

PHASE RETARDER

The present invention relates to a phase retarder.

Description of the Related Art

Phase retarders comprising a uniaxially oriented polymer film have been used as optical compensators to enhance display qualities of liquid crystal display devices.

A STN type liquid crystal display device using such phase retarders as compensators is advantageous in that it can be lighter in weight, thinner and less expensive, but disadvantageous in that it has narrow viewing angle characteristics and exhibits a low contrast ratio compared to a STN double cell type liquid crystal display device using a liquid crystal cell as optical compensators.

The STN type device has been considerably improved to alleviate its poor contrast by laminating two plies of phase retarders, but they are still unsatisfactory for the viewing angle characteristics.

The viewing angle characteristics of the liquid crystal display devices using the phase retarders as optical compensators are greatly dependent upon the viewing angle characteristics of the phase retarders

1 themselves. The viewing angle characteristics of the
phase retarders comprising uniaxially oriented polymer
films can be evaluated by using a viewing angle.

The viewing angle of phase retarders is
5 defined as a tilt angle ($\theta_{1.10}$) of a film relative to a
normal direction when a ratio of the retardation (R)
observed for the tilted film to the retardation (R_0)
observed for the normally disposed film is 1.10 with the
film being tilted by rotating around an axis which is
10 corresponding to the slow axis of the film having a
positive birefringent anisotropy, or to the fast axis of
the one having a negative birefringent anisotropy where
the observation is performed under a polarizing
microscope equipped with Senarmont compensator. The
15 higher the viewing angle, the better the viewing angle
characteristics.

As techniques for enhancing the viewing angle,
there have been proposed several methods such as a
method of shrinking the film in the direction
20 perpendicular to the stretching direction at the time of
stretching as disclosed in Japanese Patent KOKAI (Laid-
open) No. 2-191904; a method of controlling the
birefringent properties of a raw film, which has been
produced from a molten polymer or a polymer solution
25 under an electric field applied, by stretching as
disclosed in Japanese Patent KOKAI (Laid-open) No. 2-
285303; and a method of laminating a film, which has
been produced under an electric field applied, on a

1 conventional phase retarder as disclosed in Japanese
Patent KOKAI (Laid-open) No. 3-85519. However, it can
hardly be said that any of these methods has good mass
producibility.

5 Furthermore, in order to improve display
characteristics such as contrast, color and viewing
angle properties and the like, there have been developed
various liquid crystal display schemes other than the
STN type, for example, a TN liquid crystal display
10 having a birefringent optical compensating layer as
disclosed in G.B. Patent No. 1462978 and a homeotropic
liquid crystal display scheme having a birefringence
compensating layer as disclosed in Japanese Patent KOKAI
(Laid-open) No. 2-15239. However, these liquid crystal
15 displays require as optical compensator a phase retarder
comprising a film having a non-anisotropic refractive
index in the film plane ($R_0=0$) and a refractive index
different therefrom in the thickness direction normal to
the plane.

20 SUMMARY OF THE INVENTION

The present inventors have made extensive
research for overcoming the problems as described above.
As a result, it has been discovered that the use of a
layered inorganic compound enables production of a novel
25 phase retarder having an excellent performance.

1 The present invention provides a novel phase
retarder characterized by comprising a layered inorganic
compound film or sheet having an in-plane refractive
index which is different from the refractive index in
5 the thickness direction.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a chart showing iso-contrast
curves representing the viewing angle characteristics of
the FTN type LCD using the phase retarders of Examples
10 according to the present invention.

Figure 2 is a chart showing iso-contrast
curves representing the viewing angle characteristics of
the liquid crystal display device using the conventional
phase retarders.

15 DESCRIPTION OF THE PREFERRED EMBODIMENTS

The layered inorganic compounds to be used in
the present invention are such that they have a
stratified structure with a plurality of crystalline
layer units being stacked on one another and can be
20 intercalated with ions or molecules, which are
introduced between the crystalline layer units, by
various physical or chemical procedures without
destroying the structure of the crystalline layer unit
because of the relatively weak bonding strength
25 between the crystalline layer units; and that they have
such refractive index properties that the refractive



1 index in the plane of the crystalline layer unit is
different from the refractive index in the thickness
direction.

The layered inorganic compounds as above are
5 described by T. Kato and I. Kuroda in the publication
"Development and Application of intercalary compounds"
(published by CMC Co. Ltd., 1985) where layered
inorganic compounds are referred to, including, for
example, clay minerals, chalcogen compounds, zirconium
10 phosphate compounds, oxyacid salts of transition metals,
layered polysilicates, metal oxyhalogenides, and
intercalary forms thereof intercalated with ions or
molecules between the crystalline layer units. When
layered inorganic compounds having a higher refractive
15 index in the plane of the crystalline layer unit than
that in the thickness direction are used, layered
inorganic compound sheets or films comprising layered
inorganic compounds can be easily obtained. Clay
minerals can be preferably employed in the present
20 invention. The clay minerals may be classified into two
types.

The first type is such that the crystalline
layer unit is composed of a two-layer structure having a
layer of silica tetrahedrons and a layer of octahedrons
25 with central metal of aluminum, magnesium or the like
formed thereon. The second type is such that the
crystalline layer unit is composed of a three-layer
structure having a layer of octahedrons with central

- 1 metal of aluminum, magnesium or the like sandwiched
between two silica tetrahedron layers. The first type
includes kaolinite group, antigorite group, while the
second type includes smectite group, vermiculite group,
5 and mica group.

Practical clay minerals include kaolinite,
dickite, nacrite, halloysite, antigorite, chrysotile,
prophyllite, montmorillonite, hectorite, sodium
tetrasilic mica, sodium tenorite, muscovite,
10 margarite, talc, vermiculite, phlogopite,
xanthophyllite, and chlorite.

Among the clay minerals, chemically
synthesized sodium tetrasilic mica containing less
impurities, and the smectite group are preferred for
15 excellent transparency. Exemplary smectite group
materials include montmorillonite, beidellite,
nontronite, saponite, hectorite, sauconite, and
chemically synthesized products having a similar
crystalline structure.

20 The layered inorganic compounds which have
been swollen or dispersed, for example, in the form of
dispersion or gel are formed into film by solvent
casting or coating on a releasable substrate, for
example, on a polyester film having a surface treated
25 with a releasing agent and by peeling off after drying,
whereby a layered inorganic compound sheet or film
comprising layered inorganic compounds and having less
anisotropic in-plane refractive index, which is different

1 from the refractive index in the thickness direction can
be easily produced. The resultant sheets or films can
be used as phase retarders in the present invention.

Solvents to be used for swelling or dispersing
5 the layered inorganic compounds should be those which
can swell the interlayer space between the crystalline
layer units of the layered inorganic compounds, and
among them, preferred ones are those capable of swelling
the interlayer space to such an extent as to exhibit a
10 colloidal state. Exemplary solvents which can be used
for the clay minerals not formed with organic
materials between the crystalline layer units are
dimethylformamide, dimethyl sulfoxide, nitromethane,
water, methanol and ethylene glycol.

15 In order to achieve a good transparency after
film formation, such layered inorganic compounds
containing no impurity and having a mean particle size
of 5000 nm or less as determined by a dynamic light
scattering method, inter alia, clay minerals should be
20 preferably used. More preferred mean particle size is
in the range of 1000 nm to 10 nm. The synthetic
smectite group materials, mean particle size of which is
controlled in the range of visible light wave length or
less are preferred; inter alia, synthetic hectorite
25 group materials are preferred.

In production of the phase retarders using the
layered inorganic compound sheets or films according to
the present invention, a mixture of the layered

1 inorganic compounds with an optically transparent resin
is preferred because film formability, mechanical
properties and durability are improved.

The optically transparent resins to be used
5 for the mixture are, but not limited to, any one
selected from hydrophobic resins and hydrophilic ones as
desired depending upon the type of layered inorganic
compounds. Such resins may be used alone or in a blend
of a plurality of them, and inclusion of a resin
10 additive can be acceptable, if in small amount.

The ratio of the layered inorganic compounds
to the optically transparent resins is not critical,
though the ratio of the layered inorganic compounds to
the optically transparent resins by volume is preferably
15 in the range of 0.1 to 10 in view of enhancing film
formability and mechanical properties, such as crack
resistance of the layered inorganic compound sheets or
films.

Procedure for forming films from a mixture of
20 the layered inorganic compounds and the optically
transparent resins is not critical, so long as the
interlayer space between the crystalline layer units of
the layered inorganic compounds is expanded after the
film formation to attain a structure where the resin
25 molecules occupy the interlayer space between the
crystalline layer units.

For example, one may make mention of a method
comprising the steps of heat-kneading the layered

1 inorganic compounds and the optically transparent
resins, and extruding the resultant mixture to form the
sheets; a method comprising the steps of mixing a
layered inorganic compound which has been swollen or
5 dispersed in a solvent, for example, a dispersion or
gel, with the optically transparent resins, and
extruding the resultant mixture to form films; and a
method comprising the steps of mixing a layered
inorganic compound, which has been swollen or dispersed
10 in a solvent, with a solution of the optically
transparent resins dissolved therein, and casting or
coating the resultant uniform mixture on a substrate to
produce films. Preferred among these is the method
where a dispersion of the layered inorganic compounds in
15 a solvent and a solution of the optically transparent
resins dissolved are mixed to form a uniform mixture
which is cast or coated to produce films.

When a clay mineral is used as layered
inorganic compound, the hydrophilic resins to be used
20 include nonionic hydrophilic resins such as vinyl
alcohol polymers, for example, polyvinyl alcohol,
ethylene-vinylalcohol copolymers, partially saponified
polyvinyl acetate, cellulose polymers, for example,
cellulose, hydroxyethyl cellulose, carbomethoxy
25 cellulose, polyvinylpyrrolidone, polyhydroxyethyl
methacrylate, polyacrylamide, and polyethylene glycol;
cationic hydrophilic resins such as polyethyleneimine,
polyallylamine, N-type-alkylated polyvinylpyridine, and

1 chitosan; anionic hydrophilic resins such as polyacrylic
acid, sodium polyacrylate, polystyrene sulfonate, and
sodium polystyrene sulfonate.

For enhancement of the film formability and
5 the mechanical properties such as crack resistance of
the layered inorganic compound sheets or films, the use
of non-ionic hydrophilic resins, inter alia,
polyvinylalcohol polymers is preferred, and
polyvinylalcohols having a degree of saponification of
10 70% or more and a degree of polymerization of 200 to
1800 are most preferred for excellent mixability with
clay minerals, as well as transparency after film
formation.

The mixture of the layered inorganic compounds
15 and the optically transparent resins may cause an
orientation of the optically transparent resins at the
time of the film formation resulting in generation of
birefringence, but the in-plane retardation should be
preferably controlled to a value of 50 nm or less.

20 The phase retarders comprising the layered
inorganic compound sheets or films according to the
present invention may be formed on a transparent
substrate having no or a very small in-plane
birefringence to produce a phase retarder in the form of
25 a sheet or a film deposited on the transparent
substrate.

The transparent substrates to be used should
have an excellent transparency in the visible light

1 range, but have no in-plane birefringence or very small
in-plane birefringence. For example, they should have a
in-plane retardation of 50 nm or less and optical
uniformity, and be capable of forming optically uniform
5 sheets or films from a dispersion or gel obtained by
swelling or disperse the layered inorganic compounds.

The transparent substrates as above include
clean glass substrates, transparent resin substrates
produced by a film-casting process, and surface-
10 saponified cellulose base films, inter alia, the
surface-saponified cellulose base films are preferred.

As techniques for laminating the transparent
substrate and the phase retarder of the layered
inorganic compound sheet or film according to the
15 present invention, there may be mentioned a method
comprising the steps of forming the film on a releasable
substrate such as polyester film, the surfaces of which
have been treated with silicone, or stainless steel
plates processed with fluorine, then peeling the layered
20 inorganic compound film from the substrate, and
laminating the film onto one of various substrates with
an adhesive or a sticking agent; a method comprising the
steps of casting a layered inorganic compound which has
been swollen or dispersed, for example, a dispersion or
25 a gel on a transparent substrate to form a film
deposited on the substrate; a method comprising the
steps of mixing a layered inorganic compound which has
been swollen or dispersed, for example, a liquid

1 dispersion or a gel with a solution of the optically
transparent resin dissolved to produce a uniform
mixture, and casting the mixture to form a film; and a
method comprising the step of extruding a layered
5 inorganic compound on one of various transparent
substrates to produce a laminate. Among them, the
method comprising the steps of mixing uniformly a liquid
dispersion, obtained by swelling or dispersing a layered
inorganic compound in a solvent, with a solution of an
10 optically transparent resin dissolved to produce a
dispersion, which is made into a film by a casting or
coating process, is preferred.

The phase retarders comprising the layered
inorganic compound film or sheet according to the
15 present invention can be used alone or in the form of a
laminate on an optically transparent sheet or film which
have no birefringent anisotropy in the plane. They can
be preferably employed in the liquid crystal display
devices of the type requiring an optical compensator, in
20 which the in-plane refractive index and the refractive
index in the thickness direction are different from each
other.

The phase retarders comprising the layered
inorganic compound film or sheet according to the
25 present invention can be endowed with a good
viewing angle property by laminating on a birefringent
film having a negative birefringent anisotropy.

The birefringent films having a negative

1 birefringent anisotropy can be easily obtained by
stretching a film of a resin having an negative
intrinsic birefringence. The stretching can be
performed by any one of conventional techniques such as
5 tentering, stretching between rolls, and rolling, and
the like, so long as it allows uniformity in retardation
to attain.

As laminating techniques, one can employ
similar methods to those for laminating on the
10 transparent substrate as described above.

There are known various resins having negative
intrinsic birefringence. Vinyl resins having high
dielectric constant substituents in side chains are
preferred, inter alia, aromatic vinyl resins and acrylic
15 resins are more preferred because they are excellent in
optical properties.

Practical examples of such resins include
polystyrenes, poly- α -methylstyrene, polyvinylpyridine,
polyvinyl naphthalene, and polymethyl methacrylate.

20 The phase retarders obtained in this way have
excellent viewing angle properties and can be used as
optical compensator in the liquid crystal display
devices of the type requiring a wide viewing angle.

Process for attaching the present phase
25 retarders onto the liquid crystal display devices is not
critical and may be conducted as by applying a sticking
agent to one side or both sides of the phase retarder,
and attaching adhesively the phase retarder onto a

1 liquid crystal cell and/or a polarizer. Either side of
the phase retarder may be disposed on the side of the
liquid crystal cell. The phase plate may be disposed
between the front polarizer and the liquid crystal cell,
5 or between the rear polarizer and the liquid crystal.

The phase retarders of the present invention
can be easily produced and used alone or in combination
with other films and the like for improving the display
properties of various liquid crystal display devices.

10 For example, the phase retarders comprising
the layered inorganic compounds sheets or films
according to the present invention can be used as
compensators in the TN type liquid crystal display
devices which comprise:

15 a liquid crystal cell containing nematic
liquid crystal molecules having a positive dielectric
anisotropy where the molecules are placed between two
transparent substrates each having an electrode
disposed parallel thereto, such that both electrodes
20 face each other and are oriented with their
longitudinal axis parallel to the transparent
substrates, and are twisted as a whole at an angle of 80° to
 100° relative to the direction perpendicular to the
transparent substrate when no voltage is applied;

25 a pair of linear polarizers which are disposed
on the outer sides of the liquid crystal cell; and

a compensator layer disposed in at least one
place between the liquid crystal cell and the linear

1 polarizers.

Alternatively, a combination of the phase retarder, comprising the layered inorganic compound sheet or film, with a uniaxially oriented birefringent film, comprising a thermoplastic resin having a negative birefringent anisotropy, can be used as compensator in the STN type liquid crystal display device which comprises:

a liquid crystal cell containing nematic liquid crystal molecules having a positive dielectric anisotropy where the molecules are placed between two transparent substrates each having an electrode disposed parallel thereto such that both electrodes face each other and are oriented with their longitudinal axis parallel to the transparent substrates, and are twisted as a whole at an angle of 180° to 270° relative to the direction perpendicular to the transparent substrate when no voltage is applied;

a pair of linear polarizers which are disposed on the outer sides of the liquid crystal cell; and

a compensator layer disposed in at least one place between the liquid crystal cell and the linear polarizers. Such TN and STN type liquid crystal displays are also described in U.S. Patent No.

25 5,061,042.

The present invention will be illustrated with reference to the following Examples without being limited thereto. The mean particle sizes in the following

- 1 Examples were determined with BI-90 Particle Sizer
available from Brookhaven Instruments Corporation.

Example 1

- Polystyrene film (HR sheet available from
- 5 DAINIPPON INK & CHEMICALS INC.) was milled to produce a
15% solution of dichloroethane which was cast into a
film. This film was stretched 2.8 times by tentering at
135°C resulting in a birefringent film having an in-
plane retardation (R_0) = 512 nm, $\theta_{1,10} = 35^\circ$, and a
10 thickness of 28 μm . This film was corona-discharged
with a corona-discharge apparatus (MM Electrode type
corona-discharge test machine available from Softal
Electronic GmbH) under conditions of a discharge energy
of 400 W.min./m² to achieve a surface tension of 54
15 dyn/cm or more, and then applied with a 1% aqueous
dispersion of a clay mineral, i.e., synthetic smectite
particles (available from KUNIMINE KOGYO under the
tradename, SMECTON SA) having a mean particle size of
108 nm, and dried at about 28°C for 12 hours to produce
20 a phase retarder comprising a birefringent polystyrene
film having the synthetic smectite layer of a thickness
of 3.8 μm laminated thereon. This phase retarder
exhibited a wide viewing angle of $\theta_{1,10} = 59^\circ$ with in-
plane retardation value $R_0 = 512$ nm.

25 Example 2

A cast polystyrene film produced in the same

1 procedure as in Example 1 was stretched 2.8 times at
135°C by tentering to attain a birefringent film having
a thickness of 28 μm and exhibiting $\theta_{1,10} = 35^\circ$ with $R_0 =$
503 nm. This film was corona-discharged under the same
5 conditions as in Example 1 to achieve a surface tension
of 54 dyn/cm or more, and then applied with a 2% aqueous
dispersion of a clay mineral, i.e., synthetic hectorite
particles (available from Laporte Co. under the
tradename, Laponite XLG) having a mean particle size of
10 35 nm, and dried at about 28°C for 12 hours to produce a
phase retarder comprising a birefringent polystyrene
film having the synthetic hectorite layer of a thickness
of 10 μm laminated thereon. This phase retarder
exhibited a wide viewing angle of $\theta_{1,10} = 80^\circ$ or more with
15 $R_0 = 506$ nm.

Example 3

To a triacetyl cellulose film having a
thickness of 80 μm (available from Fuji Photo Film Co.
Ltd. under the tradename, FJITACK CLEAR), the surfaces
20 of which were treated by saponification, having an in-
plane retardation of 6 nm, there was applied a 1%
aqueous dispersion of a clay mineral, i.e., synthetic
smectite particles (available from KUNIMINE Industry
under the tradename, SMECTON SA) having a mean particle
25 size of 108 nm, and dried at about 28°C for 12 hours to
produce a phase retarder comprising a triacetyl
cellulose film having the synthetic smectite layer of a

1 thickness of 3.8 μm laminated thereon. The synthetic
smectite layer had a difference in refractive index
between the direction in the plane and the thickness
direction of 1.12×10^{-1} and the phase retarder had a
5 very low birefringence as represented by an in-plane
retardation of 6 nm.

Example 4

A cast polystyrene film having a very low
birefringence was obtained by casting in the same
10 procedure as in Example 1. This film was corona-
discharged under the same conditions as in Example 1 to
achieve a surface tension of 54 dyn/cm or more, and then
applied with a 0.65% aqueous dispersion of a clay
mineral, i.e., sodium tetrasiliric mica (available from
15 TOPY INDUSTRIES, LTD. under the tradename, Na-Ts) having
a mean particle size of 977 nm, and dried at about 28°C
for 12 hours to produce a phase retarder comprising a
cast polystyrene film of a very low birefringence having
a sodium tetrasiliric mica layer of a thickness of 2.5
20 μm laminated thereon. The sodium tetrasiliric mica
layer had a difference in refractive index between the
direction in the plane and the thickness direction of
 2.14×10^{-1} and the phase retarder had a very low
birefringence in the plane.

25 Example 5

A cast polystyrene film produced in the same

1 procedure as in Example 1 was stretched 2.8 times at
135°C by tentering to attain a birefringent film having
a thickness of 28 μm and exhibiting $\theta_{1,10} = 35^\circ$ with $R_0 =$
503 nm. This film was corona-discharged under the same
5 conditions as in Example 1 to achieve a surface tension
of 54 dyn/cm or more, and then applied with an aqueous
dispersion consisting of a 1 : 1 mixture of a 2% aqueous
dispersion of a clay mineral, i.e., synthetic hectorite
particles (available from Laporte Co. under the
10 tradename, Laponite XLG) having a mean particle size of
35 nm and a 2% aqueous solution of polyvinylalcohol
(available from Wako Pure Chemical Industries, Ltd.)
having a degree of polymerization of 500 and a degree of
saponification of 98.5%, and then dried at about 28°C
15 for 30 hours to produce a phase retarder comprising a
birefringent polystyrene film having a polyvinylalcohol-
containing synthetic hectorite layer of a thickness of
18 μm laminated thereon. This phase retarder exhibited
a wide viewing angle of $\theta_{1,10} = 74^\circ$ with $R_0 = 503$ nm and
20 was very good in film condition.

Example 6

To a triacetyl cellulose film having a
thickness of 80 μm (available from Fuji Photo Film Co.,
Ltd. under the tradename, FJITACK CLEAR), the surfaces
25 of which were treated by saponification, having an in-
plane retardation of 6 nm, there was applied an aqueous
dispersion consisting of a 3 : 7 mixture of a 5% aqueous

1 dispersion of a clay mineral, i.e., synthetic hectorite
particles (available from Laporte Co. under the
tradename, Laponite XLS) having a mean particle size of
35 nm and a 2.5% aqueous solution of polyvinylalcohol
5 (available from KURARAY CO., LTD.) having a degree of
polymerization of 300 and a degree of saponification of
98.5%, and then dried at about 60°C for one hour to
produce a phase retarder comprising a triacetyl
cellulose film having a polyvinylalcohol-containing
10 synthetic hectorite layer of a thickness of 12 μm
laminated thereon. The polyvinylalcohol-containing
synthetic hectorite layer had a difference in refractive
index between the direction in the plane and the
thickness direction of 0.18×10^{-1} and the phase retarder
15 had a very low birefringence in the plane as represented
by an in-plane retardation of 6 nm. This phase retarder
was very good in film condition.

Example 7

To a non-oriented glass plate, there was
20 applied an aqueous dispersion consisting of a 3 : 7
mixture of a 2% aqueous dispersion of a clay mineral,
i.e., synthetic hectorite particles (available from
Laporte Co. under the tradename, Laponite XLS) having a
mean particle size of 35 nm and a 1% aqueous solution of
25 polyvinylalcohol (available from KURARAY CO., LTD.)
having a degree of polymerization of 1000 and a degree
of saponification of 98.5%, and then dried at about 60°C

1 for one hour to produce a phase retarder comprising the
glass plate having a polyvinylalcohol-containing
synthetic hectorite layer of a thickness of 8 μm
laminated thereon. The polyvinylalcohol-containing
5 synthetic hectorite layer had a difference in refractive
index between the direction in the plane and the
thickness direction of 0.16×10^{-1} and the phase plate
had a very low birefringence in the plane. This phase
retarder was very good in film condition.

10 Example 8

To a triacetyl cellulose film having a
thickness of 80 μm (available from Fuji Photo Film Co.,
Ltd. under the tradename, FJITACK CLEAR), the surfaces
of which were treated by saponification, having an in-
15 plane retardation of 6 nm, there was applied an aqueous
dispersion consisting of a 3 : 7 mixture of a 1% aqueous
dispersion of a clay mineral, i.e., synthetic hectorite
particles (available from Laporte Co. under the
tradename, Laponite XLS) having a mean particle size of
20 35 nm and a 0.5% aqueous solution of polyvinylalcohol
(available from KURARAY CO., LTD.) having a degree of
polymerization of 2400 and a degree of saponification of
98.5%, and then dried at about 60°C for one hour to
produce a phase retarder comprising a triacetyl
25 cellulose film having a polyvinylalcohol-containing
synthetic hectorite layer of a thickness of 10 μm
laminated thereon. The polyvinylalcohol-containing

1 synthetic hectorite layer had a difference in refractive
index between the direction in the plane and the
thickness direction of 0.16×10^{-1} and the phase retarder
had a very low birefringence in the plane as represented
5 by an in-plane retardation of 6 nm. This phase retarder
was good in film condition.

Example 9

To a releasable polyester film, the surface of
which was treated with silicon, there was applied an
10 aqueous dispersion consisting of a 3 : 7 mixture of a 2%
aqueous dispersion of a clay mineral, i.e., synthetic
hectorite particles (available from Laporte Co. under
the tradename, Laponite XLS) having a mean particle size
of 35 nm and a 1% aqueous solution of polyvinylalcohol
15 (available from KURARAY CO., LTD.) having a degree of
polymerization of 1000 and a degree of saponification of
88.5%, and then dried at about 60°C for one hour. A
polyvinylalcohol-containing synthetic hectorite layer
was easily peeled off so that a phase retarder
20 comprising the polyvinylalcohol-containing synthetic
hectorite sheet of a thickness of 15 μm . This phase
retarder had a difference in refractive index between
the direction in the plane and the thickness direction
of 0.17×10^{-1} and had a very low birefringence in the
25 plane. This phase retarder was very good in film
condition.

1 Example 10

 To a triacetyl cellulose film having a
thickness of 80 μm (available from Fuji Photo Film Co.,
Ltd. under the tradename, FJITACK CLEAR), the surfaces
5 of which were treated by saponification, having an in-
plane retardation of 6 nm, there was applied an aqueous
dispersion consisting of a 3 : 7 mixture of a 2% aqueous
dispersion of a clay mineral, i.e., synthetic hectorite
particles (available from Laporte Co. under the
10 tradename, Laponite XLG) having a mean particle size of
35 nm and a 2% aqueous solution of polyvinylalcohol
(available from KURARAY CO., LTD.) having a degree of
polymerization of 1000 and a degree of saponification of
88.5%, and then dried at about 28°C for 30 hours to
15 produce a phase retarder comprising a triacetyl
cellulose film having a polyvinylalcohol-containing
synthetic hectorite layer of a thickness of 10 μm
laminated thereon. The polyvinylalcohol-containing
synthetic hectorite layer had a difference in refractive
20 index between the direction in the plane and the
thickness direction of 0.17×10^{-1} and the phase retarder
had a very low birefringence in the plane as represented
by an in-plane retardation of 6 nm. This phase plate
was very good in film condition.

25 Example 11

 A phase retarder was produced in the same
procedure as in Example 6, except that the

1 polyvinylalcohol-containing synthetic hectorite layer
had a thickness of 2.4 μm .

Then, a 25% solution of polystyrene resin
(available from SUMITOMO CHEMICAL CO., LTD.) in
5 dichloroethane was prepared, and cast into a film. This
cast film was stretched 2.0 times at 130°C by tentering
to obtain a birefringent film exhibiting $R_0 = 403 \text{ nm}$,
 $\theta_{1.10} = 38^\circ$ and having a thickness of 85 μm .

The phase retarder and the birefringent film
10 of polystyrene were stacked by means of a sticking agent
with the polyvinylalcohol-containing synthetic hectorite
layer being between the triacetyl cellulose film and the
birefringent film to produce a phase retarder. This
phase retarder exhibited good viewing angle properties
15 as $R_0 = 403 \text{ nm}$ and $\theta_{1.10} = 51^\circ$.

Example 12

A phase retarder was produced in the same
procedure as in Example 6, except that the
polyvinylalcohol-containing synthetic hectorite layer
20 had a thickness of 7.2 μm .

The phase retarder and the same birefringent
film of polystyrene as in Example 11 were stacked by
means of a sticking agent with the polyvinylalcohol-
containing synthetic hectorite layer being between the
25 triacetyl cellulose film and the birefringent film to
produce a phase retarder. This phase retarder exhibited
good viewing angle properties as $R_0 = 403 \text{ nm}$ and $\theta_{1.10} =$

- 1 80° or more.

Comparative Example 1

A cast polystyrene film obtained in the identical procedure to that in Example 1 was stretched
5 2.8 times at 135°C by tentering to produce a phase retarder. This phase retarder exhibited $R_0 = 503$ nm and $\theta_{1.10} = 35^\circ$.

Example 13

A triacetyl cellulose film having a thickness
10 of 80 μ m (available from Fuji Photo Film Co., Ltd. under the tradename, FJITACK CLEAR), the surfaces of which were treated by saponification, was used as a substrate film (in-plane retardation: 5.5 nm). Onto the substrate film, there was applied an aqueous dispersion consisting
15 of a 3 : 7 mixture of a 5.0% aqueous dispersion of a clay mineral, i.e., synthetic hectorite particles (available from Laporte Co. under the tradename, Laponite XLS) having a mean particle size of 35 nm and a 2.5% aqueous solution of polyvinylalcohol (available
20 from KURARAY CO., LTD.) having a degree of saponification of 98.5% and a degree of polymerization of 300 to produce a film having a thickness of 2.4 μ m after drying, thereby attaining a phase retarder comprising a triacetyl cellulose film having a
25 polyvinylalcohol-containing synthetic hectorite layer laminated thereon (referred to as Film A hereunder).

1 The polyvinylalcohol-containing synthetic hectorite
layer had a difference in refractive index between the
direction in the plane and the thickness direction of
0.18 $\times 10^{-1}$ and the in-plane retardation of Film A was
5 very low (5.5 nm as determined by measurement with a
polarizing microscope).

Furthermore, a cast film was obtained from the
polystyrene (available from SUMITOMO CHEMICAL CO., LTD.
under the tradename, SUMIBRIGHT E183) in the identical
10 procedure to that in Example 11. The cast film was
uniaxially stretched to produce a uniaxially oriented
birefringent film having an in-plane retardation of 390
nm as determined by measurement with the polarizing
microscope (referred to as Film B) and a uniaxially
15 oriented birefringent film having an in-plane
retardation of 406 nm (referred to as Film C).

Using these films, there were prepared a phase
retarder 1 by laminating the Film A and the Film B with
a sticking agent (Constitution: triacetyl cellulose
20 film/polyvinylalcohol-containing synthetic hectorite
layer/polystyrene film) and a phase retarder 2 by
laminating the Film A and the phase Film C with a
sticking agent (Constitution: triacetyl cellulose
film/polyvinylalcohol-containing synthetic hectorite
25 layer/polystyrene film).

The STN type liquid crystal display device
with an optical compensator film equipped on the word
processor available from FUJITSU LTD. under the

1 tradename, OASYS 30LX-401 was modified by removing the
optical compensator film therefrom. Then, the phase
retarder 1 was interposed between the upper polarizing
film and the liquid crystal cell and the phase retarder
5 2 was interposed between the lower polarizing film and
the liquid crystal cell with each triacetyl cellulose
layer of both films being on the side of the film remote
from the liquid crystal cell. In this way, a STN type
LCD was made using as a compensating phase retarders the
10 combination of the phase retarders having the layered
inorganic compound layer with the uniaxially oriented
birefringent films.

This LCD exhibited less variation in contrast
depending upon viewing angle and good viewing angle
15 characteristics. Iso-contrast curves are shown in
Figure 1, in which CR indicates a contrast ratio.

Comparative Example 2

A liquid crystal display device was
constructed in the same manner as in Example 13, except
20 that a phase retarder having an in-plane retardation of
385 nm prepared from a thermoplastic resin having a
positive birefringent anisotropy (available from
SUMITOMO CHEMICAL CO., LTD. under the tradename,
SUMIKALIGHT) was used as Film 1, and that a birefringent
25 film having an in-plane retardation of 408 nm prepared
from a thermoplastic resin having a positive
birefringent anisotropy (available from SUMITOMO

1 CHEMICAL CO., LTD. under the tradename, SUMIKALIGHT) was
used as Film 2. This liquid crystal display device was
inferior in viewing angle characteristics especially in
the vertical direction viewing angle characteristics, to
5 those of the liquid crystal display device constructed
in Example 13. Iso-contrast curves are shown in Figure
2.

Example 14

A triacetyl cellulose film having a thickness
10 of 80 μm (available from Fuji Photo Film Co., Ltd. under
the tradename, FJITACK CLEAR), the surfaces of which
were treated by saponification (in-plane retardation 6
nm) was used as a substrate film. Onto the substrate
film, there was applied an aqueous dispersion consisting
15 of a 3 : 7 mixture of a 5.0% aqueous dispersion of a
clay mineral, i.e., synthetic hectorite particles
(available from Laporte Co. under the tradename,
Laponite XLS) having a mean particle size of 35 nm and a
2.5% aqueous solution of polyvinylalcohol (available
20 from KURARAY CO., LTD.) having a degree of
polymerization of 300 and a degree of saponification of
98.5%, and then dried to produce a laminate film
comprising a triacetyl cellulose film having a
polyvinylalcohol-containing synthetic hectorite layer of
25 a thickness of 15 μm .

Using a 1% aqueous solution of
polyvinylalcohol (available from KURARAY CO., LTD.)

1 under the tradename, Poval 117) having a degree of
polymerization of 1700 and a degree of saponification of
98.5% as an adhesive, a triacetyl cellulose film having
a thickness of 80 μm (available from Fuji Photo Film
5 Co., Ltd. under the tradename, FJITACK CLEAR), the
surfaces of which were treated by saponification, and
having an in-plane retardation of 6 nm was wet-laminated
onto the side of the polyvinylalcohol-containing
synthetic hectorite layer, and dried at 80°C for one
10 hour to obtain a phase retarder (Constitution: triacetyl
cellulose film/polyvinylalcohol-containing synthetic
hectorite layer/triacetyl cellulose film).

The polyvinylalcohol-containing synthetic
hectorite layer had a difference in refractive index
15 between the direction in the plane and the thickness
direction of 0.18×10^{-1} and the in-plane retardation of
the phase film was very low (an in-plane retardation of
12 nm).

This phase film was interposed between the
20 upper polarizing film and the liquid crystal cell of a 3
inch thin film transistor TN liquid crystal color
television (available from Matsushita Electric
Industrial Co., Ltd. under tradename, PANACRYSTAL TR-
3LT1). The display exhibited less variation in contrast
25 with varying viewing angle and better viewing angle
properties compared to the case without any phase
retarder laminated.

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CLAIMS:

1. A phase retarder comprising a layered inorganic compound sheet or film in which the refractive index in the plane thereof differs from the refractive index in the thickness direction.
2. A phase retarder according to Claim 1, wherein the layered inorganic compound is clay mineral.
3. A phase retarder according to Claim 2, wherein the clay mineral has a mean particle size of 5000 nm or less.
4. A phase retarder according to any preceding claim, wherein the sheet or film contains an optically transparent resin.
5. A phase retarder according to Claim 4, wherein the optically transparent resin is a vinylalcohol polymer.
6. A phase retarder according to Claim 4 or 5, wherein the layered inorganic compound and the optically transparent resin are present in a ratio by volume of from 0.1 to 10.
7. A phase retarder according to Claim 1, 2 or 3, wherein the layered inorganic compound sheet or film is produced by swelling or dispersing in a solvent a layered inorganic compound having a refractive index in the plane thereof different from the refractive index in the thickness direction, applying the resultant gel or dispersion to a substrate, and drying.

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8. A phase retarder according to Claim 4, 5 or 6, wherein the layered inorganic compound sheet or film is produced by mixing a layered inorganic compound having a refractive index in the plane thereof different from the refractive index in the thickness direction and which has been swollen or dispersed in a solvent, with a solution of an optically transparent resin, applying the resultant mixture to a substrate, and drying.

9. A liquid crystal display device, incorporating a phase retarder according to any preceding claim as an optical compensator.

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