(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
31 August 2006 (31.08.2006)

PCT

(10) International Publication Number
WO 2006/091393 A1

(51) **International Patent Classification:**
G02B 5/30 (2006.01)

(21) **International Application Number:**
PCT/US2006/004657

(22) **International Filing Date:** 9 February 2006 (09.02.2006)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
11/064,372   23 February 2005 (23.02.2005)   US

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guid-ance Notes on Codes and Abbreviations" appearing at the begin-ning of each regular issue of the PCT Gazette.

(54) **Title:** POLARIZING LAYER WITH ADHERENT PROTECTIVE LAYER
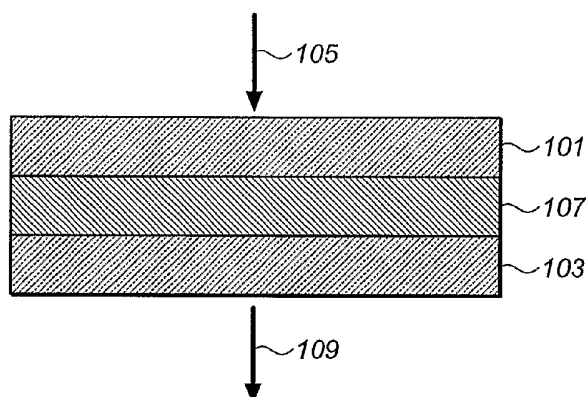
(57) **Abstract:** The invention relates to a process for forming an integral protective layer on a polarizing layer comprising coating the layer with a sol, gelling the sol, and then curing the coating to form a contiguous crosslinked adherent protective layer. In a further aspect, the invention relates to a multilayer polarizer plate comprising a polarizing polyvinyl alcohol layer bearing a contiguous integral crosslinked polymeric layer; preferably, the crosslinked polymeric layer comprises a silica-siloxane composite layer.

POLARIZING LAYER WITH ADHERENT PROTECTIVE LAYER

FIELD OF THE INVENTION

This invention relates to polarizing plates and their manufacturing

5   process. The polarizing plate according to the invention has improved

dimensional stability and optical properties suitable for use in high definition

image display devices such as Liquid Crystal Display (LCD) and Organic Light

Emitting Diode Display (OLED).

10   **BACKGROUND OF THE INVENTION**

Polarizing plates (also commonly called "polarizers") are widely

used in displays to control incoming and outgoing light. For example, in LCDs, a

liquid crystal cell is typically situated between a pair of polarizer plates. Incident

light polarized by the first polarizer plate passes through a liquid crystal cell and is

15   affected by the molecular orientation of the liquid crystal, which can be altered by

the application of a voltage across the cell. The altered light goes into the second

polarizer plate. By employing this principle, the transmission of light from an

external source, including ambient light, can be controlled. LCD's are quickly

taking over from traditional CRTs in computer monitors and TVs because of their

20   lower energy consumption and thinness.

The principle of OLED Display operation does not rely on the

polarization state of light. In OLED Displays, organic compounds emit light as a

current goes through, thus, no modulation of polarization is involved. However, in

order to reject ambient light, OLED displays use a combination of an optical

25   retardation film and a polarizer, such as a circular polarizer plate. In display

applications including LCD and OLED, it is important that the degree of

polarization, so called polarization efficiency, of the light through the polarizer

plate is high. A low degree of polarization would result in inferior display

performance.

30   Most of the polarizer plates currently used in displays are

transmission-absorptive type. They polarize incident natural light by absorbing a

component of the electric field oscillating in a particular direction. The transmitted

light is linearly polarized. In order to generate the absorption-dichromatic

polarizing element that functions over a wide range of visible spectrum, a sheet of

polyvinyl alcohol (PVA) impregnated with iodine or organic dichroic dyes is

5   stretched to produce a polarizing film. In most cases the absorption axis is parallel

to the direction of stretch. Polarizing films composed of said oriented PVA sheet

alone do not possess good humidity or temperature stability. Thus, they are

sandwiched between two protective layers **101, 103**, FIG.1, to form a polarizing

plate. Typically the protective layers are made from cellulose triacetate (TAC).

10   The incoming un-polarized light **105** transmits through the protective layer **101**,

and is polarized through the polarizing film element **107**. The linearly polarized

light **109** comes out from the opposite side through the other protective layer **103**.

The protective layers must satisfy certain quality requirements: high transparency,

low birefringence, dimensional stability against temperature and humidity, and

15   chemical stability.

For display applications, overall light efficiency is an important

factor for performance. Thus the protective film should be free from haze, high

absorption, and coloration. Preferably, transmission of the protective film is above

90%. In LCDs, the polarization state of the light is modulated by changing the

20   birefringence of the liquid crystal cell and additional birefringence contribution

from polarizer protective layers often has to be suppressed. Also, a low

birefringence protective layer enables efficient manufacturing of various

combinations of polarizer and retarders.

Long-term reliability of the polarizer plates depends on two factors:

25   chemical and dimensional stability. The function of a polarizing element **107**

relies on the alignment and the chemical state of iodine or dichroic dyes embedded

within it. In dichroic dye type polarizers, the desired absorption spectrum is given

by a mixture of dichroic dyes possessing overlapping absorption bands to cover

the intended useful light wavelength range. In iodine type polarizer films, the

30   desired absorption spectrum is given by controlling the amount of poly-iodide

ions, I_3^- and I_5^-. The degree of polarization is directly related to the degree of

alignment of these ionic species. If the ionic state or alignment is degraded, the polarization degree of light would not be satisfactory for display applications. Therefore, the protective layers have to be free from chemical species that can react with or diffuse into the polarizing element and alter the state of poly-ions or

5   dyes.

Dimensional instability of the protecting layer(s) (**101, 103**) degrades the polarizer plate performance mainly by two mechanisms: photo elasticity and change in the local polarization direction. Due to the effect of photo elasticity, a protective layer would generate undesired birefringence on its own

10   when it shrinks or expands due to temperature or humidity. With the birefringence in the protective layer, the linearly polarized light **109** exiting the polarizing element **107** will be altered to elliptically polarized light while it transmits through the second protective layer **103**. In most cases, such a birefringence caused by photo elasticity is not uniform across the plane of the polarizer and thus creates an

15   inhomogeneous brightness appearance in the display application. Even if the protective film has no photo elasticity, dimensional change can alter the local polarization direction as it is adhered to the polarizing element typically made from a film of polyvinyl alcohol.

Intrinsic birefringence describes the fundamental orientation of a

20   material at a molecular level. It is directly related to the molecular structure (bond angles, rotational freedom, presence of aromatic groups, etc.) of the material. The intrinsic birefringence is not affected by process conditions (temperature, stresses, pressures) used to make a macroscopic object.

Crystalline and liquid crystalline materials have the convenient

25   property that their intrinsic birefringence manifests itself almost perfectly when they are assembled into a macroscopic article. Layers of crystalline and liquid crystalline molecules often can be manufactured such that a preponderance of the molecules in the article are in registry with each other and thus preserve their fundamental orientation. The same is not true when making layers of an

30   amorphous polymeric material. Their intrinsic birefringence can be highly modified by the manufacturing process. Thus, the measured birefringence of an

actual article will be a resultant of its intrinsic birefringence and the manufacturing process. Because we are dealing with such amorphous polymeric materials, the following definitions refer to this measured birefringence and not intrinsic birefringence.

5   In-plane birefringence means the difference between n_x and n_y, where x and y lie in the plane of the layer. n_x will be defined as being parallel to the casting direction of the polymer, and n_y being perpendicular to the casting direction of the polymer film. The sign convention used will be $n_x - n_y$.

Out of-plane birefringence means the difference between n_z and the

10   average of n_x and n_y, where x and y lie in the plane of the layer and z lies in the plane normal to the layer. The sign convention used will be: $n_z - [(n_x + n_y)/2]$. TAC typically has a negative out of plane birefringence as its n_z is smaller than its n_x and n_y.

In-plane retardation (Re) means the product of in-plane

15   birefringence and layer thickness (t). Thus Re = t $(n_x - n_y)$

Out-of-plane retardation (Rth) means the product of out-of-plane birefringence and layer thickness (t). Thus Rth = t $(n_z - [(n_x + n_y)/2])$.

TAC film has been widely used as the protective layers of polarizer

20   plates. It is relatively simple to obtain low birefringence, especially in-plane, by adjustment of the casting process. This is due to a low intrinsic birefringence of TAC. By carefully choosing the dopant material to TAC (e.g., UV absorber, plasticizers), it is possible to prevent the degradation of the polarizing element (dyed PVA film) by chemical processes. Good optical properties (low haze,

25   relatively high transmission) and its low cost make TAC attractive for this application.

Although TAC satisfies the essential requirements of the protective layers for polarizer plates, it has problems in birefringence and dimensional stability.

30   As mentioned above, it is possible to lower the birefringence of TAC by changing the casting conditions. This holds true for in-plane

birefringence and it is typically 3×10^{-5}. However, there is typically residual out-of-plane birefringence on the order of 6×10^{-4}. Thus, TAC film with a thickness of 100 μm would have low in-plane retardation of 3 nm but the out-of-plane retardation (Rth) would be 60 nm. Such a high value of Rth is often a major

5   concern in display applications. The generation of higher out-of-plane retardation is due to the stress generated in the film normal direction during the drying of solvent used during casting. A few modes of LCD utilize this residual Rth to enhance the viewing quality of LCDs. In some applications, it is preferable to have a much lower Rth contribution from the protective layer.

10   TAC can have high residual stress generated during the solvent casting process. This often contributes to its low dimensional stability. A dimension change in TAC, such as shrinkage, leads to a local change in the polarization direction or lowering of the degree of polarization.

Another problem with TAC is its high moisture permeability. TAC

15   is generally adhered to polarizing film elements with a water soluble adhesion agent after saponification treatment of the TAC film surface. Thus, such humidity permeation leads to a delamination between the TAC and polarizing film element. Also, the ionic state of the dichroic components in the polarizing film element changes state in the presence of moisture leading to a lower degree of polarization

20   of the outcoming light.

An additional complication in the polarizer plate manufacturing process is the saponification treatment required to prepare the TAC film surface for adhesion to the PVA polarizing film element. Since this involves treatment with strong alkaline solution, it raises environmental and working safety concerns,

25   as well as being a source of protective layer non-uniformity defects. Such a strong alkaline treatment combined with the use of plasticizer and other dopant in TAC, can result in segregation, so called bleeding problems. Therefore, it is desirable to eliminate the need for saponification treatment from the polarizer plate manufacturing process.

30   JP 2001-206981 discloses a process to manufacture cellulose ester film having low Rth. The process involves dissolving cellulose ester into a solvent

containing bromopropane. As bromopropane has a higher boiling point than the more generally used solvent, methylene chloride, the slow evaporation process is intended to relax the polymer chain. Reduction in the Rth of TAC from 85 nm to 25~40 nm was claimed. However, the residual Rth is still significant and the use

5   of such a solvent poses a significant potential health hazard.

Other well-known polymeric materials having low birefringence are polynorbornene type polymers. Films of such polymers made by solvent casting or extrusion processes usually shows a few nm in Rth. Not only do such polymer films have low birefringence, also they exhibit low moisture permeation

10   and high dimensional stability. US 6,552,145 discloses use of such a polymer as a protective layer for a polarizer plate. Though various desirable characteristics are shown, the cost of such a film is generally much higher than TAC. Also, adhesion of such polymer layers to PVA is a significant challenge as compared to that of cellulose ester films. JP2001-215331 teaches art in which a protective layer film is

15   comprised of a core layer and a layer of cellulose derivative disposed on at least one side of the core layer. By having the layer of cellulose derivative, adhesion to PVA can be improved. However, such an extra coating process only increases the manufacturing cost of polarizer protective layers.

Therefore, there is a need for a new protective layer for polarizing

20   plates having low in-plane and out-of-plane birefringence and higher dimensional stability than TAC. Yet another need exists for a process to provide such a protective layer for polarizing elements that is free from the need to use strong alkaline solutions, that pose environmental and work-safety concerns.

25   **PROBLEM TO BE SOLVED BY THE INVENTION**

Accordingly, it would be desirable to provide a polarizer protective layer possessing low in-plane and out-of-plane birefringence. It would be desirable to have a polarizer protective layer with better dimensional stability. Furthermore, it would be desired to be able to form the polarizer plate using an

30   easy processing procedure.

SUMMARY OF THE INVENTION

It is an object of the invention to overcome the disadvantages of previous protective layers for polyvinyl alcohol film polarizers in the formation of
5   polarizer plates used in display devices.

It is another object to provide polarizer protective layers having low in-plane and out-of-plane birefringence.

It is yet another object to provide polarizer plates with improved dimensional stability.

10   These and other objects of the invention are accomplished by a process for forming an integral protective layer on a polarizing polyvinyl alcohol polymer film comprising coating the polarizing film with a sol, gelling the sol, and then curing the coating to form a contiguous cross-linked adherent protective layer in the production of a polarizing plate.

15

ADVANTAGEOUS EFFECTS OF THE INVENTION

The invention provides a polarizer plate protective layer having low in-plane and out-of-plane birefringence. The invention also provides a polarizer plate protective layer with good dimensional stability. The invention further
20   provides an inexpensive process for the manufacture of polarizer plates.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the cross section of a polarizer plate.

25   ## DETAILED DESCRIPTION OF THE INVENTION

The invention has numerous advantages. The invention provides a protective layer for a polarizer film that has low in-plane and out-of-plane retardation. The invention provides a less expensive method of forming a polarizer plate, as adhesive joining the protective layers to the polarizer film is not
30   required. The invention provides a polarizer plate of good dimensional stability. The invention provides a protective layer for a polarizer film with good resistance

to moisture permeation. These and other advantages will be apparent from the detailed description below.

As shown in Fig. 1 a polarizer plate may comprise three layers with a core layer of a polarizing film (107) and on both sides of the polarizing film, two
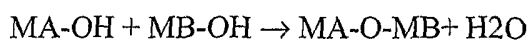5   protective layers. (101 and 103)

It has been found in the present invention that an improved polarizer plate may be formed by having a crosslinked protective layers. One way to generate the crosslinked protective layer is through sol-gel processing. It is realized by the casting of an integral layer of sol onto a polyvinyl alcohol polymer
10   polarizing film. The sol is cast onto one or both sides of the polarizing film, gelled and then cured to form a integral protective layer. Integral as used herein means the joining of two layers such that they can not be separated and maintain the integrity of the layers.

Typical sol-gel processing includes hydrolysis and condensation.
15   In hydrolysis:

$$MRx(OR')_y + H_2O \rightarrow MR_x(OR')_{y-1}\text{-}OH + R'OH$$

wherein M is a metal atom, R and R' are substituents, and x, y are integers.
20

In condensation:

$$MA\text{-}OH + MB\text{-}OH \rightarrow MA\text{-}O\text{-}MB + H2O$$
$$MA\text{-}OR + MB\text{-}OH \rightarrow MA\text{-}O\text{-}MB + ROH$$
25

wherein M is a metal atom, A, B and R are substituents.

The sol utilized in the invention may be any material that will provide a layer of low in-plane and out-of-plane birefringence and has the ability
30   to adhere to the polyvinyl alcohol polymer film to form an integral layer therewith. A polymer chain which has a Tg of less than 25oC is in a rubbery state at room

temperature and thus possessing a low birefringence because of the ability of any recovery of stress induced birefringence. However it is mechanically compliant. When it is crosslinked telechelically, it can form a material with low birefringence as well as good mechanical integrity and dimensional stability. One type of
5 telechelic cross linking is to use silica. Suitable sol materials are silicon alkoxide end grouped oligomers of siloxane, ethylene oxide, acrylate, acrylamide, vinyl and copolymers thereof. A preferred oligomer is siloxane as it provides zero in-plane and out-of-plane birefringence and good dimensional stability. The formation of an embodiment of the invention is illustrated here.

10
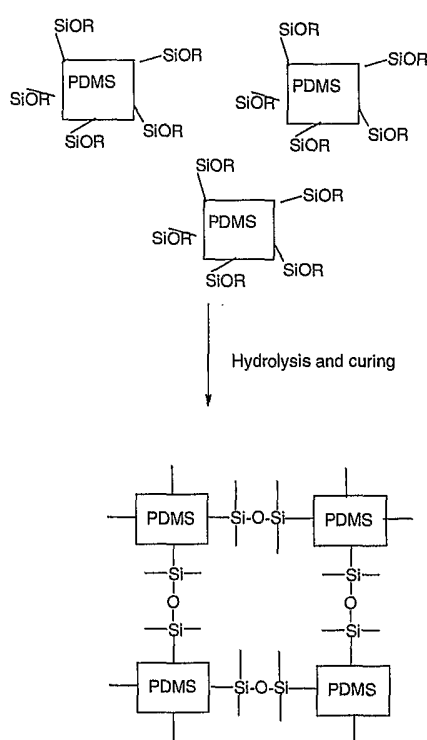
Where R is substituent, alkyl or aromatic; PDMS is polydimethylsiloxane.

There may be either no solvent or solvent present while coating the
15 sol. A variety of solvents may be used, such as THF, lower alcohols, ketones, toluene, acetate esters, formamides and dioxane. It is preferred not to use solvent so as to reduce the shrinkage of the layer upon drying, and to be benign to the environment.

Catalyst may be used to promote the hydrolysis in the preparation

of the sol and later gelation of the sol. Suitable catalysts include but are not

limited to base, acid, and titanium alkoxide or vanadium alkoxide and various

oxides. Commonly used base catalysts include ammonia, KOH and amines.

5   Commonly used acid catalysts include mineral acids, acetic acid and HF.

The gelling of the sol can be achieved through drying. Drying

temperatures may conveniently be in the range of 25°C to 75°C. Drying

temperatures may preferably be between 40°C and 75°C because too high a drying

temperature may degrade the polyvinyl alcohol polarizing film and too low a

10   drying temperature requires excessive time to dry.

The thus formed protective layer(s) can have a wide range of

thicknesses from 5 micron to 100 micron. It is preferred to have a thickness

between 10 to 60 microns such that the resulting protective layer has sufficient

physical integrity. The thickness is preferred to be thinner than conventionally

15   used TAC (about 80micron) such that the overall thickness of the polarizer plate

and finished display can be reduced.

Preparation of polarizing film

Polarizing film can be prepared on commercial scale processing

equipment designed for the production of display grade polarizers. As described,

20   for example, in US20020162483A1 Section 0224, polyvinyl alcohol (PVA) film

in excess of 98% degree of hydrolysis is swollen in water and uniaxially stretched.

The resulting film is subsequently immersed in an aqueous solution of iodine and

potassium iodide to provide the well-known complex with PVA. The polarizing

film is then further immersed in an aqueous solution of potassium iodide and boric

25   acid, washed with water, and dried.

It is common practice to produce a polarizing film by stretching a

film of polyvinyl alcohol (PVA) and then causing the poly-iodide (I^-, I_3^-, and I_5^-) to

be absorbed as a polarizing element in the resulting oriented film. Those

polarizers making use of iodine as a polarizing element have good initial

30   performance but generally have poor resistance to water or heat. Under conditions

of high temperature and high humidity these polarizers may display a problem in durability. Thus, it is well known in the art to use dichroic organic dyes as a replacement for iodine in the polarizers. Many examples of dichroic organic dyes for polarizing films may be found in the patent literature, for example: US

5   5,310,509, US 5,340,504, US 5,446,135, JP 2002296417, JP 2000329936, JP 05273788, JP 63243166, EP 549342, US 5,667,719, and the journal literature such as Proceedings of the SPIE-Int. Soc. Opt. Eng. Vol. 2407 pp. 62-72, "Highly Durable Dyed Polarizer for Use in LCD Projections." Polarizing films making use of dichroic organic dye as a polarizing element have better durability against water

10   and heat compared with polarizing films using iodine. It is common practice to use water soluble azo dyes for the manufacture of polarizing films. Combinations of two or more dyes make it possible to produce polarizing films dyed in various hues. It is common to use multiple dyes with a high degree of dichroism to provide a neutral hue to the polarizing film.

15   Examples of such dichroic organic dyes (Colour Index Generic Name) include the following but are not limited thereto: C.I. Direct Yellow 12, C.I. Direct Blue 202, C.I. Direct Red 31, C.I. Direct Yellow 44, C.I. Direct Yellow 28, C.I. Direct Orange 107, C.I. Direct Red 79, C.I. Direct Blue 71, C.I. Direct Blue 78, C.I. Direct Red 2, C.I. Direct Red 81, C.I. Direct Violet 51, C.I. Direct

20   Orange 26, C.I. Direct Red 247, C.I. Direct Blue 168, C.I. Direct Green 85, C.I. Direct Brown 223, C.I. Direct Brown 106, C.I. Direct Yellow 142, C.I. Direct Blue 1, C.I. Direct Violet 9, C.I. Direct Red 81, Chemical Abstracts Registry Number 6300-50-1, Chemical Abstracts Registry Number 134476-95-2, Chemical Abstracts Registry Number 169454-83-5, and C.I. Direct Blue 98.

25   The casting of sol on polyvinyl alcohol polarizing film can be done through conventional coating processes, such as blade, hopper, and dip coating. It can be coated simultaneously to the both sides of the polarizing film. It can also be coated one side of the polarizing film, dried and subsequently coated on the other side of the polarizing film. The inventive protective layer can be put on one

30   side of the polarizing film with the other side protective layer being TAC film.

The following examples illustrate the practice of this invention.
They are not intended to be exhaustive of all possible variations of the invention.
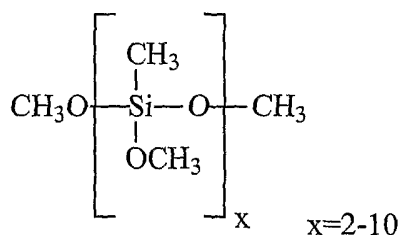Parts and percentages are by weight unless otherwise indicated.
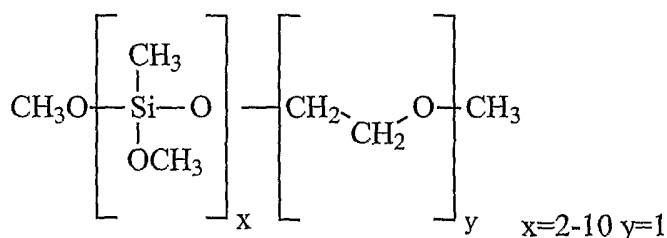
5   **EXAMPLES**

Materials:

APS-262 and APS-294 were supplied by Advanced Polymer Inc. Both materials

10   are oligomeric siloxane with methoxy end groups. The materials were analyzed
by gas chromatography mass spectrometry (GC/MS), matrix assisted laser
desorption/ionization (MALD/I) mass spectrometry, and nuclear magnetic
resonance (NMR). The analysis suggested a chemical structure as illustrated in
the following:

An **A** series

$$CH_3O-\left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ OCH_3 \end{array}\right]_x-CH_3 \qquad x=2\text{-}10$$

plus a small amount of a **B** series,

$$CH_3O-\left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ OCH_3 \end{array}\right]_x-\left[\begin{array}{c} CH_2 \\ CH_2 \\ O \end{array}\right]_y-CH_3 \qquad x=2\text{-}10 \ y=1$$

15

APS-262

An **A** series

$$\text{CH}_3\text{O}\left[\begin{array}{c}\text{CH}_3\\|\\\text{Si}-\text{O}\\|\\\text{OCH}_3\end{array}\right]_x\left[\begin{array}{c}\text{C}_6\text{H}_5\\|\\-\text{Si}-\text{O}\\|\\\text{C}_6\text{H}_5\end{array}\right]\left[\begin{array}{c}\text{CH}_3\\|\\-\text{Si}-\text{O}\\|\\\text{OCH}_3\end{array}\right]_y\text{CH}_3$$

x+y=0-5
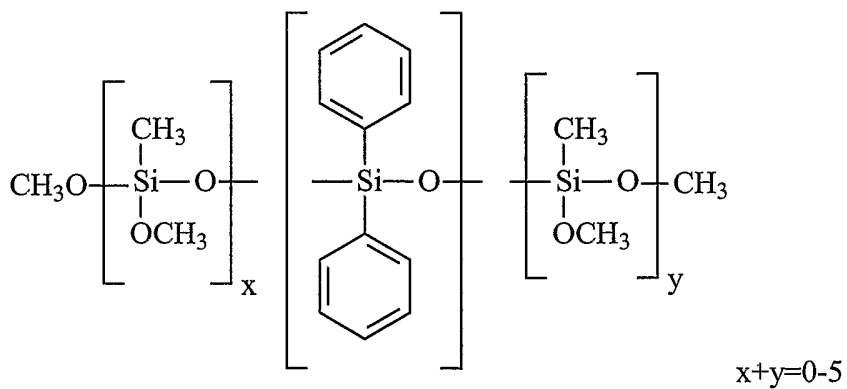
a measurable amounts of a **B** series,

$$\text{CH}_3\text{O}\left[\begin{array}{c}\text{CH}_3\\|\\\text{Si}-\text{O}\\|\\\text{OCH}_3\end{array}\right]_x\text{CH}_3 \qquad x=2\text{-}10$$
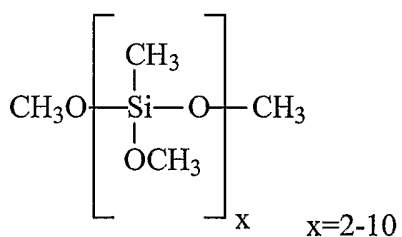
plus a small amount of a **C** series,

$$\text{CH}_3\text{O}\left[\begin{array}{c}\text{CH}_3\\|\\-\text{Si}-\text{O}\\|\\\text{OCH}_3\end{array}\right]_x\left[\begin{array}{c}-\text{CH}_2\text{CH}_2\text{O}-\end{array}\right]_y\text{CH}_3 \qquad x=2\text{-}10 \; y=1$$

5
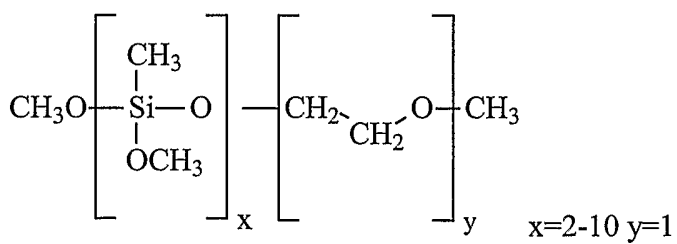
APS-294 (mixture)

Catalyst API Catalyst 5 is also provided by Advanced Polymer Inc. This catalyst
is based on titanium alkoxide.

5

Evaluation:

In-plane, out-of-plane birefringence and transmittance were measured using a
Woollam M-2000V Spectroscopic Ellipsometer.

10

Water Vapor Transmission Rate (WVTR) was measured using a Mocon tester in
compliance with ASTM-1249.

Dimensional change at elevated temperature was measured using a TA
15   Instruments TMA. The sample was heated to a set temperature at a rate of 10
oC/min, and then soaked for 5 mins at that temperature. The dimensional change
was then recorded.

Polarizer protection evaluation

20

Polarizer efficiency and photopic transmittance are two parameters to characterize
the performance of polarizer.

Polarizer plate photopic transmission and polarization efficiency were measured
25   using a Perkin-Elmer Lmabda 2spectrophotometer. Photopic transmission was
calculated as per CIE standard procedure using D65 illumination:

$$Y = k \int_{380}^{780} y(\lambda)\Phi(\lambda)d\lambda.$$

Polarization efficiency was calculated as:

$$PE = 100 \left[\frac{\left(Y_{\parallel} - Y_{\perp} \right)}{\left(Y_{\parallel} + Y_{\perp} \right)} \right]^{1/2}$$

An aging study was conducted on a polarizer. The polarizer was put in a high

5   humidity oven at 60°C, 90%RH for 500 hours. The polarizer efficiency and

photopic transmittance was measured before the aging and recorded as IPE(initial

polarizer efficiency) and IY (initial photopic transmission). After the aging, the

change in the polarizer efficiency (CPE) and photopic transmittance(CPT) were

recorded:

10

CPE=PE before aging-PE after aging

CPT=Y before aging-Y after aging

Example 1.

15

APS-294 was coated using a coating blade on bare PET film. The film is allowed

to dry at ambient conditions for 24 hours. A 44 micron dried free-standing film

was obtained after peeling from the PET film. The film showed 0.14 nm in-plane

retardation and −0.11 nm out-of-plane retardation, thus the in-plane birefringence

20   (n_x-n_y) was 3.2×10^{-6} and out-of-plane birefringence $(n_z - (n_x+n_y)/2)$ was -2.5×10^{-6}.

The transmittance of the film was 95%. The WVTR of the film was 503

$g/m^2/day$, or 0.022 $g*m/m^2/day$. The dimensional change at 150°C was 0.1%.

Comparative example 1

25

Cellulose triacetate resin was dissolved in methylene chloride and methanol (95:5)

and cast on a polished metal coating wheel. An 80 micron thick film was

obtained. The film was measured to have an in-plane retardation of 2.64 nm and

out-of-plane retardation is 51 nm. The TAC film showed an in-plane birefringence

30   of 3.3×10^{-5} and an out-of-plane birefringence of 6.3×10^{-4}. The WVTR of the film

was measured to be 513 g/m^2/day, or 0.041 g*m/m^2/day. The dimensional change at 150°C was 0.5%.

The above results show that the inventive layer is optically clear, has lower in-plane and out-of-plane birefringence, better resistance to water vapor transmission and better dimensional stability at elevated temperature than the comparative cellulose triacetate layer.

Example 2

APS-294 was coated on a PVA polarizer film with TAC protective layer on the opposite side using a coating knife. A 15 micron layer is formed on PVA after the coating was dried at ambient condition for 24 hours. The polarizer efficiency and photopic transmittance of the coated polarizer was then measured after drying. Afterwards, the coated polarizer is put in a high humidity oven at 60°C, 90%RH for 500 hours and again the polarizer efficiency and photopic transmittance was measured again.

Example 3

After removing protective layer from one side of a polarizer (Sumitomo), APS-294 was coated on a PVA polarizer film using a coating knife. A 8 micron layer is formed on PVA after the coating was dried at ambient condition for 24 hours. The polarizer efficiency and photopic transmittance of the coated polarizer was then measured after drying. Afterwards, the coated polarizer is put in a high humidity oven at 60°C, 90%RH for 500 hours and the polarizer efficiency and photopic transmittance was measured again.

Example 4

After removing protective layer from one side of a polarizer (Sumitomo), APS-294 was coated on a PVA polarizer film using a coating knife. A 11 micron layer is formed on PVA after the coating was dried at ambient condition for 24 hours. The polarizer efficiency and photopic transmittance of the coated polarizer was

then measured after drying. Afterwards, the coated polarizer is put in a high humidity oven at 60°C, 90%RH for 500 hours and the polarizer efficiency and photopic transmittance was measured again.

5   Example 5

After removing protective layer from one side of a polarizer (Sumitomo), APS-294 was coated on a PVA polarizer film using a coating knife. A 26 micron layer is formed on PVA after the coating was dried at ambient condition for 24 hours. The polarizer efficiency and photopic transmittance of the coated polarizer was

10   then measured after drying. Afterwards, the coated polarizer is put in a high humidity oven at 60°C, 90%RH for 500 hours and the polarizer efficiency and photopic transmittance was measured again.

Example 6

15   After removing protective layer from one side of a polarizer (Sumitomo), APS-262 with .5% catalyst of API-Catalyst 4, was coated on a PVA polarizer film using a coating knife. A 26 micron layer is formed on PVA after the coating was dried at ambient condition for 24 hours. The polarizer efficiency and photopic transmittance of the coated polarizer was then measured after drying. Afterwards,

20   the coated polarizer is put in a high humidity oven at 60°C, 90%RH for 500 hours and the polarizer efficiency and photopic transmittance was measured again.

Example 7

After removing both sides of protective layers from a polarizer (Palotechno), APS-

25   294 were coated on both sides of a PVA polarizer film using a coating knife. Two 8 micron layers are formed on PVA. The polarizer efficiency and photopic transmittance of the coated polarizer was then measured after drying. Afterwards, the coated polarizer is put in a high humidity oven at 60°C, 90%RH for 500 hours and the polarizer efficiency and photopic transmittance was measured again.

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Example 8

After removing both sides of protective layers from a polarizer (Palotechno), APS-294 were coated on both sides of a PVA polarizer film using a coating knife. Two 11 micron layers are formed on PVA. The polarizer efficiency and photopic

5   transmittance of the coated polarizer was then measured after drying. Afterwards, the coated polarizer is put in a high humidity oven at 60°C, 90%RH for 500 hours and the polarizer efficiency and photopic transmittance was measured again.

Example 9

10   After removing both sides of protective layers from a polarizer (Palotechno), APS-294 were coated on both sides of a PVA polarizer film using a coating knife. Two 26 micron layers are formed on PVA. The polarizer efficiency and photopic transmittance of the coated polarizer was then measured after drying. Afterwards, the coated polarizer is put in a high humidity oven at 60°C, 90%RH for 500 hours

15   and the polarizer efficiency and photopic transmittance was measured again.

Comparative example 2: a commercially available polarizer plate laminated with 80 micron TAC was used as a comparison. The polarizer efficiency and photopic transmittance of the polarizer was measured. The polarizer is then put in a high

20   humidity oven at 60°C, 90%RH for 500 hours and the polarizer efficiency and photopic transmittance was measured again.

Comparative example 3: another commercially available polarizer plate laminated with 40 micron TAC was used as a comparison. The polarizer efficiency and

25   photopic transmittance of the polarizer was measured. The polarizer is then put in a high humidity oven at 60°C, 90%RH for 500 hours and the polarizer efficiency and photopic transmittance was measured again.

Comparative example 4: another commercially available polarizer plate laminated

30   with 80 micron TAC was used as a comparison. The polarizer efficiency and photopic transmittance of the polarizer was measured. The polarizer is then put in

a high humidity oven at 60°C, 90%RH for 500 hours and the polarizer efficiency and photopic transmittance was measured again.

The polarizer evaluation results are listed in the following table.

5

	PE	CPE	CPT
Example			
2	99.78	-0.07	-4.1
3	99.96	-0.17	-0.17
4	99.96	-0.15	-0.01
5	99.97	-0.19	0
6	99.96	-0.05	-0.04
7	99.98	-0.1	0.01
8	99.94	-0.08	-0.03
9	99.88	-0.06	0
comparative example			
2	99.92	0.02	-4.1
3	99.79	0.02	-1.39
4	99.98	0.09	-3.05

The above table shows that the inventive coated polarizer sheet sustains the

10   polarizer function as well as the comparative example at a thickness range of 41 microns to 85 microns, and at either one side or both sides of a polarizing layer. The inventitive coated polarizer plates are generally thinner than the comparative examples, which have a thickness of 105 to 185 microns. Thus the inventive coated polarizer plate is advantageous to generate a thinner and cheaper polarizer

15   plate.

PARTS LIST

	101	protective layer
5	103	protective layer
	105	incoming unpolarized light
	107	polarizing film element
	109	linearly polarizer light

10

CLAIMS:

   1. A process for forming an integral protective layer on a polarizing layer comprising coating the layer with a sol, gelling the sol, and then curing the coating to form a contiguous crosslinked adherent protective layer.

   2. The process of claim 1 wherein said sol comprises an oligomeric compound having therein cross-linkable terminal groups.

   3. The process of claim 1 wherein said sol comprises oligomers of siloxane, acrylate, acrylamide, vinyl and copolymers thereof having therein silicon alkoxide terminal groups.

   4. The process of claims 2 and 3 wherein the Tg of the oligomer is lower than 25 degrees C.

   5. The process of claim 1 wherein said sol comprises a silicon alkoxide terminated siloxane oligomer.

   6. The process of claim 1 wherein said silicon alkoxide end grouped siloxane comprises diphenyl siloxane.

   7. The process of claim 1 wherein the coating is carried out without the use of solvent.

   8. The process of claim 1 wherein said sol further comprises a catalyst to promote sol preparation and gelling.

   9. The process of claim 1 wherein said curing is carried out at less than 75 degrees C.

10. The process of claim 1 wherein said polarizing polymer layer comprises polyvinyl alcohol.

11. The process of claim 1 wherein said polarizing polymer layer comprises iodine.

12. The process of claim 1 wherein said polarizing polymer layer comprises at least one dichroic organic compound.

13. The process of claim 1 wherein said integral protective layer has a thickness of between 10 and 60 micrometers.

14. The process of claim 1 wherein said integral protective layers are simultaneously coated on both sides of said polarizing polymer layer.

15. The process of claim 1 wherein said integral protective layers are sequentially coated on both sides of said polarizing polymer layer.

16. The process of claim 1 wherein said integral protective layer is coated on at least one side of said polarizing polymer layer.

17. The process of claim 1 wherein said integral protective layer is stable such that its percentage change in lateral dimension at a temperature of between 80 and 150 degrees C is less than 1%.

18. The process of claim 1 wherein said integral protective layer has a water vapor permeability of less than 0.05 g*m/m^2/day.

19. The process of claim 1 wherein said integral protective layer has an absolute in-plane birefringence of less than 10^{-5} and an absolute out-of-plane birefringence of less than 10^{-4}.

20.   The process of claim 1 wherein said integral protective layer
has an absolute in-plane retardation of less than 10nm and an absolute out-of-
plane retardation of less than 70nm.

5   21.   An multilayer polarizer plate comprising a polarizing
polyvinyl alcohol layer bearing a contiguous integral crosslinked polymeric layer.

22.   The polarizer plate of claim 21 wherein said integral
crosslinked polymeric layer comprises a silica-siloxane composite layer.

10
23.   The polarizer plate of claim 21 wherein said integral
crosslinked polymeric layer comprises a silica-diphenyl siloxane composite layer.

24.   The polarizer plate of claim 21 wherein said polarizing
15   polyvinyl alcohol layer comprises iodine.

25.   The polarizer plate of claim 21 wherein said polarizing
polyvinyl alcohol layer comprises at least one dichroic organic compound.

20   26.   The polarizer plate of claim 21 wherein said integral
crosslinked polymeric layer has a thickness of between 10 and 60 micrometers.

27.   The polarizer plate of claim 21 wherein said integral
protective layer has an absolute in-plane birefringence of less than 10^{-5} and an
25   absolute out-of-plane birefringence of less than 10^{-4}.

28.   The polarizer plate of claim 21 wherein said integral
protective layer has an absolute in-plane retardation of less than 10nm and an
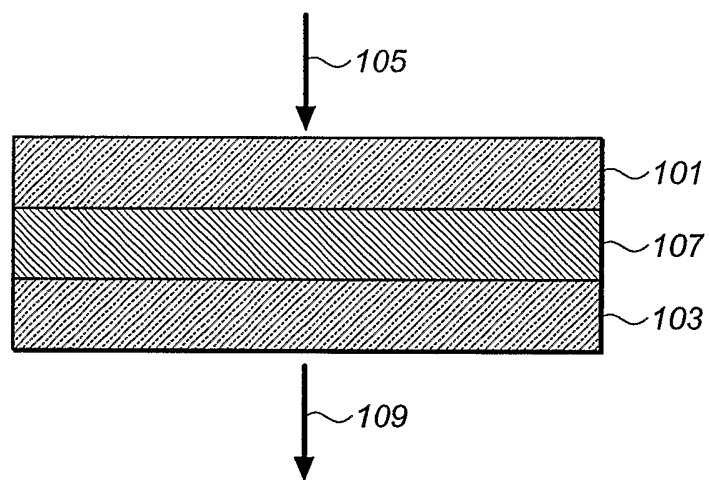absolute out-of-plane retardation of less than 70nm.

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FIG. 1

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. 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)
G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 818 624 A (DOWNEY, JR. ET AL) 4 April 1989 (1989-04-04) the whole document	1-28
X	US 4 759 611 A (DOWNEY, JR. ET AL) 26 July 1988 (1988-07-26) the whole document	1-28
A	US 5 676 885 A (STARZEWSKI ET AL) 14 October 1997 (1997-10-14) example 4	1-28
A	DD 141 076 A1 (DRECHSEL,LUDWIG,DD; MAEUSEZAHL,BARBARA,DD) 9 April 1980 (1980-04-09) claim 1	1-28

☐ 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 document 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
29 May 2006	09/06/2006

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

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