Title: COATING COMPOSITION FOR LOW REFRACTIVE LAYER, ANTI-REFLECTION FILM USING THE SAME AND IMAGE DISPLAYING DEVICE COMPRISES SAID ANTI-REFLECTION FILM

Abstract: Disclosed is a coating composition for forming a low-refractive-index layer, an antireflective film using the same, and an image display device including the antireflective film. In detail, the invention provides a coating composition including a fluorine compound, a reactive silicon compound, a (meth)acrylate compound, a polymerization initiator, and a solvent, an antireflective film using the same, and an image display device including the antireflective film. Using the coating composition, an antireflective film having low reflectance and high transmittance and exhibiting a sufficient antifouling property and high durability, can be provided, along with an image display device including the film.
Description

COATING COMPOSITION FOR LOW REFRACTIVE LAYER, ANTI-REFLECTION FILM USING THE SAME AND IMAGE DISPLAYING DEVICE COMPRISING SAID ANTI-REFLECTION FILM

Technical Field

[1] The present invention relates, generally, to a coating composition for forming a low-refractive-index layer, an antireflective film using the same, and an image display device comprising the antireflective film, and more particularly, to a coating composition for forming a low-refractive-index layer, which comprises a fluorine compound, a reactive silicon compound, a (meth)acrylate compound, a polymerization initiator and a solvent, to an antireflective film using the same, and to an image display device comprising the antireflective film.

Background Art

[2] Typically represented by LCDs (Liquid Crystal Displays), PDPs (Plasma Display Panels), CRTs (Cathode Ray Tubes) or ELDs (ElectroLuminescent Displays), the use of display devices is popular these days. Accordingly, the display device should have wear resistance and an antifouling property on the surface thereof, and furthermore, should have performance for preventing the reflection of external light, such as solar light or fluorescent light, from the surface thereof upon use outdoors and under bright illumination.

[3] In order to impart the device with such an antireflective function, methods of depositing one or more layers having refractive indexes different from each other on a plastic substrate have been initially applied. However, the deposition process is disadvantageous because the cost thereof is very high and it is impossible to apply to a film having a large area. Thus, there have been proposed methods of forming a low-refractive-index film using organic fluorine resin having a low refractive index.

[4] However, since the fluorine resin is insoluble in general solvents, a fluorine solvent should be used. When using the fluorine solvent, the preparation cost is increased. Furthermore, when a coating film is formed using only the fluorine resin, scratch resistance and hardness of the film are low, resulting in poor durability. In this regard, WO 96/22356 discloses a method of applying an amorphous tetrafluoroethylene copolymer in a state in which it is dissolved in a fluorine solvent.

[5] Therefore, with the goal of enabling the dissolution of the fluorine resin in the general solvent, the amount of fluorine should not be high. To this end, the fluorine
resin may be mixed with acrylate resin having no fluorine to thus form a coating film, and the method therefor is disclosed in Japanese Unexamined Patent Publication No. 1995-42031. However, in order to assure sufficient scratch resistance and hardness of the coating film, an acrylate resin having no fluorine should be used in an amount not less than a predetermined level. In this case, the refractive index of the coating solution is increased, undesirably deteriorating antireflective properties.  

In addition, in the case where a coating film is formed using fluorine resin, an antifouling property is decreased. Therefore, to increase the antifouling property of the coating film, disclosed are methods of introducing a silyl group into fluorine resin (Japanese Unexamined Patent Publication No. 1993-025183), of adding a hydrolysate of organosilane and a partial condensate thereof to a coating solution (Japanese Examined Patent Publication No. 1994-98703 and Japanese Unexamined Patent Publication No. 1998-21601), and of blending fluorine resin with a condensate of organosilane (Japanese Unexamined Patent Publication No. 2001-14690). Although these methods make it possible to form a coating film having high antifouling property and scratch resistance, they suffer because there is a need for an additional process upon preparation of a coating solution, and furthermore, the coating solution causes problems when stored for a long time period.

Disclosure of Invention

Technical Problem

Accordingly, the present invention has been made keeping in mind the above problems occurring in the related art, and an object of the present invention is to provide a coating composition for forming a low-refractive-index layer, which can be dissolved in general solvents and has superior antifouling property and hardness without a decrease in antireflective performance.

Another object of the present invention is to provide an antireflective film, which has superior antifouling property and hardness, using the above composition.

A further object of the present invention is to provide an image display device comprising the antireflective film.

Technical Solution

In order to accomplish the above objects, according to one aspect of the present invention, the invention provides a coating composition for forming a low-refractive-index layer, comprising (a) a fluorine compound, (b) a reactive silicon compound, (c) a (meth)acrylate compound, (d) a photoinitiator, and (e) a solvent.

According to another aspect of the present invention, the invention provides an antireflective film, comprising (a) a substrate, (b) a hard coating layer, (c) a high-refractive-index layer, and (d) a low-refractive-index layer, in which the low-
refractive-index layer is formed using the coating composition mentioned above.

According to a further aspect of the present invention, the invention provides an image display device, comprising the antireflective film mentioned above.

Hereinafter, a detailed description will be given of the present invention.

The present invention pertains to a coating composition for forming a low-refractive-index layer, comprising a fluorine compound represented by Formula 1 below:

[15] Formula 1

\[
(CH_2=CR^1COO)_2R^f
\]

[17] wherein \( R^f \) is a perfluoro group and \( R^1 \) is a hydrogen atom or a methyl group.

[18] In the fluorine compound of Formula 1, \( R^f \) may have a molecular structure as represented by Formula 2 below:

[19] Formula 2

\[
\begin{align*}
(a) & \quad F & F & R^{f2} & F & R^{f3} & F \\
(b) & \quad -C- & f & M & -C- & -C- & R^{f2} & -C- \\
(c) & \quad F & F & F & R^{f1} & F & F & F \\
\end{align*}
\]

wherein \( R^{f1} \) is a linear \( C_{1-14} \) perfluoro group, and \( R^{f2}, R^{f3}, R^{f4}, \) and \( R^{f5} \) are each a linear \( C_{1-14} \) perfluoro group.

[20]

In order to be useful as resin for forming a film, the fluorine compound of Formula 1 should preferably have easy synthesis, low refractive property, easy UV curability, and a molecular structure and a molecular weight suitable for forming a coating layer.

The amount of the fluorine compound of Formula 1 is preferably set in the range of 70-95 parts by weight, based on 100 parts by weight of the solid content of the coating composition. If the amount is less than 70 parts by weight, antireflective performance is insufficient. On the other hand, if the amount exceeds 95 parts by weight, the hardness and scratch resistance of the coating film become poor.

[21]

In the present invention, in order to impart the fluorine compound with both a low refractive property and easy UV curability, which are contrary to each other, among the compounds of Formula 1, two or more fluorine compounds that are different from
each other and are able to respectively exhibit the corresponding properties may be mixed together depending on need. Each of the two or more different fluorine compounds of Formula 1 is preferably used in an amount of 10 or more parts by weight, based on 100 parts by weight of the total amount of fluorine compound. In the case where respective fluorine compounds are used in an amount less than 10 parts by weight, properties that are expected to be realized by mixing them are not realized.

Alternatively, a coating composition for forming a low-refractive-index layer according to the present invention may comprise two or more fluorine compounds different from each other, respectively represented by Formula 1 and Formula 3 below:

\[ \text{Formula 3} \]

\[ \text{R}^1\text{O-A} \quad \left\{ \text{O-} \quad \text{CO-} \quad \text{Cr} \equiv \text{CH}_2 \right\} \text{a} \]

wherein \( \text{R}^1 \) is a \( C_{1-18} \) and \( F_{3-37} \) perfluoro group, \( A \) is a dehydrated polyhydric alcohol residue, \( R \) is a hydrogen atom or a methyl group, and \( a \) is an integer from 1 to 3.

In the fluorine compound of Formula 3, used in the present invention, the perfluoro group, \( R^1 \), may be either linear or branched, or may have a cyclic ring in the molecular structure thereof. Among these, particularly useful is perfluorononene, represented by Formula 4 below:

\[ \text{Formula 4} \]

\[ \begin{align*} 
&\text{CF}_3 \quad \text{CF} \\
&\text{CF} \quad \text{C} \\
&\text{C} \quad \text{C} \\
&\text{C} \quad \text{P}_3 \\
&\text{CF}_3 \quad \text{CF} \\
\end{align*} \]

In the fluorine compound of Formula 4, the dehydrated polyhydric alcohol residue, \(-A-\), may be obtained through a reaction of polyhydric alcohol represented by \((\text{HO-})_p\text{A}(-\text{OH})_q\). Examples of the polyhydric alcohol include, but are not limited to, any one alcohol selected from among pentaerythritol, dipentaerythritol, tripen-
taerythritol, glycerine, diglycerine, triglycerine, polyglycerine, trimethylol propane, ditemethylol propane, and trimethylol ethane, ethyleneoxide adducts thereof, propylene oxide adducts thereof, butylenes oxide adducts thereof or -caprolactone modifications thereof. Since the fluorine compound of Formula 3 has one or more \((\text{meth})\text{acrylate} \) groups at the terminal end thereof, it contributes to an increase in...
hardness and scratch resistance of a coating film through reaction with another component upon a curing process.

[33] The amount of the fluorine compound of Formula 4 is preferably set in the range of 5-40 parts by weight based on the total weight of the solid content of the composition. If the amount is less than 5 parts by weight, the hardness and scratch resistance of the coating film become insufficient. On the other hand, if the amount exceeds 40 parts by weight, antireflective performance is deteriorated.

[34] In the coating composition for forming a low-refractive-index layer according to the present invention, the reactive silicon compound may be represented by Formula 5 or 6 below:

[35] Formula 5

[36]

\[
\begin{array}{c}
X^1 \\
R^1-Si-O \left\{ \begin{array}{c}
X^2 \\
Si-O \end{array} \right\} \begin{array}{c} X^3 \\
Si-R^2 \end{array} \\
X^1
\end{array}
\]

[37] wherein \( X^1, X^2, \) and \( X^3 \), which are the same as or different from each other, are each hydrogen or a methyl group, at least one of \( R^1 \) and \( R^2 \), which are the same as or different from each other, is a curable reactive group, and \( c \) is an integer from 3 to 1000; or

[38] Formula 6

[39]

\[
\begin{array}{c}
X^1 \\
X^1-Si-O \left\{ \begin{array}{c}
R^1 \\
Si-O \end{array} \right\} \begin{array}{c} X^2 \\
X^2 \end{array} \\
X^1
\end{array}
\]

[40] wherein \( X^1 \) and \( X^2 \), which are the same as or different from each other, are each hydrogen or a methyl group, at least one of \( R^1 \) and \( R^2 \), which are the same as or different from each other, is a curable reactive group, and \( c \) is an integer from 3 to 1000.

[41] According to the present invention, the reactive silicon compound is a compound in which at least one functional group is contained in the terminal end of or in the molecule of a basic structure of each of polysiloxane, methylhydropolysiloxane, trimethyl siloxane methylhydro siloxane copolymer, dimethyl siloxane methylhydro
siloxane copolymer, and polydimethylsiloxane, which are in the form of oil. It may be used alone or in mixtures of two or more. The process of preparing the reactive silicon compound may vary depending on the type of functional group contained in the terminal end thereof.

Examples of the functional group contained in the terminal end thereof include an amino group, an epoxy group, an alicyclic epoxy group, a carbonyl group, a methacrylate group, a polyethyl group, a mercapto group, a carboxyl group, a phenol group, and a hydroxy 1 group.

The reactive silicon compound is used in an amount of 0.1-15 parts by weight, and preferably 0.2-10 parts by weight based on 100 parts by weight of the solid content of the composition. If the amount is less than 0.1 parts by weight, the antifouling property of the coating film is insufficient. On the other hand, if the amount exceeds 15 parts by weight, the outer appearance of the coating film becomes poor and a phenomenon of whiteness may occur.

According to the present invention, the (meth)acrylate compound is a monomer, an oligomer, or a polymer having a polymerizable unsaturated bond, such as a methacryloyl group or a methacryloxy group, or a cationic polymerizable functional group, such as an epoxy group, in the molecule thereof.

The (meth)acrylate compound is preferably used in an amount of 1-20 parts by weight, based on 100 parts by weight of the solid content of the composition. If the amount is less than 1 part by weight, the curing efficiency of the coating layer is not sufficiently high, or the outer appearance of the coating film may be non-uniform. On the other hand, if the amount exceeds 20 parts by weight, antireflective performance may be deteriorated.

According to the present invention, the polymerization initiator, which is typically used in a general polymerization composition, includes, for example, a photoinitiator and a radical initiator. Furthermore, a polymerization initiator, which is not susceptible to oxygen inhibition but has good initiation efficiency, is particularly useful.

The polymerization initiator is used in an amount of 0.1 to 10 parts by weight, and preferably 0.5 to 5 parts by weight, based on 100 parts by weight of the solid content of the composition. If the amount is less than 0.1 parts by weight, the hardness of the prepared coating film is insufficient. On the other hand, if the amount exceeds 10 parts by weight, the polymerization initiator itself reacts with a radical, undesirably inhibiting the polymerization.

The solid content, composed of the fluorine compound of Formula 1, the reactive silicon compound, the (meth)acrylate compound, and the polymerization initiator, preferably ranges from 1 to 20 parts by weight based on 100 parts by weight of the coating solution. If the solid content is less than 1 part by weight, the coating layer is
too thin, and thus antireflective performance is not manifested. On the other hand, if the solid content exceeds 20 parts by weight, the wavelength range showing a minimum reflectance value falls outside of the visible light range.

In the present invention, examples of the solvent include, but are not limited to, alcohol, such as methyl alcohol, ethyl alcohol, propanol, isopropanol or 1-methoxy-2-propanol, ketone, such as methyl isobutyl ketone or methylethyl ketone, ester such as methyl acetate or ethyl acetate, an aromatic compound such as toluene, xylene, or benzene, and ether, such as diethyl ether, which may be used alone or in mixtures of two or more.

Further, in order to increase scratch resistance and the antifouling property of the coating film, colloidal silica, which is modified by a fluorine silane coupling agent, may be additionally included in the composition.

In addition, the present invention pertains to an antireflective film, which comprises a substrate, a hard coating layer, a high-refractive-index layer, and a low-refractive-index layer, the low-refractive-index layer being formed using the coating composition of the present invention mentioned above.

Below, the antireflective film is specifically described with reference to the appended drawing.

FIG. 1 is a schematic sectional view illustrating the antireflective film of the present invention, comprising a substrate 10, a hard coating layer 20 for conferring scratch resistance, a high-refractive-index layer 30 for conferring antireflective performance, and a low-refractive-index layer 40.

Although the substrate 10 of the antireflective film of the present invention is not particularly limited as long as it is transparent, the use of a plastic film is preferable in terms of processability. Examples of material for the substrate include cellulose ester, such as acetylcellulose, diacetylcellulose, propionylcellulose, acetylpropionylcellulose or nitrocellulose, polyester, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate, poly-1,4-cyclohexane dimethylene terephthalate, polyethylene-1,2-diphenoyxethylene-4,4'-dicarboxylate or cyclohexane dimethylene terephthalate, and polyolefin, such as polyethylene, polypropylene or polymethylpentane. In addition, exemplary are polymethylmethacrylate, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol, polystyrene, polycarbonate, polylamid, polyethersulfone, polyetherketone, polysulfone, polyimide, and nylon. Among these, since acetylcellulose, polyethylene terephthalate or polycarbonate is highly transparent, it is particularly useful as the substrate of the optical film. In addition, it is possible to use acetylcellulose which is saponified with alkali.
Hard Coating Layer 20

The antireflective film of the present invention includes a hard coating layer 20 positioned beneath a high-refractive-index layer for increasing the hardness of the film. This hard coating layer functions to protect the substrate and increase the hardness of the film. The hard coating layer may be prepared using a coating composition comprising a UV curable resin, a photoinitiator, and a solvent, and also comprising inorganic particles depending on need.

Used in the hard coating layer, the UV curable resin preferably comprises a compound having two or more functional groups. Such a compound is exemplified by a monomer, an oligomer or a polymer having a polymerizable unsaturated bond, such as a methacryloyl group or a methacryloyloxy group, or a cationic polymerizable functional group, such as an epoxy group, in the molecule thereof, which may be used alone or in mixtures of two or more.

Preferably, the resin has an ethylene group in the molecule thereof to crosslink it upon a curing process.

The hard coating layer may further include inorganic particles, if necessary, in order to control the refractive index or to increase the hardness of the film. The inorganic particles preferably have an average diameter of 0.5 mm or less. If the average diameter of the inorganic particles exceeds 0.5 mm, the haze of the antireflective film may be increased. Examples of the inorganic particles include silicon dioxide, titanium dioxide, aluminum oxide, tin oxide, calcium carbonate, barium sulfate, talc, kaolin or calcium lactate particles.

In the present invention, the hard coating layer preferably has a thickness from 0.5 to 15 mm. If the thickness of the hard coating layer is less than 0.5 mm, hardness is insufficient. On the other hand, if the thickness exceeds 15 mm, the film may easily curl and the transmittance thereof may be decreased.

The process of applying the hard coating layer is not particularly limited, and examples thereof include any wet coating, such as roll coating, die coating, bar coating, spin coating, etc. After the coating process, the applied film is dried at 50-130 C to remove the solvent and then cured using UV light energy at 100-700 mJ/cm².

High-Refractive-Index Layer 30

Used in the antireflective film of the present invention, a high-refractive-index layer 30 may be prepared using a coating composition comprising metal oxide particles having a high refractive index, a resin having two or more UV curable functional groups, a photoinitiator, and a solvent.

Examples of the metal oxide particles include, but are not limited to, zinc oxide, tin oxide, antimony tin oxide, indium tin oxide, indium oxide, antimony oxide, zirconium
oxide, titanium oxide, tungsten oxide, zinc antimonate, and vanadium oxide. The metal oxide is preferably selected in consideration of dispersibility of the particles and of whether the refractive index is easily controlled.

The metal oxide particles have an average diameter from 0.01 to 0.5 mm. If the average diameter is less than 0.01 mm, it is difficult to disperse the particles. On the other hand, if the average diameter exceeds 0.5 mm, haze may be increased.

When the surface of the metal oxide particles is treated using a coupling agent, the dispersibility of the particles is increased and the dispersion stability of a coating solution for forming a high-refractive-index layer is increased. Examples of the coupling agent include isopropyl triisostearoyl titanate, titanium n-butoxide, titanium ethoxide, titanium 2-ethylhexyloxy, titanium isobutoxide, and titanium stearloxylo.

The resin having two or more UV curable functional groups, which is the same type as the resin used in the hard coating layer, preferably includes a monomer, an oligomer or a polymer having a polymerizable unsaturated bond, such as a methacryloyl group or a methacryloyloxy group, or a cationic polymerizable functional group, such as an epoxy group, in the molecule thereof.

The process of applying the coating solution for forming the high-refractive-index layer is not particularly limited, and examples thereof include any wet coating, such as roll coating, die coating, bar coating, spin coating, etc. After the coating process, the applied film is dried at 50-130 °C to remove the solvent, and then cured using UV light at 300-1000 mJ/cm².

The high-refractive-index layer may be formed into a two-layer structure consisting of a medium-refractive-index layer and a high-refractive-index layer, in that order, through the control of refractive index depending on need. As such, the refractive index is controlled depending on the amount of metal oxide particles.

In the case where the high-refractive-index layer is formed using the above coating solution, it has a refractive index of 1.6 or more, and preferably 1.6-2, and a thickness from 60 nm to 600 nm. This is because there is a need to finely control the thickness of the layer depending on the refractive index of the coating film to exhibit antireflective performance using light interference.

Low-Refractive-Index Layer 40

A low-refractive-index layer 40 used in the antireflective film of the present invention is prepared using a coating composition comprising a fluorine compound represented by Formula 1, a reactive silicon compound, a (meth)acrylate compound, a polymerization initiator, and a solvent. In addition, in order to enhance scratch resistance and antifouling property of the coating film, colloidal silica which is modified by a fluorine silane coupling agent may be further included, if necessary.
The process of applying the coating solution for forming the low-refractive-index layer is not particularly limited, and examples thereof include, but are not limited to, any wet coating, such as roll coating, die coating, bar coating, spin coating, etc. After the coating process, the applied film is dried at 50-130 °C to remove the solvent and then cured using UV light at 300-1300 mJ/cm².

The low-refractive-index layer thus formed has a refractive index of 1.3-1.5 and a thickness from 60 nm to 600 nm, like the high-refractive-index layer. In the low-refractive-index coating solution using the fluorine-based monomer or oligomer, the refractive index thereof is not less than 1.3. If the refractive index exceeds 1.5, antireflective performance is not sufficiently exhibited. Further, if the thickness of the low-refractive-index layer is less than 60 nm, antireflective performance is not manifested. On the other hand, if the thickness exceeds 600 nm, the wavelength range where the minimum reflectance is obtained may fall outside of the visible light range.

In the present invention, it is preferred that the difference in refractive index between the high-refractive-index layer and the low-refractive-index layer be 0.05-0.7. When the difference in refractive index between the high-refractive-index layer and the low-refractive-index layer is less than 0.05, antireflective performance becomes insufficient. On the other hand, when the difference in refractive index exceeds 0.7, it is not easy to realize sufficient antireflective performance using a wet coating process.

The antireflective film thus formed has a haze of 1% or less, an average reflectance of 3% or less in a visible light range, that is, in a wavelength range of 380 - 780 nm, a minimum reflectance less than 1% in a light wavelength range of 550-650 nm, and a contact angle with respect to water of 90 or more.

In addition, the present invention pertains to an image display device, comprising the antireflective film.

The image display device comprising the antireflective film has low reflectance and high transmittance while sufficiently exhibiting an antifouling property and durability, and thus can be widely applied to PDPs, LCDs, touch panels, etc.

Advantageous Effects

As described hereinafter, the present invention provides a coating composition for forming a low-refractive-index layer, an antireflective film using the same, and an image display device comprising the antireflective film. According to the present invention, the coating composition for forming a low-refractive-index layer is used, thus making it possible to manufacture an antireflective film having low reflectance and haze and high antifouling property and scratch resistance, and an image display device comprising the film.

Brief Description of the Drawings
FIG. 1 is a sectional view schematically illustrating the antireflective film of the present invention;

FIG. 2 is a graph illustrating the reflectance spectrum of the antireflective film obtained in Example 1; and

FIG. 3 is a graph illustrating the reflectance spectrum of the antireflective film obtained in Example 7.

Best Mode for Carrying Out the Invention

A better understanding of the present invention may be obtained in light of the following examples and comparative examples, which are set forth to illustrate, but are not to be construed as limiting the present invention.

Preparative Examples 1 to 18: Preparation of Coating Solution for Forming Low-Refractive-Index Layer

As the fluorine compound of Formula 1, a compound having \( R' \) represented by (a) in Formula 2 and a compound having \( R' \) represented by (c) in Formula 2 were used (Preparative Examples 1-6), and a fluorine compound of Formula 1 and a fluorine compound of Formula 3 were used (Preparative Examples 7-18). A reactive silicon compound and a (meth)acrylate compound exemplified by urethane acrylate oligomer (Ebecryl 5129, available from SK-UCB) were used, as shown in Table 1 below. Respective components were dissolved in a methylethylketone solvent and then mixed, after which the solid content of the composition was controlled to be 5 parts by weight using a solvent mixture of methylethylketone and methylisobutylketone. A photoinitiator, Irgacure 127 (available from Ciba-geigy), was added in an amount of 5 parts by weight based on the total weight of the solid content of the composition, and then a stirring process was conducted to completely dissolve the components.

Examples 1 to 12: Manufacture of Antireflective Film

1) Substrate

As a substrate, a PET film (A4300, available from Toyobo) having a thickness of 100 mm was used.

2) Formation of Hard Coating Layer

30 parts by weight of urethane acrylate oligomer (Ebecryl 5129, available from SK-UCB) and 20 parts by weight of dipentaerythritol acrylate (A-400, available from Nippon Kayaku) were mixed with 25 parts by weight of each of methylethylketone and toluene as solvents. A photoinitiator, Irgacure 184 (available from Ciba-geigy), was added in an amount of 1 part by weight based on the total weight of the solid content of the composition.
Using a #12 bar as a bar coater, a coating film was formed, dried at 80 °C for 2 min to thus remove the solvent, and then cured through irradiation of UV light at 300 mJ/cm².

3) Formation of High-Refractive-Index Layer

A dispersion of tin oxide (available from Catalysts & Chemicals Ind Co. Ltd.), in which tin oxide particles having an average diameter of 25 nm were dispersed in a UV curable resin, ethanol and isopropanol, was diluted to 8 wt% using isopropanol.

Using a #4 bar as a bar coater, a coating film was formed, dried at 80 °C for 2 min to thus evaporate the solvent, and then cured through irradiation of UV light at 500 mJ/cm².

4) Formation of Low-Refractive-Index Layer

Each of the coating solutions for forming the low-refractive-index layer prepared in Preparative Examples 1-12 of Table 1 was applied using a #4 bar as a bar coater to thus form a coating film, which was then dried at 80 °C for 2 min to thus evaporate the solvent, thereby forming a coating film.

The coating films thus formed were measured for average reflectance, transmittance, haze, and contact angle, and furthermore, were subjected to a steel wool test and an oil pen test. The results are shown in Table 2 below. In addition, the reflectance spectra of the antireflective films of Examples 1 and 7 are shown in FIGS. 2 and 3, respectively.

Comparative Examples 1-6

These examples were conducted in the same manner as in Examples 1-12, with the exception that the low-refractive-index layer was formed using the coating composition of each of Preparative Examples 13-18 of Table 1. The results of measurement of the properties of the coating films thus formed are given in Table 2 below.
TABLE 2

Methods of Evaluating Properties

Outer Appearance: The outer appearance of the antireflective film was observed with the naked eye. The case where a poor outer appearance of the coating film was not observed was indicated by O, the case where faint marks scratched by the bar remained thereon was indicated by D, and the case where clear marks scratched by the bar remained thereon, or where the surface of the film was opaque was indicated by x.

Average Reflectance: The reflectance was measured using a UV/VIS/NIR spectrometer (Lambda 950, available from Perkin-Elmer). The other surface of the sample was rubbed with abrasive paper, and was then coated with flat paint (CL440F-1999, available from Koryo Paint) to thus eliminate reflective light from the
other surface of the film. The incident angle was set at 8°, and the reflectance with respect to specular light among reflected light was measured. The measured reflectance values were averaged in the range of 380 ~ 780 nm.

Minimum Reflectance: The reflectance was measured using a UV/VIS/NIR spectrometer (Lambda 950, available from Perkin-Elmer). The other surface of the sample was rubbed with abrasive paper, and then coated with faint paint (CL440F-1999, available from Koryo Paint) to thus eliminate reflective light from the other surface of the film. The incident angle was set at 8°, and the reflectance with respect to specular light among reflected light was measured. Among the measured reflectance values in the range of 550-650 nm, the minimum reflectance value was recorded.

Haze: The haze was measured using a haze and turbidity meter (available from Nippon Denshoku Kogyo Co.).

Steel Wool Test: The coating film was scratched through reciprocal movements 20 times using #0000 steel wool under a load of 200 g. The degree of scratching was classified from 1 to 5. The case where the coating film was completely peeled off was represented by 1 and the case where the tested coating film was not changed was represented by 5.

Oil Pen Test: The coating film was fouled using an oil pen (available from Monami), from which the fouling was then removed through reciprocal movements 5 times using cotton cloth. The case where the fouling was completely removed was represented by 0, the case where the fouling was removed but traces thereof remained was represented by D, and the case where the fouling was not removed was represented by x.

Contact Angle: The contact angle with respect to water was measured using a contact angle analyzer (Phoenix300, available from SEO).

As is apparent from Table 2, the antireflective films of Examples 1 to 12 according to the present invention had average reflectance of 3% or less and haze of 1% or less, and exhibited superior antifouling property and higher scratch resistance without a decrease in antireflective performance, compared to those of antireflective films of Comparative Examples 1 to 6.

Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.
Claims

[1] A coating composition for forming a low-refractive-index layer, comprising:
(a) a fluorine compound represented by Formula 1 below;
(b) a reactive silicon compound;
(c) a (meth)acrylate compound;
(d) a polymerization initiator; and
(e) a solvent:

\[
(\text{CH}_2=\text{CFV COO})_2R^f
\]

wherein R' is a C\textsubscript{1-19} perfluoro group, and R' is a hydrogen atom or a methyl group.

[2] The composition as set forth in claim 1, wherein the R\textsuperscript{f} in Formula 1 is represented by Formula 2 below:

\[
\begin{align*}
\text{(a)} & \\
\text{(b)} & \\
\text{(c)} & \\
F & F & R'^2 F & R'^2 F \\
\text{C}-\text{R}'^1 \text{C} & \text{C}-\text{R}'^1 \text{C} & \text{C}-\text{R}'^1 \text{C} \\
F & F & F & F \\
\end{align*}
\]

\[
\begin{align*}
\text{(d)} & \\
\text{(e)} & \\
M & C_6 \\
\text{R}'^3 & \text{R}'^4 & \text{R}'^2 & \text{R}'^4 \\
\text{C}-\text{R}'^1 \text{C} & \text{C}-\text{R}'^1 \text{C} \\
\text{R}'^3 & F & \text{R}'^3 & \text{R}'^5 \\
\end{align*}
\]

wherein R\textsuperscript{f} is a linear C\textsubscript{1-14} perfluoro group, and R\textsuperscript{1-14}, R\textsuperscript{1-14}, and R\textsuperscript{1-14} are each a linear C\textsubscript{1-14} perfluoro group.

[3] The composition as set forth in claim 1, which comprises two or more fluorine compounds different from each other, represented by Formula 1 below:

\[
(\text{CH}_2=\text{CR}^1 \text{COO})_2R^f
\]

wherein R' is one selected from among functional groups represented by Formula 2 below, and R' is a hydrogen atom or a methyl group;
wherein $R^i$ is a linear C$_{1-10}$ perfluoro group, and $R^{f2}$, $R^{f3}$, $R^{f4}$, and $R^{f5}$ are each a linear C$_{1-14}$ perfluoro group.

[4] The composition as set forth in claim 1, which comprises two or more fluorine compounds different from each other, represented by Formula 1 and Formula 3 below:

Formula 3

$$R^f-O-A\left\{O-CO-CR=CH_2\right\}_a$$

wherein $R^f$ is a C$_{1-18}$ and F$_{3-37}$ perfluoro group, A is a dehydrated polyhydric alcohol residue, $R$ is a hydrogen atom or a methyl group, and a is an integer from 1 to 3.

[5] The composition as set forth in claim 1, which comprises, based on 100 parts by weight of a solid content thereof,

(a) 70-95 parts by weight of the fluorine compound represented by Formula 1;
(b) 0.1-15 parts by weight of the reactive silicon compound;
(c) 1-20 parts by weight of the (meth)acrylate compound; and
(d) 0.1-10 parts by weight of the polymerization initiator.

[6] The composition as set forth in claim 1, wherein the reactive silicon compound is used in an amount of 0.2-5 parts by weight based on 100 parts by weight of a solid content of the composition.

[7] The composition as set forth in claim 3, wherein each of the two or more fluorine compounds, which are different from each other, is used in an amount of 10 or more parts by weight based on 100 parts by weight of a total amount of fluorine compound.

[8] The composition as set forth in claim 4, which comprises, based on 100 parts by weight of a solid content thereof,

(a) 50-80 parts by weight of the fluorine compound represented by Formula 1; and
(b) 5-40 parts by weight of the fluorine compound represented by Formula 3.
The composition as set forth in claim 5, wherein the solid content comprising the (a), (b), (c) and (d) of the composition is 1-20 parts by weight based on a total amount of a coating solution for forming a low-refractive-index layer.

The composition as set forth in claim 4, wherein a (meth)acrylate resin is used in an amount of 3-10 parts by weight based on 100 parts by weight of a sum of the fluorine compound represented by Formula 1 and the (meth)acrylate compound.

The composition as set forth in claim 1, wherein the silicon compound is represented by Formula 5 or 6 below:

**Formula 5**

\[
\begin{array}{c}
\text{X}^1 \\
\text{R}^1 \text{Si(O)} \text{X}^2 \\
\text{Si(O)} \text{Si(O)} \text{Si(O)} \\
\text{X}^3 \\
\end{array}
\]

wherein X[^1], X[^2], and X[^3], which are the same as or different from each other, are each hydrogen or a methyl group, at least one of R[^1] and R[^2], which are the same as or different from each other, is a curable reactive group, and c is an integer from 3 to 1000; or

**Formula 6**

\[
\begin{array}{c}
\text{X}^1 \\
\text{X}^2 \\
\text{X}^3 \\
\end{array}
\]

wherein X[^1] and X[^2], which are the same as or different from each other, are each hydrogen or a methyl group, at least one of R[^1] and R[^2], which are the same as or different from each other, is a curable reactive group, and c is an integer from 3 to 1000.

The composition as set forth in claim 1, which further comprises colloidal silica modified by a fluorine silane coupling agent.

An antireflective film, comprising:

(a) a substrate;
(b) a hard coating layer;
(c) a high-refractive-index layer; and
(d) a low-refractive-index layer,

wherein the low-refractive-index layer is formed using the composition of any
one of claims 1 to 12.

[14] The film as set forth in claim 13, which has an average reflectance less than 3% in a visible light range from 380 to 780 nm.

[15] The film as set forth in claim 13, which has a minimum reflectance less than 1% in a light wavelength range from 550 to 650 nm.

[16] An image display device, comprising the antireflective film of claim 13.
### Box No. II  Observations where certain claims were found unsearchable (Continuation of item 2 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**  
   - claimed because they relate to subject matter not required to be searched by this Authority, namely

2. **Claims Nos 6, 10**  
   - claimed 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
     - The features of Claims 6 and 10 are not referred to in the description. Therefore, Claims 6 and 10 are not supported by the description as required by PCT Article 6.

3. **Claims Nos**  
   - claimed because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 64(a).

### Box No. III  Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

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 and, where applicable, the payment of a protest fee.
- The additional search fees were not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.
A. CLASSIFICATION OF SUBJECT MATTER

C09D 127/12(2006.01)1, C09D 402/02(2006.01)1, C09D 133/10(2006.01)1, C09D 183/04(2006.01)1, C08F 2022/06.01)1,
C08L 27/12(2006.01)1, C08L 33/10(2006.01)1, C08L 83/04(2006.01)1, G02B 1/10(2006.01)1, G02B 1/11(2006.01)1

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)
IPC8 C09D 127/12, 402, 133/10, 183/04, C08F 20/22, C08L 27/12, 33/10, 83/04, G02B 1/10, 1/1 1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Utility models and applications for Utility models since 1975
Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKIPASS(KIPO Internal), CA(STN), esp@cenet, ScienceDirect

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>JP 2006-28409 A (FUJI PHOTO FILM CO., LTD) 02 February 2006 (02-02-2006) see abstract, paragraphs &lt;8&gt;<del>&lt;13&gt;, &lt;21&gt;</del>&lt;22&gt;, &lt;36&gt;<del>&lt;76&gt;, &lt;88&gt;</del>&lt;89&gt;, examples, Claims</td>
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Further documents are listed in the continuation of Box C
See patent family annex

Date of the actual completion of the international search
16 JULY 2007 (16 07 2007)

Date of mailing of the international search report
16 JULY 2007 (16.07.2007)

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea
Facsimile No 82-42-472-7140

Authorized officer
LEE, Sun Kuk
Telephone No 82-42-481-5587

Form PCT/ISA/210 (second sheet) (April 2007)
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