This step is similar to that in the first embodiment of the invention.

In the second embodiment of the replenishing method for the replenishing liquid of the invention, it is also one of preferable embodiments to execute a step of calculating a deterioration of the alkali solution by an absorption of carbon dioxide gas, and making a feedback to the calculation of the consumption of the alkali solution per unit time.

Specifically, a deterioration of the alkali solution by an absorption of carbon oxide gas is calculated from a temperature, a humidity, a pressure etc. of an atmosphere at the saponification process.

In the first embodiment of the replenishing method for the replenishing liquid of the invention and the second embodiment of the replenishing method for the replenishing liquid of the invention, a deteriorated alkali solution recovers the saponifying ability by a replenishment with the replenishing liquid. Thus a

hydroxide ion concentration in the alkali solution increases.

In the invention, therefore, the saponifying ability is maintained within a predetermined range by a repetition of a deterioration of the alkali solution by a continued saponification process and a recovery of the saponifying ability by the replenishment with the replenishing liquid, whereby an alkali saponified polymer film can be produced in a stable manner even when the saponification process of the polymer film surface with the alkali solution is executed in a continuous manner.

[Saponification process]

In the following, a saponification process in the invention will be explained.

For applying a saponification process to a polymer film surface with an alkali solution, there can be employed any known method, such as a method of immersing the polymer film in the alkali solution, a method of spraying the alkali solution to the polymer film or a method coating the alkali solution on the polymer film.

In case of saponifying a surface only of the polymer film, a method of coating the alkali solution is preferable. For coating, there can be employed a known coating method.

In the method of coating the alkali solution, the saponification is preferably conducted at 25 to 120°C.

For executing the saponification process at or above 25°C, it is possible to employ a method of heating the polymer film to or above 25°C before the coating of the alkali solution, a method of heating the alkali solution in advance, or a method of a combination thereof. Among these, a method of heating the polymer film to or above 25°C in advance is preferable.

In the invention, it is preferable to execute at least a step of heating the polymer film to or above 25°C in advance, a step of coating the alkali solution on the polymer film, a step of maintaining the polymer film at a temperature at least equal to 25°C, and a step of washing off the alkali solution from the polymer film, in this order. These steps will be explained in detail in the following.

These steps are preferably executed in continuous manner while the polymer film is transported. A transporting speed of the polymer film is preferably 10 to 500 m/min, more preferably 20 to 300 m/min. Conditions of each step are preferably determined according to the transporting speed. For example in the step of coating the alkali solution on the polymer film, it is preferable to determine physical properties (specific gravity,

viscosity and surface tension), a coating method and coating conditions so as to achieve a stable coating operation.

At first there is executed a step of heating in advance the polymer film to or above 25°C. A heating of the polymer film to or above 25°C in advance increases the speed of the saponification reaction, and improves the stability.

In the step of heating in advance the polymer film to or above 25°C, the heating is preferably achieved by a collision by a hot air, a contact heat conduction by a heating roll, a microwave induction heating, or a radiation heating by an infrared heater. In particular, a contact heat conduction by a heating roller is preferable because it has a high heat conduction efficiency and can be executed with a small installation area and it enables a rapid temperature increase of the film temperature at the start of the transportation. There can be utilized an ordinary double-jacketed roller or an electromagnetic induction roll (manufactured by Tokuden Co.).

The film after heating preferably has a temperature of 25 to 100°C, more preferably 25 to 80°C and further preferably 35 to 75°C.

Then there is executed a step of coating the alkali solution onto the polymer film. In the step of coating

the alkali solution onto the polymer film, there can be advantageously employed a coater such as a die coater (extrusion coater or slide coater), a roll coater (forward roll coater, reverse roll coater or gravure coater), a rod coater (utilizing a rod wound with a fine metal wire), or a blade coater. As a specific coating method, it is possible to employ methods described in various references (for example Modern Coating and Drying Technology, Edward Cohen and Edgar B. Gutoff, Edits, VCH Publishers, Inc., 1992).

A coating amount of the alkali solution is preferably made as small as possible, in consideration of a waste disposal at a removal by rinsing afterwards. Among the coaters mentioned above, there is particularly preferred a rod coater, a die coater, a gravure coater or a blade coater, which can be operated stably even at a low coating amount.

It is preferable to restrict a variation in the coating amount to 30 % or less in a transversal direction and a longitudinal direction of the polymer film.

A coating amount of the alkali solution necessary for the saponification reaction is given, as an index, by a theoretical alkali consumption amount, which is determined according to a total saponification site number obtained by multiplying a saponification reaction site

number per unit area of the polymer film by a saponification depth necessary for realizing an adhesion with an orienting film etc.

In practice, the coating is preferably made equal to or larger than the the theoretical alkali consumption amount. Specifically, there is preferred an amount of 2 to 20 times of the theoretical alkali consumption amount, more preferably 2 to 5 times.

A temperature of the alkali solution is preferably equal to the temperature of the polymer film.

After the step of coating the alkali solution on the polymer film, there is executed a step of maintaining the polymer film at a temperature equal to or higher than 25°C. This step causes the saponification reaction to sufficiently proceed.

Heating means employed for maintaining the polymer film at a temperature equal to or higher than 25°C is preferably selected in consideration of a fact that a surface of the polymer film is wet with the alkali solution. For example, there can be preferably employed a collision of a hot air to a surface opposite to the coated surface, a contact heat conduction by a heating roll, a microwave induction heating, or a radiation heating by an infrared heater.

An infrared heater is preferable since it can

achieve heating in a non-contact manner and without involving an air flow, thereby minimizing an influence to the surface coated with the alkali solution. As the infrared heater, there can be utilized a far-infrared ceramic heater of electric, gas, oil or steam type. An infrared heater of oil or steam type utilizing oil or steam as a heating medium is preferable for explosion-proof property in an environment where an organic solvent is present.

A temperature at which the polymer film is maintained may be same as or different from the heated temperature before the alkali solution coating. Also the maintained temperature may be changed continuously or stepwise. The film temperature is preferably 25 to 100°C, more preferably 25 to 80°C and further preferably 35 to 70°C. For detecting the film temperature, there can be utilized a commercially available non-contact infrared thermometer. A feedback control may be applied to the heating means in order to control the temperature within the aforementioned range, and it is also possible to regulate the maintained temperature.

For terminating the saponification reaction of the polymer film, it is possible to employ, for example, a method of diluting the coated alkali solution to reduce the alkali concentration thereby lowering a reaction rate,

a method of neutralizing the coated alkali solution with an acidic liquid or a method of lowering the temperature of the polymer film thereby lowering a reaction rate. It is also possible to employ a method combining the method of diluting the alkali solution or the method of neutralizing the alkali solution and the method of lowering the temperature of the polymer film.

For diluting the coated alkali solution, there can be employed, for example, a method of coating a diluting solvent, a method of spraying a diluting solvent, or a method of immersing the polymer film in a container containing a diluting solvent. Among these, a method of coating a diluting solvent and a method of spraying a diluting solvent is preferable in executing an operation under continuous transportation of the polymer film. The method of coating a diluting solvent is most preferable as it can be executed with a minimum necessary amount of the diluting solvent.

Coating of the diluting solvent is preferably executed by a continuous coating method capable of re-applying the diluting solvent onto the polymer film on which the alkali solution is already coated.

The coating method can be similar to those described for the aforementioned saponification process. In order to promptly mix the alkali solution and the diluting

solvent thereby reducing the alkali concentration, there is preferred a roll coater or a rod coater in which a flow is not uniform in a small area (also called a coating bead) where the coating liquid is coated, in comparison with a die coater in which such flow becomes a laminar flow.

The diluting solvent has to be a solvent capable of dissolving the alkali agent in the alkali solution, since it has an objective of lowering the alkali concentration. Therefore, it is preferable to employ water or a mixture of an organic solvent and water.

It is preferable that the organic solvent employed in the diluting solvent does not dissolve nor swell the polymer film. It is also preferably to select a substance of a suitably low surface tension.

Such organic solvent can be that described in *Solvent Pocket Book New Edition* (Ohm-sha, 1994). Specific examples include a monohydric alcohol (such as methanol, ethanol, propanol, butanol, cyclohexanol, benzyl alcohol, fluorinated alcohol or ethylene glycol monomethyl ether), a ketone (such as acetone, methyl ethyl ketone, or methyl isobutyl ketone), an ester (such as methyl acetate, ethyl acetate, butyl acetate or ethylene glycol monomethyl ether monoacetate), a polyhydric alcohol (such as ethylene glycol, diethylene glycol or propylene glycol), an amide

(such as N,N-dimethylformamide), a sulfoxide (such as dimethylsulfoxide) and an ether (such as methyl cellosolve).

A coating amount of the diluting solvent can be determined according to the concentration of the alkali solution.

In case of a die coater which has a laminar flow in the coating bead, the coating amount is such that the original alkali concentration is diluted 1.5 to 10 times, more preferably 2 to 5 times.

In a roll coater or a rod coater, because of an uneven flow in the coating bead, the alkali solution and the diluting liquid are mixed and a mixed solution is re-applied. Therefore, since it is not possible to specify a dilution rate from the coating amount of the diluting solvent, it is preferable to measure the alkali concentration after the coating of the diluting solvent. Also in a roll coater or a rod coater, it is preferable that the original alkali concentration is diluted 1.5 to 10 times, more preferably 2 to 5 times.

As a method of terminating the saponification reaction of the polymer film, a method of neutralizing the coated alkali solution with an acidic liquid allows to promptly terminate the saponification reaction.

In order to achieve neutralization with a small

amount, a strong acid is preferable. Also in consideration of ease of rinsing, it is preferable to select an acid of which salt formed after neutralization with alkali has a high solubility in water. Hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, and chromic acid are particularly preferable.

For diluting the coated alkali solution, there can be employed, for example, a method of coating a diluting solvent, a method of spraying a diluting solvent, or a method of immersing the polymer film in a container containing a diluting solvent. Among these, a method of coating a diluting solvent and a method of spraying a diluting solvent is preferable in executing an operation under continuous transportation of the polymer film. The method of coating a diluting solvent is most preferable as it can be executed with a minimum necessary amount of the diluting solvent.

Coating of the diluting solvent is preferably executed by a continuous coating method capable of re-applying the diluting solvent onto the polymer film on which the alkali solution is already coated.

The coating method can be similar to those described for the aforementioned saponification process. In order to promptly mix the alkali solution and the diluting solvent thereby reducing the alkali concentration, there

is preferred a roll coater or a rod coater in which a flow is not uniform in a small area (also called a coating bead) where the coating liquid is coated, in comparison with a die coater in which such flow becomes a laminar flow.

A coating amount of the acid solution can be determined according to the kind of the alkali and the concentration of the alkali solution.

In case of a die coater which has a laminar flow in the coating bead, a coating amount of the acid solution is preferably 0.1 to 5 times of the coating amount of the alkali solution, more preferably 0.5 to 2 times.

In a roll coater or a rod coater, because of an uneven flow in the coating bead, the alkali solution and the acid solution are mixed and a mixed solution is re-applied. Therefore, since it is not possible to specify a neutralization rate from the coating amount of the acid solution, it is preferable to measure the alkali concentration after the coating of the acid solution. Also in a roll coater or a rod coater, it is preferable to determine the coating amount of the acid solution so as to obtain a pH value of 4 to 9 after the coating of the acid solution, more preferably a pH value of 6 to 8.

It is also possible to terminate the saponification reaction of the polymer film by lowering the temperature

of the polymer film. In this method, the saponification reaction is substantially terminated by a sufficient temperature decrease from a state maintained at the room temperature or higher for accelerating the reaction.

Means of lowering the temperature of the polymer film is preferably determined in consideration of a fact that a surface of the polymer film is wet. For example, there can be preferably employed a cold air collision to a surface opposite to the coated surface, or a contact heat conduction by a cooling roll.

A film temperature after the cooling is preferably 5 to 60°C, more preferably 10 to 50°C and most preferably 15 to 30°C.

The film temperature can be measured with a commercially available non-contact infrared thermometer. It is also possible to execute a feedback control on the cooling means to regulate the cooling temperature, thereby achieving a control in the aforementioned temperature range.

Then a step is executed for washing off the alkali solution from the polymer film. A remnant of the alkali solution not only causes the saponification reaction to proceed but also affects a coated film formation of an orienting film and liquid crystal molecules to be coated later and an orientation of the liquid crystal molecules.

For washing off the alkali solution from the polymer film, water rinsing is preferred. There can be advantageously employed a method of coating water, a method of spraying water, or a method of immersing the polymer film in a container containing water.

A water spraying method can be executed by a method utilizing a coating head (for example a fountain coater or a frog mouth coater), or a method utilizing a commercially available spray nozzle (for example manufactured by Ikeuchi Co. or Spraying Systems Inc.) utilized in air humidifying, painting or automatic tank washing. It is also possible to employ a spraying method described in "All of Coating", Masayoshi Araki, Kako Gijutsu Kenkyu-kai (1999). It is possible to arrange conical- or fan-shaped spray nozzles along a transversal direction of the polymer film in such a manner that a water flow collides with an entire width of the film.

A higher spraying speed of water provides a larger random flow mixing. However, a high speed may affect the transporting stability of the polymer film under continuous transportation. Therefore a spraying speed at collision to the polymer film is preferably 50 to 1000 cm/sec, more preferably 100 to 700 cm/sec and most preferably 100 to 500 cm/sec.

Assuming that all the water used for rinsing

contributes to the dilution of the alkali solution, a theoretical dilution rate is defined by a following equation:

theoretical dilution rate (times) = water amount [mL/m^2] used in rinsing/coating amount of alkali solution [mL/m^2]

Since water and the alkali solution are not completely mixed in practice, there is employed water of an amount larger than a water amount corresponding to a desired theoretical dilution rate.

The theoretical dilution rate, though dependent on an alkali concentration, a secondary additive, a solvent etc. in the employed alkali solution, is preferably set at 100 times or larger, more preferably 500 times or larger and further preferably 1000 times or larger. Also the theoretical dilution rate is usually selected 100,000 times or less.

For a given amount of water for rinsing, there is preferred a batch-type rinsing method of applying water in several divided portions, rather than applying the entire amount at a time. More specifically, the water is divided into certain portions which are supplied to plural rinsing means provided in tandem along the transporting direction of the polymer film. Between rinsing means and next rinsing means, there is preferably provided a suitable distance thereby promoting a dilution of the alkaline

coating liquid by diffusion.

A larger number of the rinsing means is more advantageous. However, in consideration of an installation space and a facility cost, there are usually employed 2 to 10 stages, preferably 2 to 5 stages.

Also the transported polymer film is preferably made to incline whereby the water on the polymer film flows along the film surface thereby achieving a mixing dilution by a flow in addition to the diffusion.

Furthermore, the efficiency of rinsing can be significantly improved by providing water squeezing means, for eliminating a water film on the polymer film, between the rinsing means. Specific examples of the water squeezing means include a blade employed in a blade coater, an air knife employed in an air knife coater, a rod employed in a rod coater, and a roll employed in a roll coater.

A thickness of a water film after the water squeezing means is preferably as small as possible, but a water film thickness is limited by the type of the water squeezing means. In a method of contacting a physically solid member such as a blade, a rod or a roll with the polymer film, it is necessary to leave a finite water film as a lubricating fluid since, even in case the solid member is constituted of an elastic member of a low

hardness such as rubber, there may result a scratch on the film surface or an abrasion of the elastic member. Usually there is left a water film of several micrometers or more, preferably 10 μm or more, as a lubricating fluid.

As water squeezing means capable of reducing the water film thickness extremely, an air knife is preferable. With an air knife, the water film thickness may be made close to zero, by employing sufficient air amount and air pressure. However, an excessively high air speed may cause a flapping or a skewing of the polymer film, thus affecting the transporting stability thereof. Therefore, the air speed, though dependent also on the thickness of the water film before squeezing and the transporting speed of the polymer film, is usually selected as 10 to 500 m/sec, preferably 20 to 300 m/sec and more preferably 30 to 200 m/sec.

Also for achieving uniform elimination of the water film, an air blow aperture of the air knife or an air supply method thereto is so regulated that a difference in the air speed in the transversal direction of the polymer film is within 10 %, preferably within 5 % of an average air speed.

A gap between a surface of the transported polymer film and the air blowing aperture of the air knife has an appropriate range since a smaller gap provides a higher

water squeezing ability but results in a higher possibility of causing a scratch by a contact with the polymer film. Therefore, the gap is usually selected as 10 μm to 10 cm, preferably 100 μm to 5 cm and further preferably 500 μm to 1 cm.

Also a backup roll is preferably provided at a side opposite to the rinsed surface of the film, so as to be opposed to the air knife, thereby stabilizing the gap setting and relaxing influences on the film such as a flapping, a crease or a defoamation.

For the water rinsing, purified water is preferably employed. The purified water to be employed in the invention means water having a specific resistivity of at least 1 MΩ or higher, with metal ions such as sodium, potassium, magnesium or calcium less than 1 mg/L and anions such as of chlorine or nitric acid less than 0.1 mg/L. The purified water can be easily obtained by a reverse osmosis film, an ion exchange resin, a distillation or a combination thereof.

A higher temperature of the rinsing water provides a higher rinsing ability. However, in a method of spraying water onto the transported polymer film, the water has a large contact area with the air and evaporates more at a higher temperature, thereby increasing the humidity in the environment and resulting in a danger of dewing.

Therefore, a temperature of the water is usually set within a range of 5 to 90°C, preferably 25 to 80°C and more preferably 25 to 60°C.

In case a component of the alkaline coating liquid or a product of the saponification reaction is not easily soluble in water, a solvent washing step for eliminating a water-insoluble component may be added before or after the step of washing off the alkali solution from the polymer film.

The solvent washing step can be executed in the same manner as the step of washing off the alkali solution from the polymer film, utilizing an organic solvent mentioned as the diluting solvent in the foregoing instead of water.

A drying step may be executed after the step of washing off the alkali solution from the polymer film.

The drying step is usually unnecessary in case the water film can be sufficiently eliminated by the water squeezing means such as an air knife, but may be executed for an adjustment to a desirable water content before the polymer film is wound in a roll.

It is also possible to execute a humidity adjustment with an air flow having a selected humidity.

[Application of saponified cellulose acylate]

[Optical compensation sheet]

A saponified cellulose acylate film is advantageously employed as a transparent substrate of an optical compensation sheet.

An optical compensation sheet has a layered structure in which a cellulose acylate film saponified by coating an alkali saponifying solution, a resin layer for forming an orienting film, and an optical anisotropic layer formed by fixing an orientation of liquid crystal molecules are laminated in this order.

In the formation of an orienting film, after a step of heating the cellulose acylate film, a step of coating an alkali saponifying solution on a surface of the cellulose acylate film at a side of the orienting film, a step of maintaining the temperature of the surface coated with the alkali saponifying solution, a step of terminating the reaction and a step of washing off the alkali saponifying solution from the film surface, it is possible to add a step of coating and drying an orienting film. It is also possible, after the coating and drying of the orienting film, to apply a rubbing process to the surface of the orienting film, and to coat and dry a liquid crystal molecule layer thereby completing a final optical compensation sheet.

An integral operation not only of the saponification process of the cellulose acylate film but also of

formation of the orienting film and the liquid crystal molecule layer provides a high productivity. Also the integral formation provides advantages of absence of a time lapse from the saponification process to the coating of the orienting film, little deterioration of the activated saponified surface, the rinsing step of the saponification process serving also as a wet dust elimination, and absence of loss at the roll ends resulting from plural unwinding and winding operations.

The optical compensation sheet is constituted of a transparent substrate formed by a saponified cellulose acylate film, an orienting film provided thereon, and an optical anisotropic layer formed on the orienting film and having a disk-shaped structural unit. The orienting film is preferably a film of a crosslinked polymer subjected to a rubbing process.

As a compound having a disk-shaped structural unit to be employed in the optical anisotropic layer, there can be employed a disk-shaped liquid crystalline compound of a low molecular weight (monomer) or a polymer obtained by a polymerization of the disk-shaped liquid crystalline compound. The disk-shaped compound (discotic compound) can be generally classified into a compound having a discotic crystal phase (namely a discotic nematic phase) and a compound not having a discotic crystal phase. The

disk-shaped compound generally has a negative birefringence, and the optical anisotropic layer of the invention has such negative birefringence of the discotic compound. The optical anisotropic layer of the invention utilizes such negative birefringence of the discotic compound.

[Orienting film]

An orienting film of the optical anisotropic layer is preferably formed by a rubbing process of a film formed by a crosslinked polymer. The orienting film is further preferably formed by crosslinked two polymers. One of the two polymers is a polymer crosslinkable by itself or a polymer crosslinked by a crosslinking agent. The orienting film can be formed from a polymer having a functional group or a polymer into which a functional group is introduced, by a reaction between the polymers by a light, heat or a pH change, or by employing a crosslinking agent which is a highly reactive compound for introducing a bonding group derived from the crosslinking agent between the polymers thereby crosslinking the polymers.

A crosslinking of the polymer can be executed by heating, after a coating liquid including a polymer or a mixture of a polymer and a crosslinking agent is coated on

the transparent substrate. A crosslinking process may be executed in any stage from the coating of the orienting film on the transparent substrate to the completion of the optical compensation sheet. In consideration of the orienting of the disk-structured compound (optical anisotropic layer) formed on the orienting film, it is also preferable to execute a final orienting after the disk-structured compound is oriented. Thus, in case of coating a coating liquid containing a polymer and a crosslinking agent capable of crosslinking the polymer on the transparent substrate, it is dried by heating and subjected to a rubbing process to form an orienting film, then a coating liquid containing a compound having a disk-shaped structural unit is coated on the orienting film, heated at least to a temperature for forming a discotic nematic phase and cooled to form an optical anisotropic layer.

A polymer to be employed in the orienting film can be a polymer crosslinkable by itself or a polymer crosslinked by a crosslinking agent, or a combination thereof. Examples of the polymer include a polymer such as polymethyl methacrylate, an acrylic acid/methacrylic acid copolymer, a styrene/maleimide copolymer, polyvinyl alcohol and denatured polyvinyl alcohol, poly(N-methylolacrylamide), a styrene/vinyltoluene copolymer,

chlorosulfonated polyethylene, nitrocellulose, polyvinyl chloride, chlorinated polyolefin, polyuester, gelain, polyimide, a vinyl acetate/vinyl chloride copolymer, an ethylene/vinyl acetate copolymer, carboxymethyl cellulose, polyethylene, polypropylene, or polycarbonate, and a silane coupling agent. Preferred examples of the polymer include water-soluble polymers such as poly(N-methylolacrylamide), gelatin, polyvinyl alcohol and denatured polyvinyl alcohol, and gelatin, polyvinyl alcohol and denatured polyvinyl alcohol are preferable, polyvinyl alcohol and denatured polyvinyl alcohol are more preferable, and it is particularly preferable to employ two kinds of polyvinyl alcohol or denatured polyvinyl alcohol in combination.

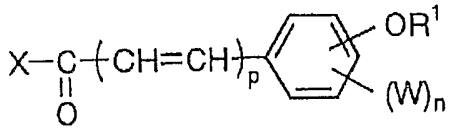
Polyvinyl alcohol preferably has a saponification degree of 70 to 100 %, more preferably 80 to 100 % and most preferably 85 to 95 %. Polyvinyl alcohol preferably has a polymerization degree of 100 to 3000. A denaturing group of denatured polyvinyl alcohol can be introduced by a copolymerization denaturing, a chain shift denaturing or a block polymerization denaturing. Examples of an introduced group in case of copolymerization denaturing include COONa, $Si(OX)_3$, $N(CH_3)_3 \cdot Cl$, $C_9H_{19}COO$, SO_3, Na, and $C_{12}H_{25}$ (wherein X represents a proton or a cation). Examples of an introduced group in case of chain shift

denaturing include COONa, SH, and $C_{12}H_{25}$. Examples of an introduced group in case of block polymerization denaturing include COOH, $CONH_2$, COOR and C_6H_5 (wherein R represents an alkyl group).

Among these, undenatured polyvinyl alcohol or alkylthio-denatured polyvinyl alcohol with a saponification degree of 85 to 95 % is most preferable.

The denatured polyvinyl alcohol is preferably a reaction product of a compound represented by a following general formula (3) and polyvinyl alcohol.

General formula (3)

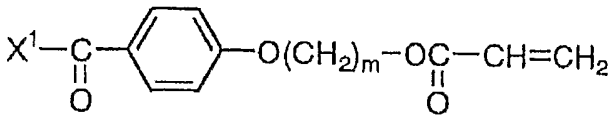


wherein R^{11} represents a non-substituted alkyl group, an acryloyl-substituted alkyl group, a methacryloyl-substituted alkyl group or an epoxy-substituted alkyl group; W represents a halogen atom, an alkyl group or an alkoxy group; X represents an atomic group necessary for forming an active ester, an acid anhydride or an acid halide; p is 0 or 1; and n represents an integer from 0 to 4.

The denatured polyvinyl alcohol is further

preferably a reaction product of a compound represented by a following general formula (4) and polyvinyl alcohol.

General formula (4)



wherein X^1 represents an atomic group necessary for forming an active ester, an acid anhydride or an acid halide, and m represents an integer from 2 to 24.

Polyvinyl alcohol to be reacted with the compound represented by the general formula (3) or (4) may also be a denatured polyvinyl alcohol (copolymerization denatured, chain shift denatured or block polymerization denatured). A method for synthesizing polyvinyl alcohol, a method of measuring a visible absorption spectrum and a method of determining an introduction rate of a denaturing group are described in detail in JP-A No. 8-33891.

Examples of a crosslinking agent for polymer (preferably water-soluble polymer, more preferably polyvinyl alcohol or denatured polyvinyl alcohol) include an aldehyde (such as formaldehyde, glyoxal, or glutaraldehyde), an N-methylol compound (such as dimethylol urea, or methyloldimethylhydantoin), a dioxane derivative (such as 2,3-dihydroxydioxane), a compound

capable of action by activation of a carboxyl group (such as carbenium, 2-naphthalenesulfonat, 1,1-bispyrrolidino-1-chloropyridinium, or 1-morpholinocarbonyl-3-(sulfonataminomethyl)), an active vinyl compound (such as 1,3,5-triacryloyl-hexahydro-s-triazine), bis(vinylsulfone)methane, or N'-methylenebis-[β-(vinylsulfon)propionamide]), an active halogen compound (such as 2,4-dichloro-6-hydroxy-s-triazine), an isooxazole and dialdehyde starch. Two or more crosslinking agents may be used in combination. There is preferred an aldehyde of a high reaction activity, particularly glutaraldehyde.

An amount of addition of the crosslinking agent is preferably 0.1 to 20 weight% with respect to polymer, more preferably 0.5 to 15 weight%. An amount of unreacted crosslinking agent remaining in the orienting film is preferably 1.0 weight% or less, more preferably 0.5 weight% or less. The crosslinking agent remaining in the orienting film in an amount exceeding 1.0 weight% cannot provide a sufficient durability. Such orienting film, in case employed in a liquid crystal display apparatus, may generate a reticulation in a use over a long period or in a prolonged standing under an atmosphere of a high temperature and a high humidity.

An orienting film can be basically formed by coating

the aforementioned polymer containing a crosslinking agent, as a material for forming the orienting film, on the transparent substrate, then drying it by heating (crosslinking) and executing a rubbing process. As explained in the foregoing, the crosslinking reaction may be executed at an arbitrary timing after the coating on the transparent substrate. In case of employing a water-soluble polymer such as polyvinyl alcohol as the material for forming the orienting film, the coating liquid preferably employs a mixed solvent formed by an organic solvent having a defoaming effect (such as methanol) and water. A weight ratio of water:methanol is preferably 0:100 to 99:1, more preferably 0:100 to 91:9. In this manner bubble formation can be suppressed, and surface defects in the orienting film and also in the optical anisotropic layer are significantly reduced.

For coating the orienting film, there is preferred spin coating, dip coating, curtain coating, extrusion coating, rod coating or roll coating. A rod coating method is particularly preferable. A film thickness after drying is preferably 0.1 to 10 μm. Heat drying can be executed at 20 to 110°C. For obtaining sufficient crosslinking, there is preferred a temperature of 60 to 100°C, particularly preferably 80 to 100°C. A drying time is from 1 minute to 36 hours, but is preferably 1 to 30

minutes. A pH value is preferably set at an optimum value for the crosslinking agent to be used, and, in case of employing glutaraldehyde, a preferred pH value is 4.5 to 5.5, particularly 5.

The orienting film is provided on the transparent substrate. The orienting film can be obtained, after crosslinking the polymer layer as explained above, by a rubbing process of a surface. The orienting film is provided for defining an orienting direction of the liquid crystal discotic compound provided thereon.

For the rubbing process, there can be employed a method widely employed as a liquid crystal orienting process for LCD. More specifically, there can be employed a method of rubbing the surface of the orienting film with water, gauze, felt, rubber, nylon fibers or polyester fibers in a fixed direction thereby obtaining an orientation. In general it is executed by a rubbing of several times with a cloth evenly planted with fibers of uniform length and thickness.

[Optical anisotropic layer]

An optical anisotropic layer of the optical compensation sheet is provided on the orienting film. The optical anisotropic layer is preferably a layer formed by a compound of a disk-shaped structural unit and having a

negative birefringence. The optical anisotropic layer is a layer of a liquid crystalline disk-shaped compound of a low molecular weight (monomer) or a layer of a polymer obtained by a polymerization (hardening) of a polymerizable liquid crystalline disk-shaped compound. Examples of the disk-shaped (discotic) compound include a benzene derivative described in C. Destrade et al., Mol. Cryst., 71, p111 (1981), a toluxene derivative described in C. C. Destrade et al., Mol. Cryst., 122, p141 (1985), a toluxene derivative described in Physics lett., A78, p.82(1990), a cyclohexan derivative described in B. Kohne et al., Angew. Chem. 96, p.70(1984), and azacrown-type and phenylacetylene-type macrocycles described in J. Lehn et. al, J. Chem. Commun., p.1794(1985) and J. Zhang et al., J. Am. Chem. Soc., 116, p.2655(1994). A discotic (disk-chaped) compound generally has a structure having these as a nucleus at the center of a molecule and radially substituted with a linear alkyl group, an alkoxy group, or a substituted benzoyloxy group as a linear chain. A disk-shaped compound includes a discotic compound having a liquid crystalline property. An optical anisotropic layer formed from a disk-shaped compound also includes a layer formed by polymerizing or crosslinking a low-molecular discotic liquid crystal, having a group reactive by light or heat, to a high molecular weight whereby the liquid

crystalline property is lost. The disk-shaped compound is described in JP-A No. 8-50206.

The optical anisotropic layer is a layer formed by a compound having a discotic structural unit and having a negative birefringence, and it is preferred that a plane of the discotic structural unit is inclined to the plane of the transparent substrate and that an angle formed by the plane of the discotic structural unit and the plane of the transparent substrate changes in a direction of the depth of the optical anisotropic layer.

An angle (inclination angle) of the plane of the discotic structural unit increases or decreases generally in the direction of depth of the optical anisotropic layer and with an increase in the distance in the optical anisotropic layer from a bottom plane of the orienting film. The inclination angle preferably increases with an increase in such distance. A change of the inclination angle includes a continuous increase, a continuous decrease, an intermittent increase, an intermittent decrease, a change including a continuous increase and a continuous decrease, and an intermittent change including an increase and a decrease. An intermittent change includes an area, in the direction of depth, where the inclination angle does not change. It is preferable that the inclination angle increases or decreases as a whole

even in case an area of no change is included. It is more preferable that the inclination angle increases as a whole, and particularly preferable that the inclination angle increases continuously.

The optical anisotropic layer can generally be obtained by coating and drying a solution, formed by dissolving a discotic compound and other compounds in a solvent, on the orienting film, then heating to a temperature for forming a discotic nematic phase, and then cooling while maintaining an oriented state (discotic nematic phase). Otherwise, the optical anisotropic layer can be obtained by coating and drying a solution, formed by dissolving a discotic compound and other compounds (also a polymerizable monomer and a photopolymerization initiator) in a solvent, on the orienting film, then heating to a temperature for forming a discotic nematic phase, executing a polymerization (for example by UV irradiation) and then cooling. The discotic liquid crystalline compound employed in the invention has a discotic nematic liquid crystal phase-solid phase transition temperature preferably of 70 to 300°C and particularly preferably 70 to 170°C.

An inclination angle of the discotic unit at the side of the substrate can be regulated by selecting generally the discotic compound or the material of the

orienting film, or by selecting the rubbing method. Also an inclination angle of the discotic unit at the surface side (air side) can be regulated by selecting the discotic compound and other compounds (such as a plasticizer, a surfactant, a polymerizable monomer and a polymer) to be employed with the discotic compound. Also a level of change of the inclination angle can be regulated by such selections.

The plasticizer, the surfactant or the polymerizable monomer can be any compound as long as it has an appropriate mutual solubility with the discotic compound and can provide a change in the inclination angle of the liquid crystalline discotic compound or does not hinder the orientation thereof. Among these, a polymerizable monomer (such as a compound having a vinyl group, a vinyloxy group, an acryloyl or a methacryloyl group) is preferred. Such compound is generally employed in 1 to 50 wt.% to the discotic compound, preferably 5 to 30 wt.%.

There can be employed any polymer as long as it has a mutual solubility with the discotic compound and can provide a change in the inclination angle of the liquid crystalline discotic compound. An example of the polymer is a cellulose ester. Preferred examples of cellulose ester include cellulose acetate, cellulose acetate propionate, hydroxypropyl cellulose and cellulose acetate

butyrate. Such polymer is employed, so as not to hinder the orientation of the discotic compound, generally in amount of 0.1 to 10 weight% to the discotic compound, preferably 0.1 to 8 weight% and particularly preferably 0.1 to 5 weight%.

[Polarizing plate]

A polarizing plate has a layered structure of an optical compensation sheet including an orienting film and an optical anisotropic layer formed by liquid crystal molecules with a fixed orientation on a polymer film, a polarizing film, and a transparent protective film, laminated in this order. For the transparent protective film, an ordinary cellulose acetate film may be employed.

The polarizing film can be an iodine-based polarizing film, a dye-based polarizing film utilizing a dichroic dye, or a polyene-based polarizing film. The iodine-based polarizing film and the dye-based polarizing film are generally produced by a polyvinyl alcohol-based film.

A relation of a phase retarding axis of the polymer film and a transmitting axis of the polarizing film varies depending on the kind of the liquid crystal display apparatus to be applied. In TN, MVA or OCB type, there is employed a substantially parallel relationship. In a

reflective liquid crystal display apparatus, there is preferred an arrangement of substantially 45°.

[Liquid crystal display apparatus]

The optical compensation plate or the polarizing plate is advantageously employed in a liquid crystal display apparatus.

A liquid crystal display apparatus of TN, MVA or OCB mode is constituted of a liquid crystal cell and two polarizing plates positioned on both sides thereof. A liquid crystal cell bears liquid crystal between two electrode substrates.

The optical compensation sheet is either positioned by one unit between the liquid crystal cell and one of the polarizing plates, or by two units between the liquid crystal cell and both polarizing plates.

In case of a liquid crystal display apparatus of OCB mode, the optical compensation plate may have, on a polymer film, an optical anisotropic layer including a disk-shaped compound or a rod-shaped liquid crystal compound. The optical anisotropic layer is formed by orienting the disk-shaped compound (or the rod-shaped liquid crystal compound) and fixing the orientation thereof.

The disk-shaped compound generally has a large

birefringence. Also the disk-shaped compound has various orientation states. Therefore, the use of a disk-shaped compound allows to produce an optical compensation sheet of an optical property that cannot be attained in the prior stretched birefringent film. The optical compensation sheet utilizing the disk-shaped compound is desribed in JP-A No. 6-214116, USP Nos. 5,583,679 and 5,646,703 and GP No. 3911620A1.

In a polarizing plate, the aforementioned polymer film can be employed as a transparent protective film to be positioned between the liquid crystal cell and the polarizing film. The aforementioned polymer film is employed only in a transparent protective film (between the liquid crystal cell and the polarizing film) of a polarizing plate, or in two transparent protective films (between the liquid crystal cell and the polarizing film) of both polarizing plates.

The liquid crystal cell is preferably of OCB mode or TN mode.

A liquid crystal cell of OCB mode is a liquid crystal display apparatus utilizing a liquid crystal cell of a bend orientation mode in which rod-shaped liquid crystal molecules are oriented in substantially opposite (symmetrical) directions in an upper part and a lower part

of the liquid crystal cell, and is described in USP Nos. 4,583,825 and 5,410,422. Since the rod-shaped liquid crystal molecules are oriented symmetrically in an upper part and a lower part of the liquid crystal cell, the liquid crystal cell of the bend orientation mode has a self optical compensating function. For this reason, this liquid crystal mode is called OCB (optically compensatory bend) liquid crystal mode. The liquid crystal display apparatus of the bend orientation mode has an advantage of a fast response. In the liquid crystal cell of TN mode, the rod-shaped liquid crystal molecules are oriented substantially horizontally and are twisted by 60 to 120°, in the absence of a voltage application. The liquid crystal cell of TN mode is most widely utilized in a color TFT liquid crystal display apparatus, and is described in many references.

EXAMPLES

In the following, specific embodiments and effects of the present invention will be further explained by examples, but the present invention is not limited to such examples.

[Example 1]

(Preparation of cellulose ester film CF-1)

A following composition was charged in a mixing tank,

and components were dissolved by heating under agitation to obtain a cellulose acetate solution A.

Composition of cellulose acetate composition A	
cellulose triacetate (substitution degree: 2.83, 6-position acyl substitution degree: 0.93, total substitution degree of 2,3-positions: 1.90, viscosity-averaged polymerization degree: 320, water content: 0.4%, viscosity in 6 weight% methylene chloride solution: 305 mPa·s)	100 parts by weight
triphenyl phosphate (plasticizer)	8 parts by weight
biphenyldiphenyl phosphate (plasticizer)	4 parts by weight
methylene chloride (first solvent)	300 parts by weight
methanol (second solvent)	60 parts by weight

Following composition was charged in a disperser and was agitated to disperse and mix components thereby preparing a matting agent solution.

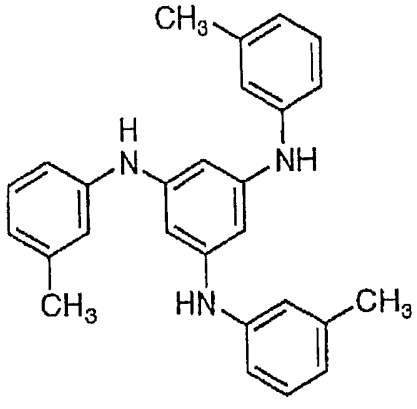
Composition of matting agent solution
silica particles of average particle size 16 nm (AEROSIL R972, manufactured by Nippon Aerosil Co.)

	2 parts by weight
methylene chloride (first solvent)	76 parts by weight
methanol (second solvent)	12 parts by weight
cellulose acetate solution A	10 parts by weight

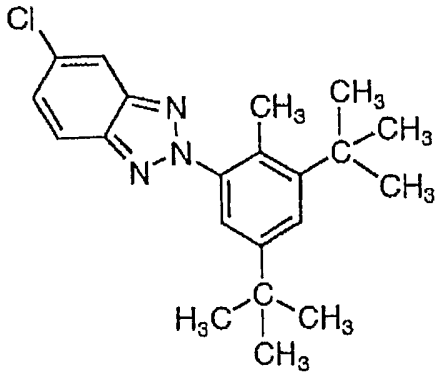
A following composition was charged in a mixing tank, and components were dissolved by heating under agitation to obtain a retardation increasing agent solution A.

Composition of retardation increasing agent solution A	
following retardation increasing agent	
	19.8 parts by weight
following UV absorbing agent (A)	0.07 parts by weight
following UV absorbing agent (B)	0.13 parts by weight
methylene chloride (first solvent)	58.5 parts by weight
methanol (second solvent)	9.0 parts by weight
cellulose acetate solution A	12.5 parts by weight

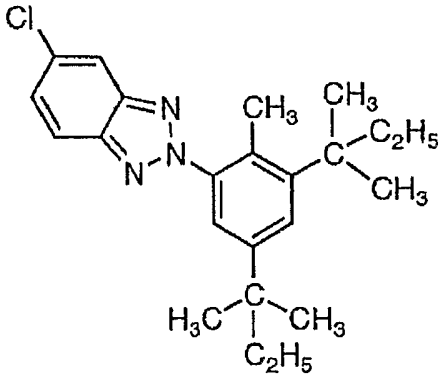
retardation increasing agent



UV absorber A



UV absorber B



95 parts by weight of the cellulose acetate solution A, 1 part by weight of the matting agent solution, and 4 parts by weight of the retardation increasing agent solution were mixed after respective filtrations, and were cast by a band casting machine. The retardation increasing agent had a weight ratio of 3.9 weight% to cellulose acetate. A film with a remaining solvent amount of 30 % was peeled off from the band, and a film with a remaining solvent amount of 15 weight% was transversally stretched by a tenter at 130°C and with a stretching rate of 30 %, and was maintained at a width after stretching for 30 seconds at 140°C. Thereafter it was detached from clips and dried at 140°C to obtain a cellulose acetate film CF-1. The obtained cellulose acetate film had a film thickness of 80 μm.

(Preparation of alkali saponifying solution (S-1) and alkali diluting liquid (SK-1))

An alkali saponifying solution and an alkali diluting liquid were prepared with following formulations.

Formulation of alkali saponifying solution (S-1)	
KOH	560 parts by weight
isopropanol	6080 parts by weight
diethylene glycol	1680 parts by weight
following nonionic surfactant	100 parts by weight
defoaming agent Surfinol DF110D (manufactured by Nisshin Chemical Industries Co.)	2 parts by weight
water	1578 parts by weight

$C_{14}H_{29}O-(CH_2CH_2O)_{10}-H$

Formulation of alkali diluting liquid (SK-1)	
isopropanol	580 parts by weight
diethylene glycol	200 parts by weight
defoaming agent Surfinol DF110D (manufactured by Nisshin Chemical Industries Co.)	1 parts by weight
purified water	9299 parts by weight

(Preparation of saponified film KF-1)

The cellulose acetate film CF-1 was heated to 30°C by passing through an electromagnetic induction heating roll

heated at 60°C, and was coated with the alkali saponifying solution (S-1) maintained at 30°C, in an amount of 15 cc/m^2 with a rod coater. After the film stayed for 10 seconds under a far-infrared steam heater manufactured by Noritake Co., Ltd. and heated at 110°C (film temperature being 30 to 50°C), the alkali diluting liquid was coated in an amount of 20 cc/m^2 with a rod coater, and the alkali was washed off. In this state, the film was maintained at a temperature of 40 to 55°C, and a KOH concentration after the coating of the alkali diluting liquid became 0.4 N. Then a water rinsing with a fountain coater and a water squeezing with an air knife were repeated three times to wash off the alkali agent, and a drying was executed by a drying zone of 70°C with a stay time of 15 seconds whereby an alkali saponified film KF-1 was prepared.

The alkali diluting liquid SK-1 had a carbonate ion concentration of 750 mg/L, a total polyvalent metal ion concentration, including calcium and magnesium, of 30 mg/L, and a chloride ion concentration of 18 mg/L.

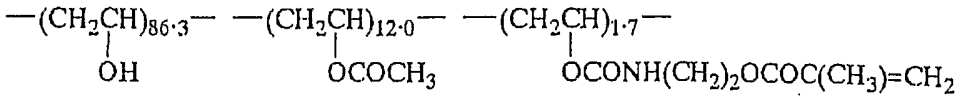
(Formation of orienting film)

On a saponified surface of the saponified film KF-1, a following orienting film coating liquid was coated with a rod coater in an amount of 30 cc/m^2, then dried for 60 seconds with a warm air of 60°C and for 150 seconds with a

hot air of 90°C, and was subjected to a rubbing process with a velvet cloth rubbing roll, positioned rectangularly to the transporting direction, thereby forming an orienting film.

Formulation of orienting film coating liquid	
denatured polyvinyl alcohol	100 parts by weight
water	1800 parts by weight
methanol	600 parts by weight
glutaraldehyde	2.5 parts by weight

denatured polyvinyl alcohol



(Preparation of optical compensation sheet (KHF-1))

On the orienting film formed on the KF-1, a discotic compound solution of a following formulation was coated with a #4 wire bar. In continuation, a heating for 2 minutes was executed in a hot air zone of 130°C connected to a coating unit, thereby orienting the disk-shaped compound. Finally the discotic compound was polymerized in an atmosphere of 80°C by a UV irradiation for 0.4 seconds with a high-pressure mercury lamp of 120 W/cm in a state of a film surface temperature of about 100°C,

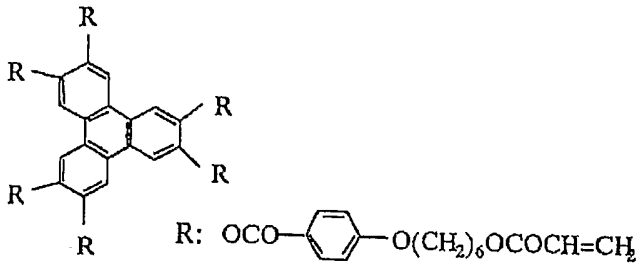
thereby forming an optical anisotropic layer and completing an optical compensation sheet KHF-1.

Formulation of discotic compound solution	
following discotic compound	2735 parts by weight
ethylene oxide-denatured trimethylol propane triacrylate (V#360, manufactured by Osaka Yuki Kagaku Co.)	80 parts by weight
polyfunctional acrylate monomer (NK ester A-TMMT, manufactured by Shin Nakamura Kgaku Kogyo Co.)	190 parts by weight
cellulose acetate butyrate (CAB551-0.2, manufactured by Eastman Chemical Co.)	60 parts by weight
cellulose acetate butyrate (CAB531-1, manufactured by Eastman Chemical Co.)	15 parts by weight
photopolymerization initiator (Irgacure 907, manufactured by Ciba-Geigy Co.)	90 parts by weight
sensitizer (Kayacure DETX, manufactured by Nippon Kayaku Co.	30 parts by weight
methyl ethyl ketone	6800 parts by weight

In the optical compensation film KHF-1, the optical anisotropic layer had a Re retardation, measured at a wavelength of 633 nm, of 38 nm. Also an angle (inclination angle) between a disk plane and a surface of

a first transparent substrate (aforementioned substrate KF-1) was 35° in average.

discotic compound



(Preparation of alkali diluting liquid (SK-2 to SK-9))

Alkali diluting liquids SK-2 to SK-9 were prepared in the same manner as the alkali diluting liquid SK-1 except that the purified water therein was changed to deionized water of a level used in a semiconductor device facility, or water mixed with city water or well water, and that amounts of ions in the alkali diluting liquid were changed as shown in Table 1.

Table 1

alkali diluting liquid	carbonate ion conc. mg/L	polyvalent ion conc. mg/L	chloride ion conc. mg/L	remarks
SK-1	750	30	18	invention
SK-2	32	0.1	0.1	invention

SK-3	90	5.2	2.1	invention
SK-4	350	28	19	invention
SK-5	1530	119	73	invention
SK-6	3330	420	289	invention
SK-7	3580	428	219	comp. ex.
SK-8	3150	509	273	invention
SK-9	2830	420	317	invention

(Preparation of optical compensation sheet (KHF-2 - KHF-9)

Alkali saponified films (KF-2 - KF-9) were prepared in the same manner as the alkali saponified film KF-1, and optical compensation films (KHF-2 - KHF-9) were prepared.

(Evaluation method of saponified film)

The obtained saponified films KHF-1 - KHF-9 were subjected to a haze measurement with an optical testing equipment NDH-300A manufactured by Nippon Denshoku Co. Results are shown in Table 2.

(Evaluation method of optical compensation sheet)

<Foreign substance defect>

Each of the obtained optical compensation films KHF-1 - KHF-9 was sandwiched between two polarizing plates in a cross Nicol arrangement and a foreign substance defect, in which a transmitted light becomes uneven by a foreign

substance, was observed visually. There was counted a number of bright spots within an image frame of 17 inches. Table 2 shows results of evaluation.

<Adhesion>

Each optical compensation sheet was cut into 30 x 25 cm, then, after a standing for 1 day under conditions of a temperature of 25°C and a relative humidity of 60%, a cellophane adhesive tape (No. 405, manufactured by Nichiban Co.) of a width of 1.2 cm and a length of 10 cm was applied in 100 units on the side of the optical anisotropic layer and each peeled off for a period of 1 second, and a peeling between the film and the orienting film was inspected. A relative level of adhesion was evaluated by a number of destructions between the coated layers among 100 cellophane tapes. Table 2 shows results of evaluation.

Table 2

alkali diluting liquid	optical compensation sheet	haze	foreign substance defect	adhesion number of abnormal peeling	remark
SK-1	KHF-1	0.8	0	0	invention
SK-2	KHF-2	0.8	0	0	invention
SK-3	KHF-3	0.8	0	0	invention

SK-4	KHF-4	0.8	0	0	invention
SK-5	KHF-5	0.9	0	0	invention
SK-6	KHF-6	0.9	0	0	invention
SK-7	KHF-7	1.3	4	3	comp. ex.
SK-8	KHF-8	1.4	7	7	invention
SK-9	KHF-9	1.4	3	4	invention

As shown in Table 2, the preferred alkali diluting liquids SK-1 to SK-6 of the invention can provide saponified films of a sufficiently low haze level, without adhesion of the alkali agent or a fatty acid salt to the saponified film at the rinsing of the alkali saponification process. Also there could be obtained satisfactory optical compensation sheets KHF-1 to KHF-6 without a foreign substance defect or a defective adhesion. On the other hand, with the alkali diluting liquid SK-7 of a comparative sample, it is understood that the saponified film obtained by an alkali dilution and a water rinsing shows a high haze, and the corresponding optical compensation sheet caused foreign substance defects and defective adhesion and is inappropriate. Also in SK-8, which is an example of the invention but in which the polyvalent metal ion concentration exceeds the preferable range and in SK-9 in which the chloride ion concentration exceeds the preferable range, the saponified films

obtained by alkali dilution and water rinsing had a haze, foreign substance defect and defective adhesion inferior to those of SK-1 to SK-6. It is thus indicated that, even among the examples of the invention, low concentrations of the polyvalent metal ion concentration and the chloride ion concentration are particularly preferable in addition the carbonate ion concentration of 3500 mg/L or less.

[Example 2]

(Preparation of cellulose ester film TF-1)

A composition of a following table 3 was charged in a mixing tank, and components were dissolved under agitation to obtain a cellulose acetate solution A.

Table 3

Composition of cellulose acetate composition A	
cellulose acetate (substitution degree: 2.83, 6-position acyl substitution degree: 0.93, 3-position acyl substitution degree of 2,3-positions: 1.90, viscosity-averaged polymerization degree: 320, water content: 0.4%, viscosity in 6 weight% methylene chloride solution: 305 mPa·s)	100.0 parts by weight
triphenyl phosphate (plasticizer)	8.0 parts by weight

dipentaerythritol hexaacetate (plasticizer)	4.0 parts by weight
methylene chloride (first solvent)	402.0 parts by weight
methanol (second solvent)	60.0 parts by weight

A composition of a following table 4 was charged in a disperser and components were dissolved by agitation to obtain a matting agent solution.

Table 4

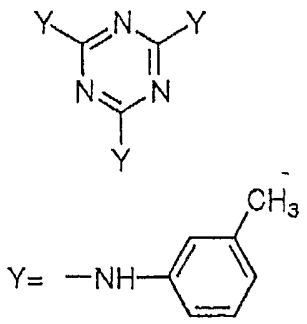
Composition of matting agent solution	
silica particles of average particle size 16 nm (AEROSIL R972, manufactured by Nippon Aerosil Co.)	2.0 parts by weight
methylene chloride (first solvent)	76.0 parts by weight
methanol (second solvent)	11.4 parts by weight
cellulose acetate solution A	10.3 parts by weight

A composition of a following table 5 was charged in a mixing tank, and components were dissolved by heating under agitation to obtain a retardation increasing agent solution A.

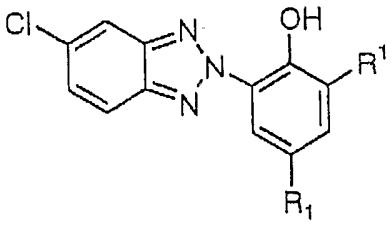
Table 5

Composition of retardation increasing agent solution A	
following retardation increasing agent	
	19.8 parts by weight
UV absorbing agent A	0.07 parts by weight
UV absorbing agent B	0.13 parts by weight
methylene chloride (first solvent)	58.4 parts by weight
methanol (second solvent)	8.7 parts by weight
cellulose acetate solution A	12.8 parts by weight

retardation increasing agent



UV absorber



(A):R^1= $-C_4H_9(t)$

(B):R^1= $-C_5H_{11}(t)$

94.6 parts by weight of the cellulose acetate solution A, 1.3 part by weight of the matting agent solution, and 4.1 parts by weight of the retardation increasing agent solution were mixed after respective filtrations, and were cast by a band casting machine. The retardation increasing agent had a weight ratio of 4.6 weight% to cellulose acetate. A film with a remaining solvent amount of 30 % was peeled off from the band, and a

film with a remaining solvent amount of 13 weight% was transversally stretched by a tenter at 130°C and with a stretching rate of 28 %, and was maintained at a width after stretching for 30 seconds at 140°C. Thereafter it was detached from clips and dried for 40 minutes at 140°C to obtain a cellulose acetate film. The obtained cellulose acetate film had a film thickness of 80 μm.

(Preparation of saponified film SF-1)

The aforementioned cellulose acetate film of a roll width of 1000 mm was heated to a film surface temperature of 30°C by passing through an electromagnetic induction heating roll heated at 60°C, and was coated with an alkali solution (S-1) of a formulation shown in table 4 with a coating amount of 13.5 cc/m^2 with a rod coater and heated to 110°C. After the film stayed for 15 seconds under a far-infrared steam heater manufactured by Noritake Co., Ltd. and purified water was coated in an amount of 3 cc/m^2 with a rod coater. In this state, the film temperature was 40°C. Then a water rinsing with a fountain coater and a water squeezing with an air knife were repeated three times, and a drying was executed by a drying zone of 70°C with a stay time of 5 seconds whereby an alkali saponified film SF-1 was prepared.

2000 m^2 of the cellulose acetate film were saponified

with 35 L of the alkali solution (S-1).

Table 6

Formulation of alkali solution (S-1)	
potassium hydroxide	8.55 weight%
water	23.235 weight%
isopropanol	54.20 weight%
surfactant (K-1: $C_{14}H_{29}O(CH_2CH_2O)_{20}H$)	1.0 weight%
dipropylene glycol	13.0 weight%
defoaming agent Surfinol DF110D (manufactured by Nisshin Chemical Industries Co.)	0.015 weight%

The alkali solution (S-1) had a viscosity of 5.5 mPa·s (25°C) and a surface tension of 22.5 mN/m (25°C).

(Preparation of comparative saponified film SFR-1)

A comparative processing liquid (SR-1) was prepared with a formulation same as that of the alkali solution (S-1) except that the surfactant (K-1), 1.0 weight%, was eliminated from the formulation of the alkali solution (S-1), and a comparative saponified film SFR-1 was prepared, utilizing such processing liquid, in the same manner as the saponified film SF-1. The alkali solution (SR-1) had a viscosity of 5.5 mPa·s (25°C) and a surface tension of 22.6 mN/m (25°C).

(Preparation of comparative saponified film SFR-2)

A comparative processing liquid (SR-2) was prepared of a formulation shown in table 7, formed by eliminating the mutually solubilizing agent from the formulation of the alkali solution (S-1) and proportionally increasing water and the organic solvent corresponding to such elimination, and a comparative saponified film SFR-2 was prepared, utilizing such processing liquid, in the same manner as the saponified film SF-1. The alkali solution (SR-2) had a viscosity of 3.5 mPa·s (25°C) and a surface tension of 22.0 mN/m (25°C).

Table 7

Formulation of alkali solution (SR-2)	
potassium hydroxide	8.55 weight%
water	27.135 weight%
isopropanol	63.30 weight%
surfactant (K-1)	1.0 weight%
defoaming agent Surfinol DF110D (manufactured by Nisshin Chemical Industries Co.)	0.015 weight%

Table 8 shows properties of the used alkali solutions (S-1, SR-1 and SR-2) and performance of the prepared saponified films (SF-1, SFR-1 and SFR-2). In the

table, A and B respectively indicate a sample immediately after the start of the saponification process and a sample after processing 2000 m^2, and the table shows observation and evaluation on each sample.

Table 8

			Ex.1	Comp.Ex.1	Comp.Ex.2
alkali solution		sample No.	S-1	SR-1	SR-2
	Property[1)]	A	+	+	+
		B	+	-	--
saponified film		sample No.	SF-1	SFR-1	SFR-2
	contact angle (°)[2)]	A	30	31	30
		B	30	30-55	30-50
	haze[3)]	A	0.33	0.34	0.33
		B	0.33	turbid	0.9
	foreign sub. turbidity[4)]	A	+	+	+
		B	+	-	-

Evaluation items marked with 1) to 4) in Table 8 were evaluated in the following manner.

1) Properties of alkali solution

Transparency of the alkali solution was visually evaluated with following evaluation criteria:

+: completely transparent without any turbidity or precipitate

-: turbidity generated

--: precipitate generated.

2) Contact angle with water

In a contact angle meter (CA-X, manufactured by Kyowa Kaimen Kagaku Co.), a liquid drop of a diameter of

1.0 mm was formed on a needle tip utilizing purified water as the liquid and in a dry state (20°C/65 %RH), and was contacted with a film surface to form a liquid drop. An angle formed between a tangential line to the liquid surface and the solid surface at a solid-liquid contact point and containing the liquid was taken as a contact angle.

On each film, the contact angle was measured in 9 points at both ends and at center of a plane of 1 square meter, and an upper limit value and a lower limit value were described. However, a range of ±1° was a fluctuation in the measurement, and a center value is shown.

3) Haze

Haze of the saponified film was measured with an optical testing equipment NHD101DP, manufactured by Nippon Denshoku Co.

4) Foreign substance, turbidity

A saponified film was cut into a length of 1 m with a full width, and such sample was observed for foreign substances and turbidity, with bare eyes and under a magnifier with a transmitting light on a light box, and evaluated under following criteria.

+: foreign substance and turbidity totally unobserved (a level of no observation in an evaluation by 10 persons)

±: weak generation of foreign substance, turbidity (a

level of observation by 2 to 5 persons in an evaluation by 10 persons)

-: strong generation of foreign substance, turbidity (a level of observation by 6 or more persons in an evaluation by 10 persons).

As shown in Table 8, in the embodiment of the invention, the alkali solution was transparent even after processing 2000 m^2 of film, and the film surface after the saponification process had a water contact angle of 30°. Also the saponified film showed little haze, and the foreign substance or the turbidity was not observed at all.

On the other hand, the comparative alkali solutions (SR-1) and (SR-2) developed turbidity or precipitate after processing 2000 m^2.

Also the comparative alkali saponified films SFR-1 and SFR-2 had, immediately after the start of saponification process (SFR-1A and SFR-2A), a performance similar to that of the film SF-1 of the invention, but, samples after processing of 2000 m^2 (SFR-1B and SFR-2B) showed a larger fluctuation of the water contact angle in the plane, an increased haze and a turbidity and foreign substances on the film surface and were not in a practically acceptable level.

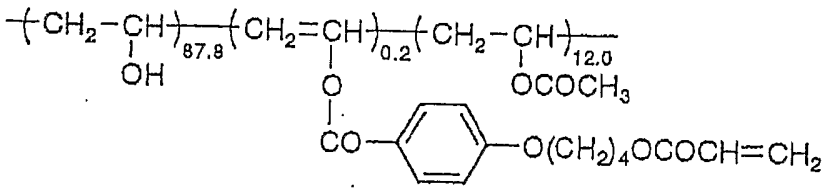
Then, the film SF-1 of the invention, showing satisfactory performance both in parts A and B of the

saponification process, was used to prepare an optical film as explained in the following and was subjected to an evaluation of the performance.

(Formation of orienting film)

On a saponified surface of a sample (SF-1A) immediately after the start of saponification and a sample (SF-1B) after a processing of 2000 m^2 of the saponified film SF-1, an orienting film coating liquid, formed by 20 parts by weight of denatured polyvinyl alcohol of a following structure, 360 parts by weight of water, 120 parts by weight of methanol and 0.5 parts by weight of glutaraldehyde, was coated with a rod coater in an amount of 30 cc/m^2, then dried for 60 seconds with a warm air of 60°C and for 150 seconds with a hot air of 90°C, and was subjected to a rubbing process with a velvet cloth rubbing roll, positioned rectangularly to the transporting direction, thereby forming an orienting film.

denatured polyvinyl alcohol

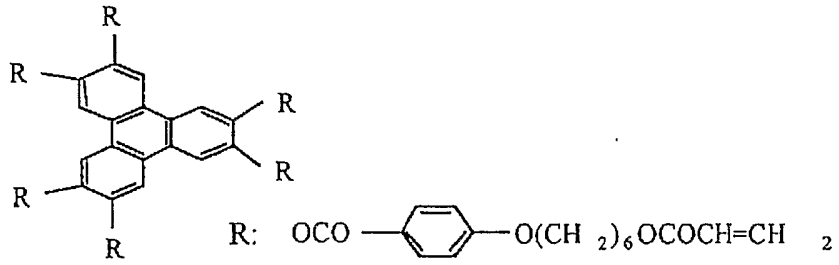


(Preparation of optical anisotropic layer)

On the orienting film formed on the samples SF-1A and SF-1B, 41.01 parts by weight of a following discotic compound, 1.22 parts by weight of ethylene oxide-denatured trimethylol propane triacrylate (V#360, manufactured by Osaka Yuki Kagaku Co.), 2.84 parts by weight of polyfunctional acrylate monomer (NK ester A-TMMT, manufactured by Shin Nakamura Kgaku Kogyo Co.), 0.90 parts by weight of cellulose acetate butyrate (CAB551-0.2, manufactured by Eastman Chemical Co.), 0.23 parts by weight of cellulose acetate butyrate (CAB531-1, manufactured by Eastman Chemical Co.), 1.35 parts by weight of a photopolymerization initiator (Irgacure 907, manufactured by Ciba-Geigy Co.), and 0.45 parts by weight of a sensitizer (Kayacure DETX, manufactured by Nippon Kayaku Co. were coated, after dissolving in 102 parts by weight of methyl ethyl ketone, with a #4 wire bar. In continuation, a heating for 2 minutes was executed in a connected hot air zone of 130°C, thereby orienting the disk-shaped compound. Finally the discotic compound was polymerized in an atmosphere of 80°C by a UV irradiation for 0.4 seconds with a high-pressure mercury lamp of 120 W/cm in a state of a film surface temperature of about 100°C, thereby forming an optical anisotropic layer. The optical anisotropic layer had a Re retardation, measured

at a wavelength of 633 nm, of 45 nm. Also an angle (inclination angle) between a disk plane and a surface of a first transparent substrate was 39° in average.

discotic compound



(Evaluation method for optical compensation sheet)

Haze

On the obtained films SF-1 - SF-4 and SFR-1, a haze measurement was conducted with an optical testing equipment NHD-101DP, manufactured by Nippon Denshoku Co.

Each optical compensation film was sandwiched between two polarizing plates in a cross Nicol arrangement and an evenness in the transmitting light was visually observed and subjectively evaluated.

+: totally absent (a level of no observation in an evaluation by 10 persons)

±: weak generation (a level of observation by 1 to 5 persons in an evaluation by 10 persons)

-: strong generation (a level of observation by 6 or more persons in an evaluation by 10 persons).

Adhesion

Each optical compensation sheet was cut into 30 x 25 cm, then, after a standing for 1 day under conditions of a temperature of 25°C and a relative humidity of 60%, a cellophane adhesive tape (No. 405, manufactured by Nichiban Co.) of a width of 1.2 cm and a length of 10 cm was applied in 5 units on the side of the optical anisotropic layer and each peeled off for a period of 1 second, and a peeling between the film and the orienting film was inspected. A relative level of adhesion was evaluated by a number of destructions between the coated layers among 10 cellophane tapes. Table 9 shows results of evaluation.

Table 9

Sample No.	saponified cellulose acylate film	haze	unevenness in transmitted light	adhesion
1	SF-1-A	0.35	+	0(number)
2	SF-1-B	0.35	+	0(number)

As shown in Table 9, SF-1 and SF-2 subjected to the saponification process of the invention were low in haze and did not show unevenness in the transmitted light. Also the adhesion was sufficient and satisfactory.

As explained in the foregoing, saponified cellulose acylate prepared by the method of the invention and an optical film utilizing the same are excellent in uniformity and satisfactory also in the adhesion.

[Example 3]

(Saponified cellulose triacetate film)

A cellulose triacetate film: Fujitac TD80UF (manufactured by Fuji Photo Film Co.) was heated to 45°C by a collision of a hot air of 100°C, then coated with a following alkali solution (S-2) maintained at 25°C in an amount of 14 cc/m^2 with a rod coater, and, after a lapse of 13 seconds, again coated with purified water in an amount of 5 cc/m^2 with a rod coater. In this state, the film had a temperature of 45°C. Then purified water of 1000 cc/m^2 was coated by an extrusion coater to execute water rinsing, and, after a lapse of 5 seconds, an air of 100 m/sec was made to collide from an air knife to the water-coated surface. After repeating the rinsing with the extrusion coater and the water squeezing by the air knife twice, drying was conducted in a drying zone of 80°C for a stay time of 10 seconds, thereby obtaining a saponified film SF-2. As in the Example 2, a film of 2000 m^2 was saponified.

Table 10

Formulation of alkali solution (S-2)	
potassium hydroxide	6.5 weight%
water	19.49 weight%
n-propanol	58.5 weight%
diethylene glycol	14.5 weight%
surfactant (K-2: ethylene diamine ethylene oxide addition product	1.0 weight%
defoaming agent Surfinol 104 (manufactured by Nisshin Chemical Industries Co.)	0.01 weight%

The alkali solution (S-2) had a viscosity of 5.6 mPa·s (25°C) and a surface tension of 22.8 N/m (25°C).

On samples of the obtained film, at the start of the saponification and after the processing of 2000 m^2 (SF-2A and SF-2B), a surface energy determined by a following method was 60 mN/m.

The surface energy was determined by a contact angle method described in "Basis and application of wetting" (Realize-sha, published December 10, 1989). Two solutions of water and methylene iodide with known surface energies were dropped on a cellulose acetate film, and an angle formed between a tangential line to a liquid drop and the film surface at a crossing point of the liquid drop

surface and the film surface and containing the liquid drop was taken as a contact angle, and the surface energy of the film was obtained by a calculation.

A polarizing plate was prepared by adsorbing iodine on a stretched polyvinyl alcohol film, then the optical compensation sheet prepared in the Example 1 was adhered on a side of the polarizing film with a polyvinyl alcohol adhesive, and the saponified film SF-2A was adhered on the other side with a polyvinyl alcohol adhesive, and a drying was executed for 10 minutes at 80°C. A transmission axis of the polarizing film was arranged parallel to a phase retarding axis of the optical compensation sheet prepared in the Example 1. A phase retarding axis of the polarizing film and a phase retarding axis of the cellulose triacetate film were arranged perpendicularly. A polarizing plate was prepared in this manner.

Also a polarizing plate was prepared in the same manner, replacing the saponified film SF-2A by SF-2B.

(Liquid crystal display apparatus)

In a liquid crystal display apparatus utilizing a TN liquid crystal cell (6E-A3, manufactured by Sharp Inc.), a pair of polarizing plates provided thereon were peeled off, and polarizing plates prepared as explained above were adhered instead respectively on an observer side and a

backlight side with an adhesive, in such a manner that the optical compensation sheet prepared in Example 1 was positioned at the side of the liquid crystal cell. A transmitting axis of the polarizing plate at the observer side and a transmitting axis of the polarizing plate at the backlight side were positioned in an O mode.

On thus prepared liquid crystal display apparatus, a measuring instrument (EZ-Contrast 160D, manufactured by ELDIM Co.) was used, and an image unevenness at a black display (L1) was visually observed.

As a result, the device employing the saponified film SF-2A or SF-2B by the method of the invention provided an sharp image of a high luminance without haze over the entire image area in both cases.

The foregoing result of visual observation indicates that the use of a cellulose acylate film, saponified by the method of the invention in a long web film, provides satisfactory optical characteristics.

[Example 4]

A cellulose acylate film provided with an antireflection film was prepared according to the description of JP-A No. 2002-182033, Example 2. Then a polyethylene terephthalate film (SAT-106TS, manufactured by Sanei Kaken) was adhered to a surface of an antistain

layer of the cellulose acylate film. A master etching processor E-380°C for an electronic platemaking system was employed as an immersion processing apparatus, and an alkali solution (S-3) of a following formulation was charged in this apparatus and was set at a liquid temperature of 45°C. After the film was immersed for a immersion time of 10 seconds, it was immersed in water to sufficiently wash off the alkali solution. It was then immersed in a 0.5% dilute sulfuric acid solution for 10 seconds, then was immersed in water and sufficiently washed. Then the film was dried at 100°C to obtain a saponified cellulose acylate film (SF-3). The polyethylene terephthalate film was removed from the cellulose triacetate film to obtain a first polarizing plate protective film.

Table 11

Formulation of alkali solution (S-3)	
potassium hydroxide	4.0 weight%
water	42.7 weight%
methyl cellosolve	40.0 weight%
tetraethylene glycol	12.0 weight%
surfactant (K-2: $C_9H_{19}Ph(OCH_2CH_2)_8SO_3Na$ (Ph: phenylene group))	1.3 weight%

defoaming agent Purlonic TR70 (manufactured by Asahi Denka Co.)	0.1 weight%

The alkali solution (S-3) had a viscosity of 2.0 mPa·s (25°C) and a surface tension of 35.0 mN/m (25°C).

(Preparation of second polarizing plate protective film)

A polyethylene terephthalate film (SAT-106TS, manufactured by Sanei Kaken) was adhered to a surface of another cellulose triacetate film prepared in the aforementioned method. After a saponification process same as in the preparation of the first second polarizing plate protective film, the polyethylene terephthalate film was eliminated to obtain a second polarizing plate protective film.

(Preparation of polarizing plate)

A polyvinyl alcohol film of a thickness of 75 μm (manufactured by Kuraray Co.) was immersed for 5 minutes in an aqueous solution containing 7 parts by weight of iodine and 105 parts by weight of potassium iodide in 1000 parts by weight of water, thereby causing iodine adsorption on the film. Then the film was monoaxially stretched 4.4 times in the longitudinal direction in a 4 weight% aqueous solution of boric acid of 40°C, and dried

in a tensioned state to obtain a polarizing film. A saponified surface of the cellulose triacetate film constituting the first polarizing plate protective film was adhered to a surface of the polarizing film with a polyvinyl alcohol adhesive, and a saponified surface of the cellulose triacetate film constituting the second polarizing plate protective film was adhered to the other surface of the polarizing film with a polyvinyl alcohol adhesive.

(Evaluation of polarizing plate)

100 polarizing plates were prepared in the aforementioned method, and were respectively adhered to glass plates with an acrylic adhesive, and these were placed in a chamber of constant temperature and constant humidity and were subjected to a durability test of 1000 hours in total, during which the interior of the chamber of constant temperature and constant humidity was switched between an atmosphere of 70°C, 93 %RH and an atmosphere of 25°C, 93 %RH every 12 hours. On the 100 samples taken out from the chamber of constant temperature and constant humidity, peeling and bubble generation between the polarizing plate and the glass plate were inspected and were not found in any of the 100 samples.

Also in a commercially available liquid crystal

monitor of thin film transistor (TFT) type, polarizing plates on both sides were peeled off and the aforementioned polarizing plates were adhered on both sides, and presence of unevenness in black display and white display was visually evaluated. A visual defect such as an unevenness was not observed at all over the entire image area.

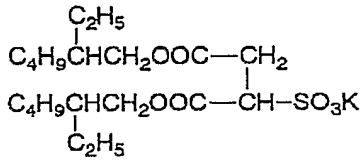
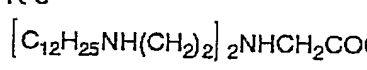
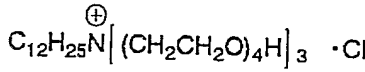
[Example 5]

(Saponified cellulose triacetate film)

An antireflection film described in Example 4 was provided on a surface of a cellulose acylate film, and a surface not coated with the antireflection film was heated to 45°C by a collision of a hot air of 80°C, then coated with each of following alkali solutions (S4 - 7) of formulations shown in Table 12, maintained at 35°C, in an amount of 5 cc/m^2 with a rod coater, and, after a lapse of 10 seconds, again coated with purified water in an amount of 5 cc/m^2 with a rod coater. In this state, the film had a temperature of 45°C. Then purified water of 1000 cc/m^2 was coated by an extrusion coater to execute water rinsing, and, after a lapse of 5 seconds, an air of 100 m/sec was brown from an air knife. After repeating twice the rinsing with the extrusion coater and the water squeezing by the air knife, drying was conducted in a drying zone of

80°C for a stay time of 10 seconds, thereby obtaining saponified films SF-2 - SF-7.

Table 12

saponified film	alkali processing liquid (S)	alkali agent	water (distilled water)	organic solvent	surfactant	humidifier	other additives
SF	S-4	KOH(7.0)	33.0	2-butanol (24) ethanol (24.5)	K-4 sorbitan monostearate PEO ether (1.5)	trimethylol propane (10)	Surfinol 104 (0.01)
SF	S-5	KOH(8.5)	30.5	isopropanol (32) ethanol (24)	K5  (1.0)	propylene glycol (8) glycerin (6)	ibid.
SF	S-6	NaOH(6.0)	32.5	propylene glycol monomethyl ether (32.5)	K-6  (1.4)	diethylene glycol (10) D-lactose (3)	ibid.
SF	S-7	KOH(8.5)	76.8	isopropanol (49.4)	K-7  (1.3)	propylene glycol (14)	ibid.

note: parenthesized number indicates weight%.

As to the organic solvents in Tables 6, 7, 10, 11 and 12, solubility parameter ($[mJ/m^3]^{1/2}$) and I/O value, though described before, are shown in the following.

Organic solvent	Solubility parameter	I/O value
isopropanol	23.5	2.00
n-propanol	24.3	1.67
methyl cellosolve	23.3	2.00
2-butanol	22.1	1.25
ethanol	26.0	2.50
propylene glycol monomethyl ether	20.7	1.50
methanol	29.7	5.00

The alkali solutions (S-4 - S-7) had a viscosity of 1.8 to 6 mPa·s (25°C) and a surface tension of 20 to 30 mN/m (25°C).

The films (SF-4 - 7) had a contact angle with water within a range of 30 to 35°.

Then, polarizing plates were prepared from saponified film of SF-4 to SF-7 as a substitute for saponified film prepared in the Example 4. The spolarizing plates were evaluated by the method in the Example 4, as a result, equivalent property of Example 4 was shown.

[Example 6 and comparative example]

A peeling film (manufactured by Rintec Co.) was adhered to a surface of a cellulose triacetate film of a roll width of 1000 mm (Fujitac TD80UF (manufactured by Fuji Photo Film Co.)). A master etching processor E-380II for an electronic platemaking system was employed as an immersion processing apparatus for the film, and an alkali solution (S-1) of a following formulation was charged in this apparatus and was set at a liquid temperature of 40°C. After the film was immersed for a immersion time of 45 seconds, it was immersed in water to sufficiently wash off the alkali solution. It was then immersed in a 0.5% dilute sulfuric acid solution for 10 seconds, then was immersed in water and sufficiently washed. Then the film was dried at 100°C and the peeling film was peeled off to obtain a saponified cellulose acylate film (SF-1).

Table 13

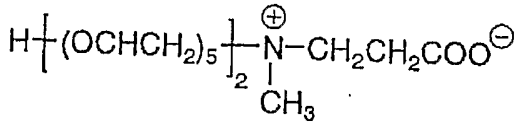
Formulation of alkali solution (S-1)	
potassium hydroxide	6.0 weight%
water	87.5 weight%
propylene glycol	5.0 weight%
surfactant (K-1: following structure)	

1.5 weight%

defoaming agent Surfinol DF110D (manufactured by Nisshin Kagaku Kogyo Co.) 0.010 weight%

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surfactant K-1



30 L of the alkali solution (S-1) were used to saponify 1000 m^2 of the aforementioned cellulose acetate film.

(Preparation of comparative saponified film SFR-1)

A comparative processing liquid (SR-1) was prepared with a formulation same as that of the alkali solution (S-1) except that the surfactant (K-1), 1.0 weight%, was eliminated from the formulation of the alkali solution (S-1), and a comparative saponified film SFR-1 was prepared, utilizing such processing liquid, in the same manner as the saponified film SF-1.

(Preparation of comparative saponified film SFR-2)

A 6.0 weight% aqueous solution of sodium hydroxide was prepared as a comparative processing liquid (SR-2) instead of the alkali solution (S-1), and a comparative

saponified film SFR-2 was prepared, utilizing such processing liquid, in the same manner as the saponified film SF-1.

Properties of the used alkali solutions (S-1, SR-1 and SR-2) and performance of the prepared saponified films (SF-1, SFR-1 and SFR-2) were evaluated in following methods and are shown in Table 14. In the table, A and B respectively indicate a sample immediately after the start of the saponification process and a sample after processing 1000 m^2, and the table shows observation and evaluation on each sample.

(Evaluation of saponified film)

The saponifying alkali solutions and the saponified films were evaluated on the following items.

1) Properties of alkali solution

Transparency of the alkali solution was visually evaluated with following evaluation criteria:

+: completely transparent without any turbidity or precipitate

-: turbidity generated

--: precipitate generated.

2) Contact angle with water

In a contact angle meter (CA-X, manufactured by

Kyowa Kaimen Kagaku Co.), a liquid drop of a diameter of 1.0 mm was formed on a needle tip utilizing purified water as the liquid and in a dry state (20°C/65 %RH), and was contacted with a film surface to form a liquid drop. An angle formed between a tangential line to the liquid surface and the solid surface at a solid-liquid contact point and containing the liquid was taken as a contact angle.

On each film, the contact angle was measured in 9 points at both ends and at center of a plane of 1 square meter, and an upper limit value and a lower limit value were described. However, a range of ±1° was a fluctuation in the measurement, and a center value is shown.

3) Foreign substance, turbidity

A saponified film was cut into a length of 1 m with a full width, and such sample was observed for foreign substances and turbidity, with bare eyes and under a magnifier with a transmitting light on a light box, and evaluated under following criteria.

+: foreign substance and turbidity totally unobserved (a level of no observation in an evaluation by 10 persons)

±: weak generation of foreign substance, turbidity (a level of observation by 2 to 5 persons in an evaluation by 10 persons)

-: strong generation of foreign substance, turbidity (a

level of observation by 6 or more persons in an evaluation by 10 persons).

Table 14

			Ex.1	Comp.Ex.1	Comp.Ex.2
alkali solution		sample No.	S-1	SR-1	SR-2
	Property	A	+	+	+
		B	+	-	--
saponified film		sample No.	SF-1	SFR-1	SFR-2
	contact angle (°)	A	38	39	40
		B	38	40-55	40-50
	foreign sub. turbidity	A	+	+	+
		B	+	-	-

As shown in Table 14, in the embodiment of the invention, the alkali solution was transparent without yellow coloration even after processing 1000 m^2 of film, and no precipitate or deposit was observed in the processing tank after the recovery of the liquid after processing. The surface of the saponified film (SF-1) had a water contact angle of 38° at the start and after the processing of 1000 m^2. Also the saponified film showed no foreign substance or turbidity at all and the transparency was satisfactory.

On the other hand, the comparative alkali solutions (SR-1) and (SR-2) developed yellowing coloring, turbidity or precipitate after processing 1000 m^2.

Also the comparative alkali saponified film SFR-1

had, immediately after the start of saponification process (SFR-1A and SFR-2A), a performance similar to that of the film SF-1 of the invention, but, samples after processing of 1000 m^2 (SFR-1B and SFR-2B) showed a larger fluctuation of the water contact angle in the plane, an increased haze and a turbidity and foreign substances on the film surface and were not in a practically acceptable level. The comparative alkali saponified film SFR-2, in the conditions (temperature and time) of Example 6, showed insufficient saponification, showing a large water contact angle with an extremely large fluctuation within the plane.

(Polarizing plate)

Then, the film SF-1 of the invention, showing satisfactory performance both in parts A and B of the saponification process, was used to prepare an optical film as explained in the following and was subjected to an evaluation of the performance.

The saponified film (SF-1) was adhered on both sides of a polyvinyl alcohol polarizing film of a thickness of 25 μm (average polymerization degree: 3500, average saponification degree: 99.5 mol.%, stretched 5 times) utilzing aa polyvinyl alcohol adhesive (3% aqueous solution, dry coating thickness 0.01 μm) and dried for 1 minute at 100°C to obtain a polarizing plate.

(Evaluation of polarizing plate)

Then, a following test was conducted in order to investigate an adhesion between the triacetyl cellulose film and the polarizing film in the polarizing plate.

<Punching test>

After the polarizing plate was let to stand for 500 hours under conditions of 65°C and 95 %RH, it was punched with a cutter (TCM-500A, manufactured by Toko Co.) with a circular blade of a diameter of 35 mm and an adhesion was evaluated with following criteria:

+: no peeling observed between the film (SF-1) and the polarizing film;

-: peeling observed between the film (SF-1) and the polarizing film.

As a result, the adhesion was extremely satisfactory with + results.

<Peeling test>

100 polarizing plates were prepared in the aforementioned method, and were respectively adhered to glass plates with an acrylic adhesive, and these were placed in a chamber of constant temperature and constant humidity and were subjected to a durability test of 1000 hours in total, during which the interior of the chamber of constant temperature and constant humidity was switched

between an atmosphere of 70°C, 93 %RH and an atmosphere of 25°C, 93 %RH every 12 hours. On the 100 samples taken out from the chamber of constant temperature and constant humidity, peeling and bubble generation between the polarizing plate and the glass plate were inspected and were not found in any of the 100 samples.

Also in a commercially available liquid crystal monitor of thin film transistor (TFT) type, polarizing plates on both sides were peeled off and the aforementioned polarizing plates were adhered on both sides, and presence of unevenness in black display and white display was visually evaluated. A visual defect such as an unevenness was not observed at all over the entire image area.

[Example 7]

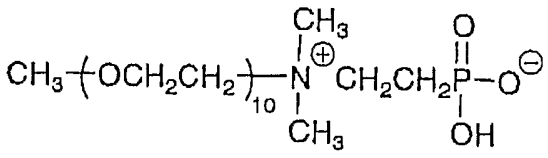
A cellulose acylate film provided with an antireflection film was prepared according to the description of JP-A No. 2002-182033, Example 1. A processed surface of the cellulose acylate film opposite to the antireflection layer was passed through an electromagnetic induction heating roll heated at 60°C to elevate the film surface to a temperature of 30°C, then an alkali solution (S-2) of a following formulation was coated with a coating amount of 10 cc/m^2 with a rod coater and heated to 110°C by staying

for 15 seconds under a far-infrared steam heater manufactured by Noritake Co., Ltd. and purified water was coated in an amount of 3 cc/m^2 with a rod coater. In this state, the film temperature was 40°C. Then a water rinsing with a fountain coater and a water squeezing with an air knife were repeated three times, and a drying was executed by a drying zone of 70°C with a stay time of 5 seconds whereby an alkali saponified film SF-2 was prepared.

Table 15

<Formulation of alkali processing liquid (S-2)>	
potassium hydroxide	5.7 weight%
water	33.3 weight%
n-propyl alcohol	49.8 weight%
ethylene glycol	10.0 weight%
surfactant (K-2: following structure)	1.2 weight%
defoaming agent Purlonic TR70 (manufactured by Asahi Denka Co.)	0.01 weight%

surfactant (K-2)



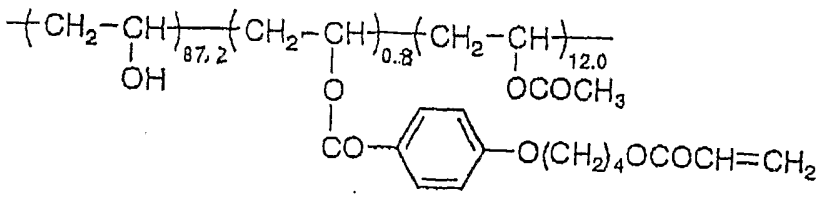
In the obtained film, samples (SF-2A and SF-2B) at the start of the saponification and after processing 2000 m^2 both had a water contact angle of 33°. Also the saponified film showed no foreign substance or turbidity was not at all, and the transparency was satisfactory.

Then, the film SF-2 of the invention, showing satisfactory performance both in parts A and B of the saponification process, was used to prepare an optical film as explained in the following and was subjected to an evaluation of the performance.

(Formation of orienting film)

On a saponified surface of a sample (SF-2A) immediately after the start of saponification and a sample (SF-2B) after a processing of 2000 m^2 of the saponified film SF-1, an orienting film coating liquid, formed by 20 parts by weight of denatured polyvinyl alcohol of a following structure, 360 parts by weight of water, 120 parts by weight of methanol and 0.5 parts by weight of glutaraldehyde, was coated with a rod coater in an amount of 30 cc/m^2, then dried for 60 seconds with a warm air of 60°C and for 150 seconds with a hot air of 90°C, and was subjected to a rubbing process with a velvet cloth rubbing roll thereby forming an orienting film.

denatured polyvinyl alcohol

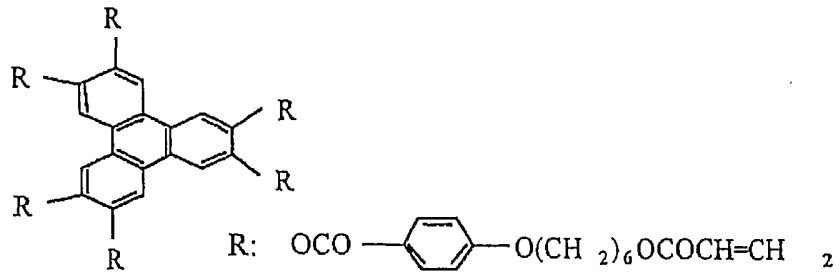


(Preparation of optical anisotropic layer)

On the orienting film formed on the samples SF-2A and SF-2B, 41.01 parts by weight of a following discotic compound, 1.22 parts by weight of ethylene oxide-denatured trimethylol propane triacrylate (V#360, manufactured by Osaka Yuki Kagaku Co.), 2.84 parts by weight of polyfunctional acrylate monomer (NK ester A-TMMT, manufactured by Shin Nakamura Kgaku Kogyo Co.), 0.90 parts by weight of cellulose acetate butyrate (CAB551-0.2, manufactured by Eastman Chemical Co.), 0.23 parts by weight of cellulose acetate butyrate (CAB531-1, manufactured by Eastman Chemical Co.), 1.35 parts by weight of a photopolymerization initiator (Irgacure 907, manufactured by Ciba-Geigy Co.), and 0.45 parts by weight of a sensitizer (Kayacure DETX, manufactured by Nippon Kayaku Co. were coated, after dissolving in 102 parts by weight of methyl ethyl ketone, with a #4 wire bar. In continuation, a heating for 2 minutes was executed in a connected hot air zone of 130°C, thereby orienting the

disk-shaped compound. Finally the discotic compound was polymerized in an atmosphere of 80°C by a UV irradiation for 0.4 seconds with a high-pressure mercury lamp of 120 W/cm in a state of a film surface temperature of about 100°C, thereby forming an optical anisotropic layer. The optical anisotropic layer had a Re retardation, measured at a wavelength of 633 nm, of 45 nm. Also an angle (inclination angle) between a disk plane and a surface of a first transparent substrate was 39° in average.

discotic compound



(Evaluation method for optical compensation sheet)

Haze

On the optical compensation sheets prepared from SF-2A and SF-2B, a haze measurement was conducted with an optical testing equipment NHD 101DP, manufactured by Nippon Denshoku Co.

Unevenness in transmitted light

Each optical compensation film was sandwiched

between two polarizing plates in a cross Nicol arrangement and an evenness in the transmitting light was visually observed and subjectively evaluated.

+: totally absent (a level of no observation in an evaluation by 10 persons)

±: weak generation (a level of observation by 1 to 5 persons in an evaluation by 10 persons)

-: strong generation (a level of observation by 6 or more persons in an evaluation by 10 persons).

Adhesion

Each optical compensation sheet was cut into 30 x 25 cm, then, after a standing for 1 day under conditions of a temperature of 25°C and a relative humidity of 60%, a cellophane adhesive tape (No. 405, manufactured by Nichiban Co.) of a width of 1.2 cm and a length of 10 cm was applied in 5 units on the side of the optical anisotropic layer and each peeled off for a period of 1 second, and a peeling between the film and the orienting film was inspected. A relative level of adhesion was evaluated by a number of destructions between the coated layers among 10 cellophane tapes.

SF-2A and SF-2B, subjected to the saponification of the invention, showed low haze and did not show an unevenness in the transmitted light. Also the adhesion was sufficient.

As explained above, the saponified cellulose acylate film prepared by the method of the invention and the optical film employing the same are excellent in uniformity and also have satisfactory adhesion.

[Example 8]

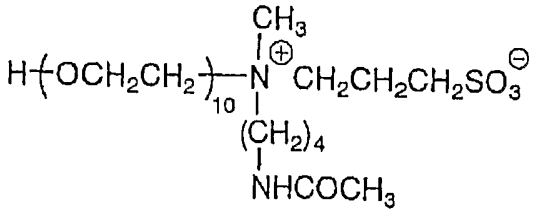
(Saponified cellulose triacetate film)

A cellulose triacetate film: Fujitac TD80UF (manufactured by Fuji Photo Film Co.) was heated to 45°C by a collision (emission heating) of a hot air of 100°C, then coated with a following alkali solution (S-3) maintained at 25°C in an amount of 14 cc/m^2 with a rod coater, and, after a lapse of 13 seconds, again coated with purified water in an amount of 5 cc/m^2 with a rod coater. In this state, the film had a temperature of 45°C. Then purified water of 1000 cc/m^2 was coated by an extrusion coater to execute water rinsing, and, after a lapse of 5 seconds, an air of 100 m/sec was made to collide (spray) from an air knife to the water-coated surface. After repeating the rinsing with the extrusion coater and the water squeezing by the air knife twice, drying was conducted in a drying zone of 80°C for a stay time of 10 seconds, thereby obtaining a saponified film SF-3. A film of 2000 m^2 was saponified.

Table 16

<Formulation of alkali solution (S-3)>	
potassium hydroxide	6.5 weight%
water	32.0 weight%
isopropanol	48.3 weight%
diethylene glycol	12.0 weight%
surfactant (K-3: following structure	1.2 weight%
defoaming agent Surfinol 104 (manufactured by Nisshin Chemical Industries Co.)	0.01 weight%

surfactant (K-3)



On samples of the obtained film, at the start of the saponification and after the processing of 2000 m^2 (respectively called SF-3A and SF-3B), a surface had a contact angle with water of 30° and a fluctuation of the contact angle was within an error of measurement over the entire surface, indicating a uniform saponification.

Also each film sample (SA-3A and SF-3B) had a

surface energy, determined by a following method, of 60 mN/m.

The surface energy was determined by a contact angle method described in "Basis and application of wetting" (Realize-sha, published December 10, 1989). Two solutions of water and methylene iodide with known surface energies were dropped on a cellulose acetate film, and an angle formed between a tangential line to a liquid drop and the film surface at a crossing point of the liquid drop surface and the film surface and containing the liquid drop was taken as a contact angle, and the surface energy of the film was obtained by a calculation.

The saponified films did not show foreign substance or turbidity, and were satisfactory in transparency.

(Polarizing plate)

A polarizing film was prepared by adsorbing iodine on a stretched polyvinyl alcohol film, then the optical compensation sheet prepared in the Example 7 was adhered on a side of the polarizing film with a polyvinyl alcohol adhesive, and the saponified film SF-3A was adhered on the other side with a polyvinyl alcohol adhesive, and a drying was executed for 10 minutes at 80°C. A transmission axis of the polarizing film was arranged parallel to a phase retarding axis of the optical compensation sheet prepared

in the Example 7. A transmission axis of the polarizing film and a phase retarding axis of the cellulose triacetate film were arranged perpendicularly. A polarizing plate was prepared in this manner.

Also a polarizing plate was prepared in the same manner, replacing the saponified film SF-3A by SF-3B.

(Liquid crystal display apparatus)

In a liquid crystal display apparatus utilizing a TN liquid crystal cell (6E-A3, manufactured by Sharp Inc.), a pair of polarizing plates provided thereon were peeled off, and polarizing plates prepared as explained above were adhered instead respectively on an observer side and a backlight side with an adhesive, in such a manner that the optical compensation sheet prepared in Example 7 was positioned at the side of the liquid crystal cell. A transmitting axis of the polarizing plate at the observer side and a transmitting axis of the polarizing plate at the backlight side were positioned in an O mode.

On thus prepared liquid crystal display apparatus, a measuring instrument (EZ-Contrast 160D, manufactured by ELDIM Co.) was used, and an image unevenness at a black display (L1) was visually observed.

As a result, the device employing the saponified film SF-3A or SF-3B by the method of the invention

provided an sharp image of a high luminance without haze over the entire image area in both cases.

The foregoing result of visual observation indicates that the use of a cellulose acylate film, saponified by the method of the invention in a long web film, provides satisfactory optical characteristics.

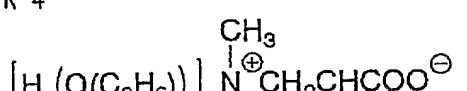
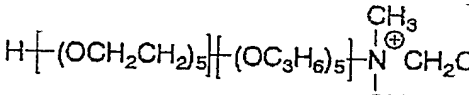
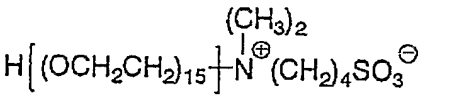
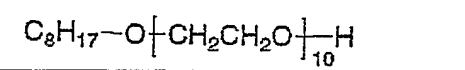
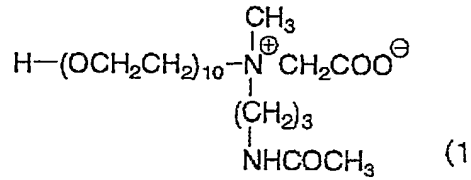
[Example 9 - 12]

(Saponified cellulose triacetate film)

An antireflection film described in Example 7 was provided on a surface of a cellulose acylate film, and a surface not coated with the antireflection film was heated to 45°C by a collision (emission heating) of a hot air of 80°C, then coated with each of following alkali solutions (S4 - 7) of formulations shown in Table 17, maintained at 35°C, in an amount of 7 cc/m^2 with a rod coater, and, after a lapse of 20 seconds, again coated with purified water in an amount of 5 cc/m^2 with a rod coater. In this state, the film had a temperature of 45°C. Then purified water of 1000 cc/m^2 was coated by an extrusion coater to execute water rinsing, and, after a lapse of 5 seconds, an air of 100 m/sec was brown from an air knife. After repeating twice the rinsing with the extrusion coater and the water squeezing by the air knife, drying was conducted in a drying zone of 80°C for a stay time of 10 seconds, thereby

obtaining saponified films SF-4 - SF-7.

[Table 17]

Example	saponified film	alkali processing liquid (S)	alkali agent	solvent (weight%)	surfactant	specific water-solvent compound	defoaming agent
9	SF-4	S-4	KOH(7.0)	water (33) 2-butanol (24) ethanol (26.8)	K-4  (1.2)	trimethylol propane (5) glycerin (3)	Purlonic TR70 0.01
10	SF-5	S-5	KOH(7.5)	water (40.6) methyl cello-solve (40.6)	 K5 (1.3)	dipropylene glycol (10)	ibid 0.01
11	SF-6	S-6	NaOH(6.0)	water (49.6) propylene glycol monomethyl ether (33.1)	K-6  (0.8)  (0.5)	diethylene glycol (7) D-lactone (3)	Surfinol DF110P 0.012
12	SF-7	S-7	KOH(8.5)	water (28.1) isopropanol (52.3)	K-7  (1.1)	propylen glycol (10)	ibid 0.012

Each of the e ofilms (SF-4 - 7) has a contact angle with water within a rangf 30 to 35°.

Then polarizing plates were prepared with the saponified films SF-4 to SF-7 instead of the saponified film employed in Example 8. Evaluation of the performance of the polarizing plates as in Example 8 showed comparable performance to the sample of Example 8.

[Example 13 and Comparative Example 3]

A film was saponified in the same manner as in Example 6, except that the alkali processing liquid (S-3) employed in Example 8 was used instead of the alkali processing liquid (S-1) in Example 6 (saponified film SF-8).

(Preparation of comparative saponified film SFR-3)

A saponified film (SFR-3) was prepared in the same manner as in Example 13, except that the alkali processing liquid (S-3) was replaced by an alkali processing liquid (SR-3) of a following formulation.

Table 18

Comparative alkali processing liquid (SR-3)	
potassium hydroxide	6.5 weight%

water	32.0 weight%
isopropanol	48.3 weight%
diethylene glycol	12.0 weight%
surfactant (following structure)	
$C_4H_9CH(C_2H_5)CH_2OOC-CH_3$	
|	
$C_4H_9CH(C_2H_5)CH_2OOC-CH-SO_3K$	1.2 weight%
defoaming agent Surfinol 104 (manufactured by Nisshin Chemical Industries Co.)	0.01 weight%

Properties of the alkali processing liquids (S-3, SR-3) and performance of the prepared saponified films (SF-8, SFR-3) were investigated as in Example 6.

After a processing of 1500 m^2 from the start of saponification process, the liquid of the invention remained same as immediately after the start, but the comparative alkali processing liquid (SR-3) developed turbidity and precipitate.

Also a sample of the saponified film (SFR-3) after processing 1500 m^2 showed a larger fluctuation of the water contact angle within the plane and a larger haze.

As explained above, the invention provided satisfactory stability of the alkali processing liquid and a satisfactory performance of the saponified film even with an increased process amount.

[Example 14]

1-1. Production of alkali saponified polymer film

A cellulose triacetate film of a roll width of 1000 mm (Fujitac TD80UF, manufactured by Fuji Photo Film Co. was heated to a film surface temperature of 40°C by passing through an electromagnetic induction heating roll heated at 60°C. Then a surface of the film was coated with an alkali solution (S-1) of a following formulation, having a specific conductivity of 220 mS/cm at 40°°C, with a coating amount of 10 cc/m^2 with a rod coater. The film was further transported so as to stay for 15 seconds under a far-infrared steam heater manufactured by Noritake Co., Ltd. heated to 110°C. Then purified water was coated in an amount of 3 cc/m^2 with a rod coater. In this state, the film temperature was 40°C. Then a water rinsing with a fountain coater and a water squeezing with an air knife were repeated three times, and a drying was executed by a drying zone of 70°C with a stay time of 5 seconds whereby an alkali saponified film (SF-1) was prepared. In this manner the cellulose triacetate film was saponified for 6000 m^2.

The alkali solution was contained in an alkali solution tank, and was fed to a coating process unit by a constant rate pump. An excessive liquid after coating was returned to the alkali solution tank and was used in

circulation. The alkali solution tank was also provided with an agitating apparatus, an electroconductometer for measuring the saponifying ability of the alkali solution, and means capable of automatically charging a replenishing liquid (H-1) of a following formulation by a predetermined amount based on the measured electrical conductivity, which were used at the saponification. The saponification process was executed under a replenishment of the replenishing liquid (H-1) in such a manner that the alkali solution was maintained at a specific conductivity of 220 ± 10 mS/cm.

Table 19

Formulation of alkali solution (S-1)	
sodium hydroxide	4.0 parts by weight
water	90.985 parts by weight
propylene glycol	4.0 parts by weight
surfactant (K-1: $C_{14}H_{29}O(CH_2CH_2O)_2OH$)	1.0 part by weight
defoaming agent Surfinol DF110D (manufactured by Nisshin Chemical Industries Co.)	0.015 parts by weight

Table 20

Formulation of replenishing liquid (H-1)	
sodium hydroxide	6.0 parts by weight
water	88.90 parts by weight
propylene glycol	4.0 parts by weight
surfactant (K-1: $C_{14}H_{29}O(CH_2CH_2O)_2OH$)	1.1 parts by weight

1-2. Evaluation of alkali solution and alkali saponified polymer film

The alkali solution after the saponification process and the alkali saponified polymer film obtained above were evaluated in the following manner.

(1) Property of alkali solution

Transparency of the alkali solution after the saponification process was visually observed. As a result, the alkali solution was free from turbidity or precipitate and was completely transparent.

Also the alkali solution was discharged from the alkali solution tank after the saponification process, and an internal wall of the alkali solution tank was visually inspected. As a result, no precipitate nor deposit was observed on the internal wall.

(2) Contact angle with water

In a contact angle meter (CA-X, manufactured by

Kyowa Kaimen Kagaku Co.), a liquid drop of a diameter of 1.0 mm was formed on a needle tip utilizing purified water as the liquid and in a dry state (20°C/65 %RH), and was contacted with a surface of the obtained alkali saponified polymer film to form a liquid drop. An angle formed between a tangential line to the liquid surface and the solid surface at a solid (film)-liquid (purified water) contact point and containing the liquid was taken as a contact angle. At plural positions of every 1000 m from the start, the film was cut with a full width and a length of 1 m in the longitudinal direction, and the contact angle was measured in 9 points at both ends and at center in the cutout square.

As a result, an average contact angle was 35° in any of the positions of evenry 1000 m from the start.

(3) Foreign substance and turbidity in alkali saponified polymer film

The obtained alkali saponified polymer film was cut into a length of 1 m with a full width, and the cut sample was observed for foreign substances and turbidity, with bare eyes and under a magnifier with a transmitting light on a light box.

As a result, the alkali saponified polymer was free from foreign substance or turbidity and was transparent.

Also similar results were obtained in case an AC

impedance meter for measuring the saponifying ability of the alkali solution, instead of the electroconductometer.

[Example 15]

2-1. Production of alkali saponified polymer film

A cellulose acylate film provided with an antistain layer having an antireflection function was prepared according to the description of JP-A No. 2002-182033, Example 1, [0020] to [0026]. Then a polyethylene terephthalate film (SAT-106TS, manufactured by Sanei Kaken) was adhered to a surface of the antistain layer of the obtained cellulose acylate film.

A master etching processor (E-380II, manufactured by Fuji Photo Film Co.) for an electronic platemaking system was employed as an immersion processing apparatus, and an alkali solution (S-2) of a following formulation, having a specific conductivity of 5.5 mS/cm, was charged in this apparatus and was set at a liquid temperature of 30°C.

After the cellulose acylate film adhered with the polyethylene terephthalate film was immersed for a immersion time of 10 seconds, it was immersed in water to sufficiently wash off the alkali solution. It was then immersed in a 0.5% dilute sulfuric acid solution for 10 seconds, then was immersed in water and sufficiently washed. Then the film was dried at 100°C to obtain a

alkali saponified polymer film (SF-2). The alkali saponified polymer film (SF-2) was saponified on a surface where the cellulose acylate film was exposed, but was protected on a surface having the antistain layer from the alkali solution by the polyethylene terephthalate film. The saponification process was executed with a process amount of 1000 m^2/day, over 4000 m^2 in 4 days.

The immersion apparatus was provided with means of measuring a process area per unit time of the polymer film, an electroconductometer, and means replenishing a replenishing liquid (H-2) of a following formulation based on the measured process area and the measured electrical conductivity, which were used at the saponification.

Table 21

Formulation of alkali processing liquid (S-3)	
potassium hydroxide	4.0 weight%
water	29.0 weight%
isopropyl alcohol	54.0 weight%
ethylene glycol	11.7 weight%
surfactant (K-2: $C_9H_{19}Ph(OCH_2CH_2)_8SO_3Na$ (Ph: phenylene group))	1.3 weight%
defoaming agent Purlonic TR70 (manufactured by Asahi Denka Co.)	0.01 weight%

Table 22

Formulation of replenishing liquid (H-2)	
potassium hydroxide	4.8 weight%
water	29.0 weight%
isopropyl alcohol	54.0 weight%
ethylene glycol	11.7 weight%
surfactant (K-2: $C_9H_{19}Ph(OCH_2CH_2)_8SO_3Na$ (Ph: phenylene group))	1.3 weight%
defoaming agent Purlonic TR70 (manufactured by Asahi Denka Co.)	0.005 weight%

2-2. Evaluation of alkali solution and alkali saponified polymer film

The alkali solution after the saponification process and the alkali saponified polymer film obtained above were evaluated in the same manner as in Example 1. As a result, the alkali solution after the saponification process was transparent, and no stain was observed in the alkali solution tank.

Also on thus obtained alkali saponified polymer film, portions at the start and at the end of the saponification process for each process day were evaluated in the same manner as in Example 1. As a result, the alkali saponified polymer film was free from foreign substance or

turbidity and was transparent.

2-3. Production of polarizing plate

The polyethylene terephthalate film was removed from the alkali saponified polymer film obtained above to obtain a first polarizing plate protective film. Separately a second polarizing plate protective film was obtained in a similar as the first polarizing plate protective film.

A polyvinyl alcohol film of a thickness of 75 μm (manufactured by Kuraray Co.) was immersed for 5 minutes in an aqueous solution containing 7 parts by weight of iodine and 105 parts by weight of potassium iodide in 1000 parts by weight of water, thereby causing iodine adsorption on the film. Then the film was monoaxially stretched 4.4 times in the longitudinal direction in a 4 weight% aqueous solution of boric acid of 40°C, and dried in a tensioned state to obtain a polarizing film.

A surface of the polarizing film and a saponified surface of the cellulose triacetate film constituting the first polarizing plate protective film were adhered with a polyvinyl alcohol adhesive, and the other surface of the polarizing film and a saponified surface of the cellulose triacetate film constituting the second polarizing plate protective film was adhered with a polyvinyl alcohol adhesive, thereby obtaining a polarizing plate.

2-4. Evaluation of polarizing plate

(1) Durability test

100 polarizing plates were prepared in the aforementioned method, and were respectively adhered to glass plates with an acrylic adhesive, and these were placed in a chamber of constant temperature and constant humidity and were subjected to a durability test of 1000 hours in total, during which the interior of the chamber of constant temperature and constant humidity was switched between an atmosphere of 70°C, 93 %RH and an atmosphere of 25°C, 93 %RH every 12 hours. After taking out from the chamber of constant temperature and constant humidity, peeling and bubble generation between the polarizing plate and the glass plate were inspected.

As a result, peeling and bubble generation were not found in any of 100 samples.

(2) Visual defect

Also in a commercially available liquid crystal monitor of thin film transistor (TFT) type, polarizing plates on both sides were peeled off and the aforementioned polarizing plates were adhered on both sides, and presence of unevenness in black display and white display was visually evaluated.

As a result, a visual defect such as an unevenness

was not observed at all over the entire image area.

[Example 16]

3-1. Production of alkali saponified polymer film

A cellulose triacetate film: Fujitac TD80UF (manufactured by Fuji Photo Film Co.) of a roll form with a width of 1000 mm was heated to a film surface temperature of 30°C by a collision of a warm air. Then a surface of the film was coated with an alkali solution (S-3) of a following formulation maintained at 25°C in an amount of 12 mL/m^2 with a rod coater. After a lapse of 20 seconds, Purified water was coated in an amount of 5 mL/m^2 with a rod coater. In this state, the film had a temperature of 30°C. Then purified water of 1000 mL/m^2 was coated by an extrusion coater to execute water rinsing, and, after a lapse of 5 seconds, an air of 100 m/sec was made to collide from an air knife. After repeating the rinsing with the extrusion coater and the water squeezing by the air knife twice, drying was conducted in a drying zone of 80°C for a stay time of 10 seconds, thereby obtaining an alkali saponified polymer film (SF-3). A film of 6000 m^2 was saponified in this manner.

The alkali solution was contained in an alkali solution tank, and was fed to a coating process unit by a constant rate pump. An excessive liquid after coating was

returned to the alkali solution tank and was used in circulation. Immediately after the rod coater in the coating step, there was provided means for measuring a process area per unit time of the polymer film, and the alkali solution tank was provided with an agitating apparatus, and means capable of automatically charging a replenishing liquid (H-3) of a following formulation by a predetermined amount based on the measured process area, which were used at the saponification.

Table 23

Formulation of alkali solution (S-3)	
potassium hydroxide	5.5 parts by weight
water	19.49 parts by weight
n-propanol	59.5 parts by weight
diethylene glycol	14.5 parts by weight
surfactant (K-3: ethylenediamine ethyleneoxide addition product (20 mole addition product)	1.0 part by weight
defoaming agent Surfinol DF110D (manufactured by Nisshin Chemical Industries Co.)	0.01 parts by weight

Table 24

Formulation of replenishing liquid (H-3)	
potassium hydroxide	6.5 parts by weight
water	19.49 parts by weight
n-propanol	58.5 parts by weight
diethylene glycol	14.5 parts by weight
surfactant (K-3: ethylenediamine ethyleneoxide addition product (20 mole addition product)	1.0 part by weight
defoaming agent Surfinol DF110D (manufactured by Nisshin Chemical Industries Co.)	0.01 parts by weight

3-2. Evaluation of alkali solution and alkali saponified polymer film

The alkali solution after the saponification process and the alkali saponified polymer film obtained above were evaluated in the same manner as in Example 14. As a result, the alkali solution after the saponification process was transparent, and no stain was observed in the alkali solution tank.

[Example 17]

(Preparation of alkali saponifying solution(S-2) and alkali neutralizing liquid (ST-10)

An alkali saponifying solution (1.7 N) and an alkali

neutralizing liquid of following formulations were prepared.

Table 25

Formulation of alkali saponifying aqueous solution (S-2)	
NaOH	680 parts by weight
following anionic surfactant	110 parts by weight
defoaming agent: Purlonic TR701 (Asahi Denka Co.)	1 part by weight
purified water	9209 parts by weight

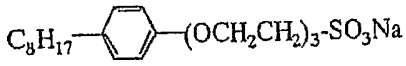


Table 26

Formulation of alkali neutralizing liquid (ST-10)	
acetic acid	800 parts by weight
L-aspartic acid	199 parts by weight
defoaming agent Surfinol DF110D (manufactured by Nisshin Chemical Industries Co.)	1 part by weight
purified water	9000 parts by weight

(Preparation of saponified film (KF-10)

A cellulose triacetate film: Fujitac TD80UF (manufactured by Fuji Photo Film Co.) was heated to 45°C by a collision of a hot air of 100°C, then coated with an alkali saponifying solution (S-3) maintained at 30°C in an amount of 8 cc/m^2 with a rod coater, and, after a lapse of 10 seconds, again coated with an alkali neutralizing liquid (ST-10) in an amount of 20 cc/m^2 with a rod coater. In this state, the film had a temperature of 45°C. Then purified water of 1000 cc/m^2 was coated by an extrusion coater to execute water rinsing, and, after a lapse of 5 seconds, an air of 100 m/sec was made to collide from an air knife to the water-coated surface. After repeating the rinsing with the extrusion coater and the water squeezing by the air knife twice, drying was conducted in a drying zone of 80°C for a stay time of 10 seconds, thereby obtaining a saponified film KF-10. The saponified film had a water contact angle of 47°, and a surface free energy of 68 mN/m.

The alkali neutralizing liquid (ST-10) had a carbonate ion concentration of 860 mg/L, a total polyvalent metal ion concentration, including calcium and magnesium, of 2.3 mg/L, and a chloride ion concentration of 1.1 mg/L.

(Preparation of optical compensation sheet (KHF-10))

An optical compensation film (KHF-10) was prepared in a similar manner as the optical compensation film KHF-1 in Example 1.

As a result of evaluation of performance, it showed excellent performance similar to the optical compensation film KHF-1.

[Example 18]

(Preparation of polarizing plate (HB-1 - HB-10))

A polarizing film was prepared by adsorbing iodine on a stretched polyvinyl alcohol film, then the optical compensation sheet prepared in the Example 1 or 17 (KHF-1 - KHF-10) was adhered on a side of the polarizing film with a polyvinyl alcohol adhesive, and a commercially available cellulose triacetate film (Fujitac TD80UF, manufactured by Fuji Photo Film Co.) saponified as in Example 1 was adhered on the other side, and a drying was executed for 10 minutes at 80°C.

A transmission axis of the polarizing film was arranged parallel to a phase retarding axis of the optical compensation sheet. A transmission axis of the polarizing film and a phase retarding axis of the commercially available cellulose triacetate film were arranged perpendicularly.

A transmission axis of the polarizing film and a phase retarding axis of the cellulose triacetate film were arranged perpendicularly. Polarizing plates (HB-1 - HB-10) were prepared in this manner.

(Assembling and evaluation of TN liquid crystal display apparatus)

In a liquid crystal display apparatus utilizing a TN liquid crystal cell (6E-A3, manufactured by Sharp Inc.), a pair of polarizing plates provided thereon were peeled off, and polarizing plates prepared as explained above were adhered instead respectively on an observer side and a backlight side with an adhesive, in such a manner that the optical compensation sheet was positioned at the side of the liquid crystal cell. The liquid crystal display apparatus was so assembled that a transmitting axis of the polarizing plate at the observer side and a transmitting axis of the polarizing plate at the backlight side were positioned in an O mode.

On thus prepared liquid crystal display apparatus, a measuring instrument (EZ-Contrast 160D, manufactured by ELDIM Co.) was used, and an image unevenness at a black display (L1) was visually observed.

As a result shown in Table 27, the liquid crystal display apparatus employing the optical compensation films

HB-7 to HB-9, employing alkali diluting liquids of a carbonate ion concentration, a polyvalent metal ion concentration and a chloride ion concentration higher than in the invention shows a haze over the entire image area thereby decreasing the luminance, but a high luminance was obtained in HB-1, HB-2, HB-3, HB-4, HB-5, HB-6 and HB-10.

Table 27

Polarizing plate	Optical compensation sheet	Alkali diluting liquid or neutralizing liquid used	Unevenness in image
HB-1	KHF-1	SK-1	none
HB-2	KHF-2	SK-2	none
HB-3	KHF-3	SK-3	none
HB-4	KHF-4	SK-4	none
HB-5	KHF-5	SK-5	none
HB-6	KHF-6	SK-6	none
HB-7	KHF-7	SK-7	haze all over
HB-8	KHF-8	SK-8	haze all over
HB-9	KHF-9	SK-9	haze all over
HB-10	KHF-10	SK-10	none

[Example 19]

(Assembling and evaluation of vertical alignment liquid crystal display apparatus)

In a liquid crystal display apparatus utilizing a vertical alignment liquid crystal cell (VL-1530S, manufactured by Fujitsu Inc.), a pair of polarizing plates provided thereon were peeled off, and polarizing plates prepared in Example 18 were adhered instead respectively on an observer side and a backlight side with an adhesive, in such a manner that the optical compensation sheet was positioned at the side of the liquid crystal cell. The liquid crystal display apparatus was assembled in a Nicol arrangement in which a transmitting axis of the polarizing plate at the observer side was in a vertical direction and a transmitting axis of the polarizing plate at the backlight side was in a horizontal direction.

On thus prepared liquid crystal display apparatus, a measuring instrument (EZ-Contrast 160D, manufactured by ELDIM Co.) was used, and an image unevenness at a black display (L1) was visually observed.

The liquid crystal display apparatus employing the polarizing plate utilizing the optical compensation film obtained with the alkali saponifying aqueous solution of the invention showed a high luminance and a satisfactory liquid crystal display apparatus without an unevenness in the image could be obtained.

[Example 20]

(Assembling and evaluation of bend orientation liquid crystal display apparatus)

A bend orientation liquid crystal cell was prepared, and polarizing plates prepared in Example 18 were adhered respectively on an observer side and a backlight side with an adhesive, in such a manner that the optical compensation sheet was positioned at the side of the liquid crystal cell.

A rubbing direction of the liquid crystal cell and a rubbing direction of the optical anisotropic layer opposed thereto were arranged antiparallel.

On thus prepared liquid crystal display apparatus, a measuring instrument (EZ-Contrast 160D, manufactured by ELDIM Co.) was used, and an image unevenness at a black display (L1) was visually observed.

The liquid crystal display apparatus employing the polarizing plate utilizing the optical compensation film obtained with the alkali saponifying aqueous solution of the invention showed a high luminance and a satisfactory liquid crystal display apparatus without an unevenness in the image could be obtained.

[Example 21]

(Preparation of saponified film (KF-11) and

polarizing plate protecting film)

A cellulose acylate film provided with an antireflection layer was prepared according to the description of JP-A No. 2002-182033, Example 1. Then a polyethylene terephthalate film (SAT-106TS, manufactured by Sanei Kaken) was adhered to a surface of the antistain layer of the obtained cellulose acylate film. A master etching processor E-380II for an electronic platemaking system was employed as an immersion processing apparatus for the film, and an alkali saponifying solution (S-1) of a following formulation was charged in this apparatus and was set at a liquid temperature of 50°C. After the film was immersed for a immersion time of 30 seconds, it was immersed in an alkali diluting liquid (SK-11) to dilute the alkali saponifying solution. It was then immersed in an alkali neutralizing liquid (ST-12) for 10 seconds, and was then sufficiently washed by immersing in a purified water tank. Then the film was dried at 100°C to obtain a alkali saponified cellulose acylate film (KF-11) of 8000 m (10000 m^2). The polyethylene terephthalate film was eliminated from the cellulose triacetate film to obtain a first polarizing plate protective film.

Table 28

Formulation of alkali diluting liquid (SK-11)	
nonionic surfactant (used in S-1)	30 parts by weight
defoaming agent Surfinol DF110D (manufactured by Nisshin Chemical Industries Co.)	1 part by weight
purified water	9769 parts by weight

Table 29

Formulation of alkali neutralizing liquid (ST-12)	
L-aspartic acid	100 parts by weight
purified water	9900 parts by weight

The alkali diluting liquid (SK-11), at the preparation of 300 L, had a carbonate ion concentration of 330 mg/L, a total polyvalent metal ion concentration, including calcium and magnesium, of 44 mg/L, and a chloride ion concentration of 12 mg/L. After the processing, it had a carbonate ion concentration of 3030 mg/L, a total polyvalent metal ion concentration, including calcium and magnesium, of 227 mg/L, and a chloride ion concentration of 32 mg/L.

The alkali neutralizing liquid (ST-12), at the preparation of 300 L, had a carbonate ion concentration of 360 mg/L, a total polyvalent metal ion concentration,

including calcium and magnesium, of 52 mg/L, and a chloride ion concentration of 18 mg/L. After the processing, it had a carbonate ion concentration of 1420 mg/L, a total polyvalent metal ion concentration, including calcium and magnesium, of 118 mg/L, and a chloride ion concentration of 25 mg/L.

An optical absorbance at 400 nm of the alkali saponifying solution was measured before the saponification process and the processing of 10000 m^2, and was 0.00 before processing and 1.88 after processing.

A polyvinyl alcohol film of a thickness of 75 μm (manufactured by Kuraray Co.) was immersed for 5 minutes in an aqueous solution containing 7 parts by weight of iodine and 100 parts by weight of potassium iodide in 1000 parts by weight of water, thereby causing iodine adsorption on the film. Then the film was monoaxially stretched 4.0 times in the longitudinal direction in a 4 weight% aqueous solution of boric acid of 40°C, and dried in a tensioned state to obtain a polarizing film. A surface of the polarizing film and a saponified surface of the first polarizing plate protective film were adhered with a polyvinyl alcohol adhesive, and the other surface and a cellulose acylate film surface of the optical compensation sheet (KHF-1) prepared in Example 1 and subjected to a saponification process was adhered and a

drying was executed for 10 minutes at 80°C, thereby obtaining a polarizing plate (HB-11).

(Evaluation of polarizing plate)

100 polarizing plates were prepared in the aforementioned method, and were respectively adhered to glass plates with an acrylic adhesive, and these were placed in a chamber of constant temperature and constant humidity and were subjected to a durability test of 1200 hours in total, during which the interior of the chamber of constant temperature and constant humidity was switched between an atmosphere of 70°C, 93 %RH and an atmosphere of 25°C, 93 %RH every 12 hours. Peeling and bubble generation between the polarizing plate and the glass plate were inspected, and peeling and bubble generation were not found in any of 100 samples.

A TN liquid crystal display apparatus was assembled, and, on thus prepared liquid crystal display apparatus, a measuring instrument (EZ-Contrast 160D, manufactured by ELDIM Co.) was used, and an image unevenness at a black display (L1) was visually observed. There was not observed at all a defect such as an unevenness in the image could be obtained over the entire image area.

[INDUSTRIAL APPLICABILITY]

The method of alkali-saponifying a cellulose acylate film with an alkali solution of the present invention can achieve a uniform and precise alkali saponification of the film surface without generating a defect such as haze on the film and can saponify one surface selectively with a high productivity. The alkali saponified film can be easily incorporated in an optical compensation sheet for a large-sized liquid crystal display apparatus without a display defect. Also there can be obtained a cellulose acylate film for a transparent substrate, having an excellent adhesion between a transparent substrate and an orienting film of an optical compensation sheet.

The method of the invention, in case of continuously saponifying a polymer film, allows to execute the saponification process in stable manner without a decrease in the work efficiency or a problem in waste disposal even in case of a large process amount.

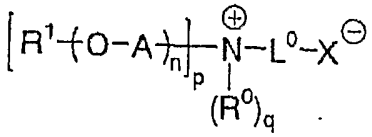
CLAIMS

1. A method of alkali-saponifying a cellulose acylate film with an alkali solution comprising an alkali agent, water, an organic solvent, a surfactant and a mutually solubilizing agent.

2. The method according to claim 1, wherein said organic solvent has an inorganic/organic value (I/O value) of 0.5 or higher and a solubility parameter of 16 to 40 $[mJ/m^3]^{1/2}$.

3. The method according to claim 1 or 2,wherein said surfactant is at least one selected from the group consisting of a nonionic surfactant, an anionic surfactant, a cationic surfactant and an amphoteric surfactant.

4. A method of alkali-saponifying a cellulose acylate film with an alkali solution comprising an alkali agent and a surfactant, wherein said surfactant is an amphoteric surfactant represented by a following general formula (I):



wherein A represents an alkylene group; L^0 represents a

group connecting a nitrogen atom and X^-; X^- represents $-COO^-$, $-SO_3^-$ or $-PO_3H^-$; R^0 represents a hydrocarbon group; R^1 represents a hydrogen atom or a hydrocarbon group; n represents an integer of from 1 to 50; p and q each represents an integer of 1 or 2 and p + q = 3.)

5. The method according to any of claims 1 to 3, wherein said mutually solubilizing agent is at least one selected from polyol compounds having a solubility of water of 30 g or higher to 100 g of the mutually solubilizing agent at 25°C.

6. The method according to claim 4, wherein said alkali solution includes an alkali agent of 0.1 to 25 % by weight ,and water or a mixed solvent of water and a hydrophilic organic solvent.

7. The method according to any of claims 1 to 6, wherein said alkali solution has a concentration of the alkali agent of 0.1 to 25 % by weight, a surface tension of 45 mN/m or less, and a viscosity of 0.8 to 20 mPa·s.

8. The method according to any of claims 1 to 7, wherein said alkali solution includes at least one selected from hydrophilic compounds having a boiling point

of 120°C or higher, and capable of dissolving water in an amount of 50 g or more in 100 g of the hydrophilic compound.

9. The method according to any of claims 1 to 8, wherein said alkali solution includes a defoaming agent.

10. A method of alkali-saponifying a cellulose acylate film with an alkali solution comprising: a step of processing a cellulose acylate film with an alkali solution; and a step of washing off said alkali solution from the film with an alkali diluting liquid or a neutralizing liquid, wherein the alkali diluting liquid or the neutralizing liquid has a carbonate ion concentration of 3500 mg/L or less.

11. The method according to claim 10, wherein the alkali diluting liquid or the neutralizing liquid has a polyvalent metal ion concentration of 500 mg/L or less and a chlorine ion concentration of 300 mg/L of less.

12. The method according to claim 10 or 11, wherein the alkali diluting liquid or the neutralizing liquid includes a surfactant.

13. The method according to any of claims 10 to 12, wherein a solvent of the alkali diluting liquid or the neutralizing liquid is water, or a mixture of water and an organic solvent.

14. The method according to any of claims 10 to 13, wherein the alkali diluting liquid or the neutralizing liquid includes a defoaming agent.

15. The method according to any of claims 10 to 14, wherein the step of processing a cellulose acylate film with said alkali solution includes a step of coating the alkali solution to the cellulose acylate film.

16. The method according to any of claims 1 to 15, which includes a step of coating said alkali solution on the cellulose acylate film at the room temperature or higher and a step of washing off said alkali solution from said cellulose acyalte film.

17. A surface saponified cellulose acylate film obtained by the method according to any of claims 1 to 16.

18. An optical film comprising the surface saponified cellulose acylate film according to claim 17.

19. A method of replenishing an alkali solution with a replenishing liquid in producing an alkali saponified polymer film by a continuous saponification process of a polymer film surface with said alkali solution, which comprises:

a step of measuring a saponifying ability of said alkali solution;

a step of determining a replenishing mode for the replenishing liquid in such a manner that the saponifying ability of the alkali solution after a replenishment with said replenishing liquid becomes within a predetermined range, based on said measured saponifying ability; and

a step of replenishing said alkali solution with said replenishing liquid in said determined replenishing mode.

20. The method according to claim 19, further comprising

a step of measuring a process area per unit time of said polymer film, wherein said predetermined range is determined based on said measured process area per unit time.

21. The method according to claim 20, wherein the

saponifying ability of said alkali solution is measured by at least one selected from a group consisting of a pH measurement of the alkali solution, a measurement of an electrical conductivity of the alkali solution, a measurement of an electrical impedance of the alkali solution, a measurement of an electrode voltage between current-controlled electrodes, and a measurement of an electrode potential between current-controlled electrodes.

22. A method of replenishing an alkali solution with a replenishing liquid in producing an alkali saponified polymer film by a continuous saponification process of a polymer film surface with said alkali solution, comprising:

a step of measuring a process area per unit time of said polymer film;

a step of calculating a consumption of the alkali solution per unit time from the measured process area per unit time, based on a pre-memorized amount of the alkali solution necessary for a saponification process per unit area of said polymer film;

a step of determining a replenishing mode for the replenishing liquid in such a manner that the saponifying ability of the alkali solution after a replenishment with said replenishing liquid becomes within a predetermined

range, based on said calculated consumption per unit time; and

a step of replenishing said alkali solution with said replenishing liquid in said determined replenishing mode.

23. The method according to claim 22, wherein said saponifying process comprises a step of heating the polymer film in advance to 25°C or higher, a step of coating the polymer film with the alkali solution, a step of maintaining the polymer film at a temperature of 25°C or higher, and a step of washing off the alkali solution from the polymer film, in this order.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP03/ 15428

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl⁷ C08J7/00,G02B5/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl⁷ C08J7/00-7/18,G02B5/30

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Japanese Utility Model Gazette 1926-1996, Japanese Publication of Unexamined Utility Model Applications 1971-2003, Japanese Registered Utility Model Gazette 1994-2003, Japanese Gazette Containing the Utility Model 1996-2003

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI/L

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	JP 2003-313326 A(FUJI PHOTO FILM CO.,LTD)2003.11.06 CLAIM1-18 AND [0038]-[0064]&US 20030194668 A&CN 1439667 A	1-3,6-18
A	JP 7-62120 A(DAIICHI SHOKO CO.,LTD)1995.03.07 CLAIM1-8 (NO FAMILIES)	1-23
A	JP 1-268729 A(TOYOBO KK)1989.10.26 CLAIM1-4 (NO FAMILIES)	1-23
A	JP 60-147446 A(NIPPON POLYTECH CO.,LTD)1985,08.03 CLAIM1 (NO FAMILIES)	1-23

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18.02.2004	02.3.2004
Name and mailing address of the ISA/JP **Japan Patent Office** 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer YOSHIZAWA EIICHI 4J 9543 Telephone No. +81-3-3581-1101 Ext. 3455

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONALSEARCHREPORT

International application No.
PCT/JP03/15428

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

THE INVENTION DESCRIBED IN CLAIM 1-3,5 IS AN ALKALI SOLUTION CONTAINING A MUTUALLY SOLUBILIZING AGENT.
THE INVENTION DESCRIBED IN CLAIM 4,6 IS AN ALKALI SOLUTION CONTAINING AN AMPHOTERIC SURFACTANT.
THE INVENTION DESCRIBED IN CLAIM 10-15 IS AN ALKALI DILUTING LIQUID HAS A CARBONATE ION CONCENTRATION OF 3500 mg/L OR LESS.
THE INVENTION DESCRIBED IN CLAIM 19-23 COMPRISES STEPS OF MEASURING,DETERMINING AND REPLENISHING.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☑ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.