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(54) Title: ANTI-REFLECTIVE HARD COAT AND ANTI-REFLECTIVE ARTICLE

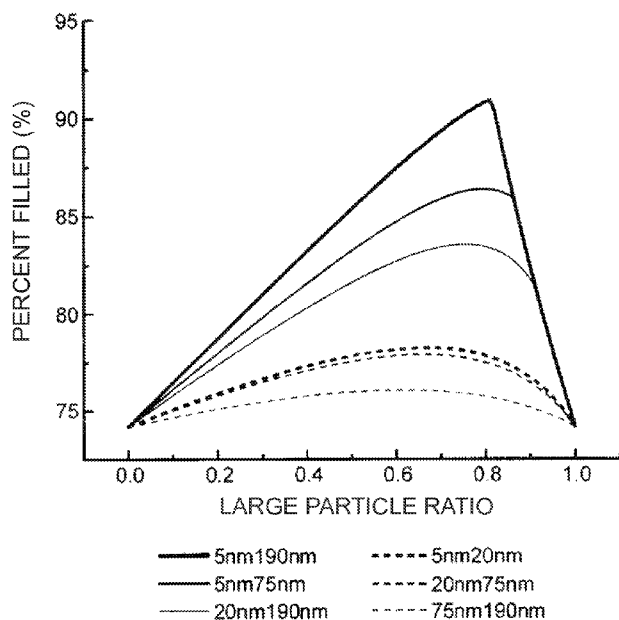


Fig. 1

(57) Abstract: An anti-reflective hard coat contains a nanoparticle mixture and a binder and has a dry-etched surface. The nanoparticles constitute from 40 to 95 mass% of an entire mass of the anti-reflective hard coat. From 10 to 50 mass% of the nanoparticles have an average particle size within a range of 2 to 200 nm. From 50 to 90 mass% of the nanoparticles have an average particle size within a range of 60 to 400 nm. A ratio of the average particle size of nanoparticles having an average particle size within the range of 60 to 400 nm to the average particle size of nanoparticles having an average particle size within a range of 2 to 200 nm is from 2:1 to 200:1. The particle size distribution of the nanoparticles is bimodal or multimodal.



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**ANTI-REFLECTIVE HARD COAT AND ANTI-REFLECTIVE ARTICLE****Cross Reference To Related Application**

This application claims priority to Japanese Patent Application JP 2012-170716, filed on August 1, 2012, the disclosure of which is incorporated by reference in their entirety.

**Technical Field**

The present disclosure relates to an anti-reflective hard coat and an anti-reflective article.

**Background**

Anti-reflective (AR) coatings are used to obtain clear video images by preventing the projection of interior lights or the like onto a display. Moreover, hard coat treatment is also sometimes performed for the purpose of providing a display surface with scratch resistance against scratching resulting from wiping with a cloth or the like or contact with fingernails or the like.

Japanese Unexamined Patent Application Publication No. 2006-297680 describes "a low-refractive-index thin film in which a solid substrate is alternately immersed in (A) a fine particle dispersion containing electrolytes at a concentration of from 0.01 to 0.25 mol/liter and (B) a polymer solution having an ionicity of an opposite charge as the surface charge of the fine particles, whereby a microparticle laminate film is formed with microparticles and a polymer alternately laminated on the substrate, and the microparticle laminate film has a pore structure that does not allow the scattering of visible light."

Japanese Unexamined Patent Application Publication No. 2002-079616 describes "a transparent coating substrate consisting of a substrate and a transparent coating provided on the substrate surface, the transparent coating having (i) a matrix containing a fluorine-substituted alkyl group-containing silicone component and (ii) an outer shell layer, wherein the interior part contains inorganic compound particles so as to be porous or hollow, and the porous or hollow quality is maintained in the transparent coating."

Japanese Unexamined Patent Application Publication No. H07-092305 describes "a low-refractive-index anti-reflective film in which (1) a portion consisting of a mixture of air and organic ultrafine particles having surface roughness formed by exposure of the surface of organic ultrafine particles with a refractive index of at most 1.45 is formed in the outermost layer of the anti-reflective film, (2) a portion consisting of organic ultrafine particles in which the outermost layer of the organic ultrafine particles themselves is crosslinked or fused is formed inside the anti-reflective film extending from the outermost layer, and (3) the anti-reflective film has a refractive index which increases gradually from the outermost layer toward the bottom."

Japanese Translation of Published PCT Application No. 2012-514238 describes a composite

formed by a process having "a step of providing a matrix containing a nanodispersion phase and a step of forming an anisotropic surface with a random nanostructure by etching the matrix using a plasma," wherein the composite serves as an article with a nanostructure useful as an anti-reflective article.

Hard coat materials containing SiO<sub>2</sub> nanoparticles modified by a photo-curing silane coupling agent are described in U.S. Patent Nos. 5104929 and 7074463.

There is also a strong demand for display surfaces to be provided with anti-smudge properties. Hard coat materials having anti-smudge properties and having an easily washable surface obtained by curing a polymerizable composition containing a fluorine compound having a hexafluoropropylene oxide site are described in U.S. Patent No. 7718264 and U.S. Patent Application Publication No. 2008/0124555.

### Summary

An object of the present disclosure is to provide an anti-reflective hard coat and an anti-reflective article with excellent scratch resistance.

One embodiment of the present disclosure provides an anti-reflective hard coat including a nanoparticle mixture and a binder, the anti-reflective hard coat having a dry-etched surface; the nanoparticles constituting from 40 to 95 mass% of an entire mass of the hard coat; from 10 to 50 mass% of the nanoparticles having an average particle size within a range of 2 to 200 nm; from 50 to 90 mass% of the nanoparticles having an average particle size within a range of 60 to 400 nm; a ratio of the average particle size of nanoparticles having an average particle size within the range of 60 to 400 nm to the average particle size of nanoparticles having an average particle size within the range of 2 to 200 nm being within a range of 2:1 to 200:1.

Another embodiment of the present disclosure provides an anti-reflective article including a substrate having a first surface and a layer of the anti-reflective hard coat disposed on the first surface of the substrate.

The anti-reflective hard coat of the present disclosure filled with a high level of nanoparticles demonstrates both excellent scratch resistance and impact resistance and exhibits high anti-reflective characteristics arising from a moth-eye structure formed on a dry-etched surface.

The above description should not be considered a disclosure of all of the embodiments of the present invention or all of the advantages of the present invention.

### Brief Description of the Drawings

FIG. 1 is a graph showing the results of simulations between the mass ratios and filling rates of a small particle group and a large particle group for combinations of several particle sizes (small particle group/large particle group).

FIG. 2 is a cross-sectional view of the anti-reflective article of an embodiment of the present disclosure.

FIG. 3 is a cross-sectional view of the anti-reflective article of another embodiment of the

present disclosure.

FIG. 4 is a cross-sectional view of a display unit including the anti-reflective article of an embodiment of the present disclosure.

FIG. 5 is a cross-sectional view of a display unit including the anti-reflective article of another embodiment of the present disclosure.

FIG. 6 is a cross-sectional view of a display unit including the anti-reflective article of another embodiment of the present disclosure.

FIG. 7 is a chart showing the results of measurements of the transmission rates of Example 1 and Comparative Example 1.

FIG. 8 is a chart showing the results of measurements of the transmission rates of Example 2 and Comparative Example 2.

FIG. 9 is a chart showing the results of measurements of the transmission rates of Example 3 and Comparative Example 3.

FIG. 10 is a chart showing the results of measurements of the transmission rates of Example 4 and Comparative Example 4.

FIG. 11 is a chart showing the results of measurements of the transmission rates of Examples 5 to 8 and Comparative Examples 5 and 6.

FIG. 12 is a chart showing the results of measurements of the transmission rates of Examples 9 and 10 and Comparative Examples 5 and 7.

FIG. 13 is a chart showing the results of measurements of the transmission rates of Examples 11 and 12 and Comparative Examples 5 and 8.

### **Detailed Description**

The present invention will be described in further detail hereinafter with the purpose of illustrating representative embodiments of the present invention, however, the present invention is not limited to these embodiments.

In the present disclosure, "(meth)acrylic" refers to "acrylic or methacrylic", and "(meth)acrylate" refers to "acrylate or methacrylate". In addition, an "anti-reflective hard coat" refers to a hard coat in which the reflection of light in the visible light range is reduced or suppressed in at least some areas of the hard coat surface. Further, a "dry-etched surface" refers to a surface that has been at least partially subjected to dry etching.

The anti-reflective hard coat of one embodiment of the present disclosure includes a nanoparticle mixture and a binder and has a dry-etched surface.

Examples of representative binders contained in the anti-reflective hard coat include resins obtained by polymerizing a curable monomer and/or a curable oligomer and resins obtained by polymerizing sol-gel glass. More specific examples include acrylic resins, urethane resins, epoxy resins, phenol resins, and polyvinyl alcohol resins. Further, the curable monomer or curable oligomer can be selected from known curable monomers or curable oligomers in this technical field, and it is possible to use a mixture of two or more curable monomers, a mixture of two or more curable oligomers, or a

mixture of one or two or more curable monomers and one or two or more curable oligomers. In several embodiments, examples of resins include dipentaerythritol pentaacrylate (available from the Sartomer Company (Exton, PA) under the product name "SR399", for example), pentaerythritol triacrylate isophorone diisocyanate (IPDI) (available from Nippon Kayaku Co., Ltd. (Tokyo Japan) under the product name "UX-5000", for example), urethane acrylate (available from Nippon Synthetic Chemical Industry Co., Ltd. (Osaka, Japan) under the product names "UV1700B" and "UB6300B", for example), trimethylhydroxyl diisocyanate/hydroxyethyl acrylate (TMHDI/HEA, available from the Daicel-Cytec Company, Ltd. (Tokyo Japan) under the product name "EBECRYL 4858", for example), polyethylene oxide (PEO) modified bis-A-diacrylate (available from the Nippon Kayaku Co., Ltd. (Tokyo Japan) under the product name "R551", for example), PEO modified bis-A-epoxy acrylate (available from Kyoisha Chemical Co., Ltd. (Osaka, Japan) under the product name "3002M", for example), silane-based UV curable resins (available from the Nagase ChemteX Corporation (Osaka, Japan) under the product name "SK501M", for example), and 2-phenoxyethyl methacrylate (available from the Sartomer Company under the product name "SR340", for example), and compounds polymerized using these mixtures. For example, improvements in the adhesiveness to polycarbonates are observed when 2-phenoxyethyl methacrylate is used within the range of approximately 1.0 to 20 mass%. Simultaneous improvements in the hardness, impact resistance, and flexibility of the hard coat are observed when a difunctional resin (for example, PEO modified bis-A-diacrylate "R551") and trimethylhydroxyl diisocyanate/hydroxyethyl acrylate (TMHDI/HEA) (available from the Daicel-Cytec Company, Ltd. (Tokyo Japan) under the product name "EBECRYL 4858", for example) are used.

The amount of the binder in the anti-reflective hard coat is typically from approximately 5 to 60 mass% and, in several embodiments, is from approximately 10 to 40 mass% or from approximately 15 to 30 mass% of the total mass of the anti-reflective hard coat. According to the present disclosure, an anti-reflective hard coat can be formed even if the amount of the binder is relatively small.

The anti-reflective hard coat may be further cured with another curable monomer or a curable oligomer as necessary. Examples of representative curable monomers or curable oligomers include polyfunctional (meth)acrylic monomers and polyfunctional (meth)acrylic oligomers selected from a group comprising: (a) compounds having two (meth)acrylic groups such as 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol monoacrylate monomethacrylate, ethylene glycol diacrylate, alkoxyated aliphatic diacrylate, alkoxyated cyclohexane dimethanol diacrylate, alkoxyated hexanediol diacrylate, alkoxyated neopentyl glycol diacrylate, caprolactone modified neopentyl glycol hydroxypivalate diacrylate, caprolactone modified neopentyl glycol hydroxypivalate diacrylate, cyclohexane dimethanol diacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, ethoxyated (10) bisphenol-A-diacrylate, ethoxyated (3) bisphenol-A-diacrylate, ethoxyated (30) bisphenol-A diacrylate, ethoxyated (4) bisphenol-A-diacrylate, hydroxypivalaldehyde modified trimethylol propane diacrylate, neopentyl glycol diacrylate, polyethylene glycol (200) diacrylate, polyethylene glycol (400) diacrylate, polyethylene glycol (600) diacrylate, propoxyated neopentyl glycol diacrylate, tetraethylene glycol diacrylate, tricyclodecane dimethanol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate, and the like; (b)

compounds having three (meth)acrylic groups such as glycerol triacrylate, trimethylol propane triacrylate, ethoxylated triacrylate (for example, ethoxylated (3) trimethylol propane triacrylate, ethoxylated (6) trimethylol propane triacrylate, ethoxylated (9) trimethylol propane triacrylate, ethoxylated (20) trimethylol propane triacrylate, and the like), pentaerythritol triacrylate, propoxylated triacrylate (for example, propoxylated (3) glyceryl triacrylate, propoxylated (5.5) glyceryl triacrylate, propoxylated (3) trimethylol propane triacrylate, propoxylated (6) trimethylol propane triacrylate, and the like), trimethylol propane triacrylate, tris-(2-hydroxyethyl) isocyanurate triacrylate, and the like; (c) compounds having four (meth)acrylic groups such as ditrimethylol propane tetraacrylate, dipentaerythritol pentaacrylate, ethoxylated (4) pentaerythritol tetraacrylate, pentaerythritol tetraacrylate, caprolactone modified dipentaerythritol hexaacrylate, and the like; (d) oligomer (meth)acrylic compounds such as urethane acrylate, polyester acrylate, epoxy acrylate, and the like; polyacrylamide analogs of the above; and combinations thereof. Such compounds are commercially available, and at least several of these compounds are available from the Sartomer Company, UCB Chemicals Corporation (Smyrna, GA), the Aldrich Chemical Company (Milwaukee, WI), and the like. Examples of other useful (meth)acrylates include hydantoin portion-containing poly(meth)acrylates, such as are disclosed in U.S. Patent No. 4262072.

A preferable curable monomer or curable oligomer contains at least three (meth)acrylic groups. Preferable commercially available curable monomers or curable oligomers include those available from the Sartomer Company such as trimethylol propane triacrylate (TMPTA) product name: "SR351"), pentaerythritol tri/tetraacrylate (PETA) (product names: "SR444" and "SR295"), and dipentaerythritol pentaacrylate (product name: "SR399"). Further, mixtures of polyfunctional (meth)acrylates and monofunctional (meth)acrylates such as a mixture of PETA and 2-phenoxyethyl acrylate (PEA) can also be used.

The nanoparticle mixture contained in the anti-reflective hard coat constitutes from approximately 40 to 95 mass% of the total mass of the anti-reflective hard coat and, in several embodiments, constitutes from approximately 60 to 90 mass% or from approximately 70 to 85 mass% of the total mass of the anti-reflective hard coat. The nanoparticle mixture contains from approximately 10 to 50 mass% of nanoparticles having an average particle size within the range of approximately 2 to 200 nm (hereafter called the small particle group or the first nanoparticle group) and from approximately 50 to 90 mass% of nanoparticles having an average particle size within the range of approximately 60 to 400 nm (hereafter called the large particle group or the second nanoparticle group). For example, the nanoparticle mixture may be obtained by mixing the first nanoparticle group with an average particle size of approximately 2 to 200 nm and the second nanoparticle group with an average particle size of approximately 60 to 400 nm at a mass ratio of approximately 10:90 to 50:50.

The average particle size of the nanoparticles can be measured with a transmission electron microscope (TEM) using technology commonly used in this technical field. In the measurement of the average particle size of the nanoparticles, a sol sample for a TEM image can be prepared by dripping a sol sample into a 400-mesh copper TEM grid having an ultra-thin carbon substrate on the upper surface of mesh lace-like carbon (available from Ted Pella Inc. (Redding, CA)). Some liquid droplets can be

removed by bringing the droplets into contact with filter paper as well as the side or bottom portion of the grid. The remaining sol solvent can be removed by heating or allowing the solution to stand at room temperature. This allows the particles to rest on the ultra-thin carbon substrate and to be imaged with the least interference from the substrate. Next, the TEM image can be recorded at many positions spanning the entire grid. Sufficient images are recorded to enable the measurement of the particle sizes of 500 to 1000 particles. Next, the average particle size of the nanoparticles can be calculated based on the particle size measurements of each of the samples. TEM images can be obtained using a high-resolution transmission electron microscope (using an LaB<sub>6</sub> source) operating at 300 KV (available from the Hitachi High Technologies Corporation under the product name "Hitachi H-9000"). The images can be recorded using a camera (available from Gatan, Inc. (Pleasanton, CA) under the product name "GATAN ULTRASCAN CCD", for example: model No. 895, 2k x 2k chip). The images can be taken at a magnification of 50,000 and 100,000 times. Images can be taken at a magnification of 300,000 times for several samples.

The nanoparticles are typically inorganic particles. Examples of inorganic particles include inorganic oxides such as alumina, tin oxide, antimony oxide, silica (SiO, SiO<sub>2</sub>), zirconia, titania, ferrite, and the like, as well as mixtures thereof, or mixed oxides thereof; metal vanadate, metal tungstate, metal phosphate, metal nitrate, metal sulfate, metal carbide, and the like. An inorganic oxide sol can be used as inorganic oxide nanoparticles. In the case of silica nanoparticles, for example, a silica sol obtained using liquid glass (sodium silicate solution) as a starting material can be used. A silica sol obtained from liquid glass may have a very narrow particle size distribution depending on the manufacturing conditions; therefore, when such a silica sol is used, an anti-reflective hard coat having desired characteristics can be obtained by more accurately controlling the filling rate of nanoparticles in the anti-reflective hard coat.

The average particle size of the small particle group is within the range of approximately 2 to 200 nm. The particle size is preferably from approximately 2 to 150 nm, from approximately 3 to 120 nm, or from approximately 5 to 100 nm. The average particle size of the large particle group is within the range of approximately 60 to 400 nm. The particle size is preferably from approximately 65 to 350 nm, from approximately 70 to 300 nm, or from approximately 75 to 200 nm.

The nanoparticle mixture contains a particle size distribution of at least two different types of nanoparticles. The particle size distribution of the nanoparticle mixture may exhibit bimodality or multimodality with peaks at the average particle size of the small particle group and the average particle size of the large particle group. In addition to the particle size distribution, the nanoparticles may be the same or different from one another (for example, surface-modified or not surface-modified compositionally). In several embodiments, a ratio of the average particle size of nanoparticles having an average particle size within the range of approximately 2 to 200 nm to the average particle size of nanoparticles having an average particle size within the range of approximately 60 to 400 nm is within the range of 2:1 to 200:1 and, in several embodiments, is within the range of 2.5:1 to 100:1 or 2.5:1 to 25:1. Examples of preferable combinations of average particle sizes include combinations of 5 nm/190 nm, 5 nm/75 nm, 20 nm/190 nm, 5 nm/20 nm, 20 nm/75 nm, 75 nm/190 nm, and 5 nm/20 nm/190 nm.



By using a mixture of nanoparticles of different sizes, it is possible to fill the anti-reflective hard coat with a large amount of nanoparticles and thereby increase the hardness of the anti-reflective hard coat.

In addition, the transparency (haze or the like) and hardness can be varied by selecting the type, amount, size, and ratio of the nanoparticles, for example. In several embodiments, an anti-reflective hard coat having both a desired transparency and hardness can be obtained.

The mass ratio (%) of the small particle group and the large particle group can be selected in accordance with the particle size used or the combination of particle sizes used. A preferable mass ratio can be selected in accordance with the particle size used or the combination of particle sizes used by using software available under the product name "CALVOLD2" and can be selected based on a simulation between the mass ratio and filling rate of the small particle group and the large particle group for the combination of particle sizes (small particle group/large particle group), for example (see also "Verification of a Model for Estimating the Void Fraction in a Three-Component Randomly Packed Bed," M. Suzuki and T. Oshima: Powder Technol., 43, 147-153 (1985)). The simulation results are illustrated in FIG. 1. According to this simulation, the mass ratio (small particle group:large particle group) for a combination of 5 nm/190 nm is from approximately 45:55 to 13:87 or from approximately 40:60 to 15:85. The mass ratio for a combination of 5 nm/75 nm is preferably from approximately 45:55 to 10:90 or from approximately 35:65 to 15:85. The mass ratio for a combination of 20 nm/190 nm is preferably from approximately 45:55 to 10:90. The mass ratio for a combination of 5 nm/20 nm is preferably from approximately 50:50 to 20:80. The mass ratio for a combination of 20 nm/75 nm is preferably from approximately 50:50 to 22:78. The mass ratio for a combination of 75 nm/190 nm is preferably from approximately 50:50 to 27:73.

In several embodiments, using a preferable combination of particle sizes and nanoparticles makes it possible to increase the amount of nanoparticles with which the anti-reflective hard coat is filled and to adjust the transparency and hardness of the resulting anti-reflective hard coat.

The thickness of the hard coat is typically within the range of approximately 80 nm to 30  $\mu$ m (in several embodiments, from approximately 200 nm to 20  $\mu$ m or from approximately 1 to 10  $\mu$ m), however, the hard coat can sometimes be used effectively even when the thickness deviates from these ranges. Using a mixture of nanoparticles of different sizes sometimes makes it possible to obtain an anti-reflective hard coat with a greater thickness and higher hardness.

The surface of the nanoparticles may be modified using a surface treatment agent as necessary. A surface treatment agent typically has a first terminal bonding to the particle surface (via covalent bonds, ionic bonds, or strong physisorption) and a second terminal which gives the particles compatibility with resins and/or reacts with resins during curing. Examples of surface treatment agents include alcohols, amines, carboxylic acids, sulfonic acids, phosphonic acids, silanes, and titanates. The preferred type of treatment agent is determined, in part, by the chemical nature of the nanoparticle surface. When silica or another siliceous filler are used as nanoparticles, a silane is preferable. Silanes and carboxylic acids are preferred for metal oxides. Surface modification may be performed before, during, or after mixing with a curable monomer or a curable oligomer. When a silane is used, the reaction between the silane and the nanoparticle surface is preferably performed before mixing with

the curable monomer or the curable oligomer. The required amount of the surface treating agent is determined by several factors such as the particle size and type of the nanoparticles and the molecular weight and type of the surface treating agent. It is typically preferable for one layer of a surface treating agent to be deposited onto the surface of the particles. The required deposition procedure or reaction conditions are also determined by the surface treating agent that is used. When a silane is used, it is preferable to perform surface treatment for approximately 1 to 24 hours at a high temperature under acidic or basic conditions. A high temperature or long period of time is typically unnecessary in the case of a surface treating agent such as a carboxylic acid.

Representative examples of surface treating agents include compounds such as isooctyltrimethoxysilane, polyalkyleneoxide alkoxysilane (available from Momentive Specialty Chemicals, Inc. (Columbus, OH) under the product name "SILQUEST A1230", for example), N-(3-triethoxysilyl propyl) methoxyethoxy ethoxyethyl carbamate, 3-(methacryloyloxy) propyl trimethoxysilane (available from Alfa Aesar (Ward Hill, MA) under the product name "SILQUEST A174", for example), 3-(acryloyloxy) propyl trimethoxysilane, 3-(methacryloyloxy) propyl triethoxysilane, 3-(methacryloyloxy) propyl methyl dimethoxysilane, 3-(acryloyloxy) propyl methyl dimethoxysilane, 3-(methacryloyloxy) propyl dimethyl ethoxysilane, 3-(methacryloyloxy) propyl dimethyl ethoxysilane, vinyl dimethyl ethoxysilane, phenyl trimethoxysilane, n-octyl trimethoxysilane, dodecyl trimethoxysilane, octadecyl trimethoxysilane, propyl trimethoxysilane, hexyl trimethoxysilane, vinyl methyl diacetoxysilane, vinyl methyl diethoxysilane, vinyl triacetoxysilane, vinyl triethoxysilane, vinyl triisopropoxysilane, vinyl trimethoxysilane, vinyl triphenoxysilane, vinyl tri(t-butoxy) silane, vinyl tri(isobutoxy) silane, vinyl triisopropenoxysilane, vinyl tris-(2-methoxyethoxy) silane, styryl ethyl trimethoxysilane, mercapto propyl trimethoxysilane, 3-glycidoxy propyl trimethoxysilane, acrylic acid, methacrylic acid, oleic acid, stearic acid, dodecanoic acid, 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MEEAA),  $\beta$ -carboxyethyl acrylate, 2-(2-methoxyethoxy)acetic acid, and methoxy phenyl acetic acid and mixtures thereof.

The binder of the anti-reflective hard coat may further contain known additives such as an ultraviolet absorbent, an anti-smudge agent, a defogging agent, a leveling agent, an ultraviolet reflecting agent, or an anti-static agent.

In some embodiments, the ultraviolet absorbent is contained in the binder of the anti-reflective hard coat. According to this embodiment, it is possible to provide the anti-reflective hard coat with wavelength selectivity (absorption of ultraviolet rays and transmission of visible light). The ultraviolet absorbent can be mixed with the curable monomer or the curable oligomer. A known agent may be used as the ultraviolet absorbent. For example, ultraviolet absorbents such as benzophenone absorbents (available from BASF AG under the product name "Uvinul 3050", for example), benzotriazole absorbents (available from BASF AG under the product name "Tinuvin 928", for example), triazine absorbents (available from BASF AG under the product name "Tinuvin 1577", for example), salicylate absorbents, diphenylacrylate absorbents, and cyanoacrylate absorbents and hindered amine light stabilizers (HALSs) (available from BASF AG under the product name "Tinuvin 292", for example) may be used. By using a known ultraviolet absorbent and a hindered amine light stabilizer in combination,

it is possible to further increase the ultraviolet absorption of the anti-reflective hard coat in comparison to when the respective components are used alone.

The amount of the ultraviolet absorbent that is added may be, for example, within the range of approximately 0.01 to 20 parts by mass (in several embodiments, from approximately 0.1 to 15 parts by mass or from approximately 0.2 to 10 parts by mass) with respect to a total of 100 parts by mass of the nanoparticles, the curable monomer, and the curable oligomer. In some embodiments, the anti-reflective hard coat containing the ultraviolet absorbent can achieve ultraviolet transmittance of less than 3%.

In some embodiments, the anti-smudge agent is contained in the binder of the anti-reflective hard coat. Anti-smudge agents have been observed to improve the washability of the anti-reflective hard coat surface (for example, through prevention of adhesion of fingerprints, oil resistance, dust prevention, and/or anti-smudge functions). A fluorinated (meth)acrylic compound may be used as an anti-smudge agent. Examples of fluorinated (meth)acrylic compounds include the HFPO urethane acrylate or modified HFPO described in Japanese Unexamined Patent Application Publication No. 2008-538195. The fluorinated (meth)acrylic compound may be included in the binder of the anti-reflective hard coat as an unreacted fluorinated (meth)acrylic compound, as a reaction product resulting from a reaction with a curable monomer or a curable oligomer, or as a combination thereof. A silicone polyether acrylate (available from Evonic Goldschmidt GmbH (Essen, Germany) under the product name "TEGORAD2250", for example) can also be used as an anti-smudge agent.

In the present disclosure, HFPO refers to a perfluoroether site expressed by  $F(CF(CF_3)CF_2O)_nCF(CF_3)-$  ( $n$  is from 2 to 15) and a compound containing such a perfluoroether site.

The anti-smudge agent is preferably a polyfunctional fluorinated (meth)acrylic compound. The polyfunctional fluorinated (meth)acrylic compound has a plurality of (meth)acrylic groups and can therefore react with a curable monomer or a curable oligomer as a crosslinking agent or can interact non-covalently with functional groups contained in the binder in a plurality of sites. As a result, the durability of the anti-smudge properties can be increased. When a polyfunctional fluorinated (meth)acrylic compound is used as the anti-smudge agent, it may be possible to also increase scratch resistance by reducing the coefficient of friction of the anti-reflective hard coat surface. When a polyfunctional fluorinated (meth)acrylic compound having three or more (meth)acrylic groups is used, it is possible to further increase the durability of the anti-smudge properties.

Since perfluoroether groups provide the anti-reflective hard coat with excellent anti-smudge properties, the polyfunctional fluorinated (meth)acrylic compound is preferably a perfluoroether compound having two or more (meth)acrylic groups.

The polyfunctional perfluoroether (meth)acrylates described in Japanese Unexamined Patent Application Publication No. 2008-538195 and Japanese Unexamined Patent Application Publication No. 2008-527090, for example, can be used as perfluoroether compounds having two or more (meth)acrylic groups. Specific examples of such polyfunctional perfluoroether (meth)acrylates include:



- HFPO-C(O)NHC(CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>)<sub>3</sub>;  
 HFPO-C(O)N(CH<sub>2</sub>CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>)<sub>2</sub>;  
 HFPO-C(O)NHCH<sub>2</sub>CH<sub>2</sub>N(C(O)CH=CH<sub>2</sub>)CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>;  
 HFPO-C(O)NHCH(CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>)<sub>2</sub>;  
 5 HFPO-C(O)NHC(CH<sub>3</sub>)(CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>)<sub>2</sub>;  
 HFPO-C(O)NHC(CH<sub>2</sub>CH<sub>3</sub>)(CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>)<sub>2</sub>;  
 HFPO-C(O)NHCH<sub>2</sub>CH(OC(O)CH=CH<sub>2</sub>)CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>;  
 HFPO-C(O)NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>)<sub>2</sub>;  
 HFPO-C(O)OCH<sub>2</sub>C(CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>)<sub>3</sub>;  
 10 HFPO-C(O)NH(CH<sub>2</sub>CH<sub>2</sub>N(C(O)CH=CH<sub>2</sub>))<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>NC(O)-HFPO;  
 CH<sub>2</sub>=CHC(O)OCH<sub>2</sub>CH(OC(O)HFPO)CH<sub>2</sub>OCH<sub>2</sub>CH(OH)CH<sub>2</sub>OCH<sub>2</sub>CH(OC(O)HFPO)CH<sub>2</sub>OCOCH=CH  
 2;  
 HFPO-CH<sub>2</sub>O-CH<sub>2</sub>CH(OC(O)CH=CH<sub>2</sub>)CH<sub>2</sub>OC(O)CH=CH<sub>2</sub>; and the like.

The polyfunctional perfluoropolyether (meth)acrylate described above can be synthesized, for  
 15 example, via a first step of reacting a poly(hexafluoropropylene oxide) ester such as HFPO-C(O)OCH<sub>3</sub>  
 or a poly(hexafluoropropylene oxide) acid halide: HFPO-C(O)F with a material containing at least three  
 alcohols or primary or secondary amino groups to produce an HFPO-ester having an HFPO-amide  
 polyol or polyamine, an HFPO-ester polyol or polyamine, an HFPO-amide, or a mixed amine and an  
 alcohol group and a second step of (meth)acrylating the alcohol group and/or amine group with a  
 20 (meth)acryloyl halide, a (meth)acrylic acid anhydride, or a (meth)acrylic acid. Alternatively, the  
 polyfunctional perfluoropolyether (meth)acrylate can be synthesized using a Michael-type addition  
 reaction of a reactive perfluoroether such as an adduct of HFPO-C(O)N(H)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N(H)CH<sub>3</sub> and  
 trimethylol propane triacrylate (TMPTA) and a poly(meth)acrylate.

A preferable polyfunctional fluorinated (meth)acrylic compound is one in which the  
 25 perfluoroether site is bivalent and (meth)acrylic groups bond with both terminals directly or via other  
 groups or bonds (ether bonds, ester bonds, amide bonds, urethane bonds, or the like). Although not  
 bound by any particular theory, it is thought that such a compound forms a firm bond with the  
 anti-reflective hard coat so as to improve the durability of the anti-smudge properties, and the  
 perfluoroether site between (meth)acrylic groups migrates to the anti-reflective hard coat surface so as to  
 30 be easily oriented in the in-plane direction. As a result, it may be possible to sufficiently express  
 anti-smudge properties.

The polyfunctional fluorinated (meth)acrylic compound may contain siloxane units. When  
 the nanoparticles are inorganic oxides, the polyfunctional fluorinated (meth)acrylic compound  
 containing siloxane units is more firmly held onto the anti-reflective hard coat not only by the reaction  
 35 between the (meth)acrylic groups and the curable monomer or the curable oligomer, but also by  
 interactions between siloxane bonds and the nanoparticles, which is thought to further increase the  
 durability of the anti-smudge properties. The nanoparticles are preferably silica nanoparticles which  
 are chemically similar to and have high affinity with siloxane bonds.

The polyfunctional fluorinated (meth)acrylic compound containing siloxane units can be synthesized, for example, by adding (hydrosilating) a perfluoropolyether compound having one or two or more unsaturated ethylene groups to a straight-chain or cyclic oligosiloxane or polysiloxane (hydrogen siloxane) containing three or more Si-H bonds in the presence of a platinum catalyst or the like at a volume of less than one equivalent with respect to the Si-H bonds, similarly adding (hydrosilating) a hydroxyl group-containing unsaturated ethylene compound to the remaining Si-H bonds in the presence of a platinum catalyst or the like, and then reacting the hydroxyl groups with an epoxy (meth)acrylate, urethane (meth)acrylate, or the like. The partial molecular weight of the perfluoroether site calculated from the chemical formula may be from 500 to 30,000.

In order to sufficiently express the anti-smudge properties imparted by the fluorinated site, it is preferable for the siloxane units to be cyclic siloxane units derived from tetramethyl cyclotetrasiloxane, pentamethyl cyclopentasiloxane, or the like. The number of silicon atoms constituting the cyclic siloxane units is preferably from 3 to 7.

An example of a polyfunctional fluorinated (meth)acrylic compound containing siloxane units is a perfluoropolyether compound having two or more (meth)acrylic groups as described in Japanese Unexamined Patent Application Publication No. 2010-285501, for example. For example, the compounds of formulas (19) and (21) in this publication have structures in which cyclic siloxanes with four silicon atoms respectively bond to both terminals of a bivalent perfluoropolyether group:  $-\text{CF}_2(\text{OCF}_2\text{CF}_2)_p(\text{OCF}_2)_q\text{OCF}_2-$  ( $p/q=0.9$ ,  $p+q=45$ ), and three acryloyloxy groups bond with each of these cyclic siloxanes via urethane groups, which is suited to the anti-reflective hard coat of the present disclosure.

The amount of the anti-smudge agent that is added may be, for example, within the range of approximately 0.01 to 20 parts by mass (in several embodiments, from approximately 0.1 to 10 parts by mass or from approximately 0.2 to 5 parts by mass) with respect to a total of 100 parts by mass of the nanoparticles, the curable monomer, and the curable oligomer.

In some embodiments, the defogging agent is contained in the binder of the anti-reflective hard coat. The anti-reflective hard coat of this embodiment can prevent condensation when an article containing the anti-reflective hard coat is used in an environment with substantial changes in temperature. The defogging agent can be mixed with the curable monomer or the curable oligomer. Anionic, cationic, nonionic or amphoteric surfactants can be used as the defogging agent, examples of which include sorbitan surfactants such as sorbitan monostearate, sorbitan monomyristate, sorbitan monopalmitate, sorbitan monobehenate, and esters of sorbitan, alkylene glycol condensates, and fatty acids; glycerin surfactants such as glycerin monopalmitate, glycerin monostearate, glycerin monolaurate, diglycerin monopalmitate, glycerin dipalmitate, glycerin distearate, glycerin monopalmitate/monostearate, triglycerin monostearate, triglycerin distearate, or alkylene oxide adducts thereof; polyethylene glycol surfactants such as polyethylene glycol monostearate, polyethylene glycol monopalmitate, and polyethylene glycol alkyl phenyl ether; trimethylol propane surfactants such as trimethylol propane monostearate; pentaerythritol surfactants such as pentaerythritol monopalmitate and pentaerythritol monostearate; alkylene oxide adducts of alkyl phenol; esters of sorbitan/glycerin

condensates and fatty acids and esters of sorbitan alkylene glycol condensates and fatty acids; diglycerin diolate sodium lauryl sulfate, sodium dodecyl benzene sulfonate, cetyl trimethyl ammonium chloride, dodecylamine hydrochloride, lauryl amide laurate ethyl phosphate, triethyl cetyl ammonium iodide, oleylamino diethylamine hydrochloride, dodecylpyridinium salts, and isomers thereof. The defogging agent may also have functional groups which react with the curable monomer or the curable oligomer.

The amount of the defogging agent that is added may be, for example, within the range of approximately 0.01 to 20 parts by mass (in several embodiments, from approximately 0.1 to 15 parts by mass or from approximately 0.2 to 10 parts by mass) with respect to a total of 100 parts by mass of the nanoparticles, the curable monomer, and the curable oligomer.

A hard coat precursor that can be used to form an anti-reflective hard coat contains the nanoparticle mixture described above, a curable monomer and/or a curable oligomer, a reaction initiator, and, if necessary, a solvent such as methyl ethyl ketone (MEK) or 1-methoxy-2-propanol (MP-OH) and the additives described above such as an ultraviolet absorbent, an anti-smudge agent, a defogging agent, a leveling agent, an ultraviolet reflecting agent, an anti-static agent, or the like. The hard coat precursors of some embodiments contain a nanoparticle mixture and a binder, wherein the nanoparticles constitute from 40 to 95 mass% of the total mass of the nanoparticles and the binder. From 10 to 50 mass% of the nanoparticles have an average particle size within the range of 2 to 200 nm, and from 50 to 90 mass% of the nanoparticles have an average particle size within the range of 60 to 400 nm. The ratio of the average particle size of nanoparticles having an average particle size within the range of 60 to 400 nm to the average particle size of nanoparticles having an average particle size within the range of 2 to 200 nm is within the range of 2:1 to 200:1.

As is generally known in this technical field, a hard coat precursor can be prepared by combining specific components of the hard coat precursor. For example, the hard coat precursor can be prepared by preparing a modified or non-modified nanoparticle sol of two or more different sizes with a desired solid content by mixing a curable monomer and/or a curable oligomer together with a reaction initiator in a solvent and adding a solvent. A light initiator or thermal polymerization initiator known in this technical field, for example, may be used as the reaction initiator. Depending on the curable monomer and/or the curable oligomer used, it may be unnecessary to use a solvent.

When surface-modified nanoparticles are used, the hard coat precursor can be prepared as follows, for example. An inhibitor and a surface modifier are added to a solvent in a container (for example, in a glass vial), and the resulting mixture is added to an aqueous solution in which nanoparticles are dispersed and is then stirred. The container is sealed and placed in an oven for several hours (for example, 16 hours) at a high temperature (for example, 80°C). Next, a rotary evaporator, for example, is used at a high temperature (for example, 60°C) to remove the water from the solution. By pouring the solvent in the solution and then evaporating the solution, the remaining water is removed from the solution. It is sometimes preferable to repeat the latter half of the steps several times. The concentration of the nanoparticles can be adjusted to a desired concentration (mass%) by adjusting the volume of the solvent.

Technology for applying the hard coat precursor (solution) to the surface of a substrate is

known in this technical field, and examples include bar coating, dip coating, spin coating, capillary coating, spray coating, gravure coating, screen printing, and the like. The coated hard coat precursor is dried as necessary and can be cured with a known polymerization method in this technical field such as optical polymerization using ultraviolet rays or electron beams, thermal polymerization, or the like. In this way, a hard coat can be formed on a substrate.

Next, dry etching is performed on the hard coat surface. As a result of dry etching, the binder is preferentially etched while the nanoparticles act as an etching mask, so a moth-eye structure having multiple prismatic structures is generated on the hard coat surface. The dry etching that is used may be a type of dry etching that is well known in this technical field, and examples include methods such as ion etching, plasma etching, radical etching, reactive ion etching (RIE), reactive ion beam etching (RIBE), plasma etching, molecular beam etching, atmospheric pressure plasma treatment, air corona treatment, and the like. Plasma etching, reactive ion etching (RIE), and reactive ion beam etching (RIBE) are preferable from the perspectives of minimal damage to the substrate, good in-plane uniformity, high vertical anisotropy in etching, and high productivity, and plasma etching can be used particularly advantageously. Dry etching may be performed on the entire hard coat surface, or dry etching may be performed partially on only the required areas of the hard coat surface. For example, dry etching may be performed selectively on the hard coat surface by masking areas that are not required to have an anti-reflective function or adhesiveness.

Various process pressure conditions ranging from atmospheric pressure to a vacuum may be used in accordance with the type of dry etching. For example, when plasma etching or reactive ion etching is performed, the pressure may be set to at least approximately 1 mTorr (approximately 0.13 Pa) or at least approximately 5 mTorr (approximately 0.67 Pa) and at most approximately 20 mTorr (approximately 2.7 Pa) or at most approximately 10 mmTorr (approximately 1.3 Pa).

Etching gases that can typically be used in dry etching include  $\text{ArO}_2$ ,  $\text{H}_2$ ,  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{CHF}_3$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CF}_3\text{Br}$ ,  $\text{N}_2$ ,  $\text{NF}_3$ ,  $\text{Cl}_2$ ,  $\text{CCl}_4$ ,  $\text{HBr}$ ,  $\text{SF}_6$ , and the like. The flow rate of the etching gas is adjusted in accordance with various conditions such as the type of dry etching, the volume of the chamber used, the electrode area, the pressure inside the chamber, and the like. For example, when plasma etching or reactive ion etching is performed, the flow rate may be set to at least approximately 1 sccm or at least approximately 5 sccm and at most approximately 1000 sccm or at most approximately 200 sccm.

The frequency of an RF (radio frequency) power oscillator that can be used in dry etching is typically 13.56 MHz, but other frequencies may also be used. For example, when a capacitively-coupled vacuum plasma with oscillation of 13.56 MHz is used, the RF power output is typically within the range of approximately 100 W to 20 kW, and the power density is preferably within the range of approximately 0.1 to 1.0 watts/cm<sup>2</sup> (in several embodiments, from approximately 0.2 to 0.3 watts/cm<sup>2</sup>).

The dry etching temperature is determined so that the hard coat and the substrate are not damaged excessively and is within the range of approximately -60°C to 100°C. The dry etching time is determined so that the etching depth of the hard coat is from approximately 10 to 500 nm and is typically within the range of approximately 1 second to 2 minutes.

Since the anti-reflective hard coat of the present disclosure is filled with a high level of nanoparticles, the depth of a plurality of concavities formed after dry etching is smaller than the wavelength of visible light and, preferably, at most 1/4 the wavelength of visible light such as from 100 to 200 nm, for example, or smaller. Therefore, the anti-reflective hard coat demonstrates anti-reflective characteristics and exhibits excellent scratch resistance due to a comparatively large number of nanoparticles remaining on the dry-etched surface.

In the anti-reflective hard coat of the present disclosure, the exposure area of the nanoparticles increases due to dry etching, so silane coupling treatment may be further performed on the dry-etched surface as necessary. Such silane coupling treatment makes it possible to further provide the surface of the anti-reflective hard coat with other functions such as smudge resistance or fog resistance.

Silane coupling treatment can be performed with a known method using a hydrophilic or hydrophobic silane coupling agent. Examples of hydrophilic silane coupling agents include amino-modified alkoxy silanes, epoxy-modified alkoxy silanes such as glycidyl-modified alkoxy silanes, polyether-modified alkoxy silanes, zwitter ion alkoxy silanes, and the like. Examples of hydrophobic silane coupling agents include chlorosilanes such as dimethyldichlorosilane, trimethylchlorosilane, allyldimethylchlorosilane, and allylphenyldichlorosilane, hexamethyldisilazane, alkyl alkoxy silanes, phenyl alkoxy silanes, vinyl alkoxy silanes, and the like.

The hydrophilicity can be enhanced by further applying a modified silicone oil such as an amino-modified silicone oil or an epoxy-modified silicone oil to the silane coupling-treated surface. The hydrophobicity can be enhanced by further applying a dimethyl silicone oil, a methyl phenyl silicone oil, an alkyl-modified silicone oil, or the like to the silane coupling-treated surface.

One embodiment of the present disclosure provides an anti-reflective article having a layer of the aforementioned anti-reflective hard coat on the surface of a substrate. In an anti-reflective article of an embodiment of the present disclosure illustrated in FIG. 2, a hard coat layer 14 having a dry-etched surface 15 is disposed on a first surface of a substrate 12. Examples of substrates that can be used in the anti-reflective article include transparent substrates such as films, plastics (polymer plates), and sheet glass. In the present disclosure, "transparent" means that the total light transmission rate in the visible light range (380 to 780 nm) is at least 90%. Examples of representative films include films formed from polyolefins (for example, polyethylene (PE), polypropylene (PP), or the like), polyurethanes, polyesters (for example, polyethylene terephthalate (PET) or the like), poly(meth)acrylates (for example, polymethyl methacrylate (PMMA) or the like), polyvinyl chlorides, polycarbonates, polyamides, polyimides, phenol resins, cellulose diacetates, cellulose triacetates, polystyrenes, styrene-acrylonitrile copolymers, acrylonitrile-butadiene-styrene copolymers (ABS), epoxies, polyacetates, or glass. Examples of representative plastics (polymer plates) include plastics formed from polycarbonates (PC), polymethylmethacrylates (PMMA), styrene-acrylonitrile copolymers, acrylonitrile-butadiene-styrene copolymers (ABS), blends of PC and PMMA, or laminates of PC and PMMA.

A thickness of the film is within the range of approximately 5 to 500  $\mu\text{m}$  (in several embodiments, from approximately 10 to 200  $\mu\text{m}$  or from approximately 25 to 100  $\mu\text{m}$ ). A thickness of the plastic (polymer plate) is within the range of approximately 0.5 mm to 10 cm (in several



embodiments, from approximately 0.5 to 5 mm or from approximately 0.5 to 3 mm). A thickness of the sheet glass is within the range of approximately 5 to 500  $\mu\text{m}$  or from approximately 0.5 mm to 10 cm (in several embodiments, from approximately 0.5 to 5 mm or from approximately 0.5 to 3 mm). These substrates may sometimes be used effectively even when the thickness deviates from the ranges  
5 described above.

The anti-reflective article may have the aforementioned anti-reflective hard coat on a plurality of surfaces of the substrate. For example, the substrate may have first and second surfaces, and the aforementioned anti-reflective hard coat may be disposed on the first and second surfaces of the substrate. The second surface may be on the opposite side as the first surface when viewed from the  
10 substrate. That is, the first and second surfaces may be two opposing surfaces of the substrate. In the anti-reflective article 20 illustrated in FIG. 3, for example, a hard coat layer 24 having a dry-etched surface 25 is respectively disposed on each of the first surface of the substrate 22 and the second surface opposing the first surface. When a plurality of anti-reflective hard coat layers are used in this way, the anti-reflective characteristics of the anti-reflective article can be enhanced. A laminate of a plurality of  
15 anti-reflective hard coat layers may also be disposed on the surface of the substrate.

In several embodiments, the surface of the substrate is primed or a primer layer is disposed on the surface of the substrate in order to improve the adhesion of the anti-reflective hard coat and the substrate. In particular, when the substrate is a film with poor adhesiveness such as polypropylene, polyvinyl chloride, or the like, priming or a primer layer is particularly effective.  
20

Priming is known in this technical field, and examples include plasma treatment, corona discharge treatment, flame treatment, electron beam irradiation, surface roughening, ozone treatment, chemical oxide treatment using chromic acid or sulfuric acid, and the like.

Examples of materials used for the primer layer include (meth)acrylic resins (homopolymers of (meth)acrylates, copolymers of two or more types of (meth)acrylates, or copolymers of (meth)acrylates and other polymerizable monomers), urethane resins (for example, 2-solution curable urethane resins consisting of a polyol and an isocyanate curing agent), (meth)acryl-urethane copolymers (for example, acryl-urethane block copolymers), polyester resins, butyral resins, vinyl chloride-vinyl acetate copolymers, ethylene-vinyl acetate copolymers, chlorinated polyolefins such as chlorinated polyethylenes or chlorinated polypropylenes, and copolymers and derivatives thereof (for example,  
25 chlorinated ethylene-propylene copolymers, chlorinated ethylene-vinyl acetate copolymers, acryl-modified chlorinated polypropylenes, maleic anhydride modified chlorinated polypropylenes, and urethane modified chlorinated polypropylenes), and the like. When the substrate is a polypropylene film, it is advantageous for the primer to contain a chlorinated polypropylene or a modified chlorinated polypropylene.  
30

The primer layer can be formed by applying a primer solution prepared by dissolving the aforementioned resins in a solvent using a known method in this technical field and then drying the solution. A thickness of the primer layer is typically within the range of approximately 0.1 to 20  $\mu\text{m}$  (in several embodiments, from approximately 0.5 to 5  $\mu\text{m}$ ).  
35

In some embodiments, the anti-reflective article may have an adhesive layer on the dry-etched

surface. The dry-etched surface has minute surface roughness, which yields excellent adhesiveness with the adhesive layer. In this embodiment, using an adhesive layer makes it possible to easily provide other articles with anti-reflecting characteristics. A rubber adhesive, acrylic adhesives, polyurethane adhesives, a polyolefin adhesives, polyester adhesives, and silicon adhesives or pressure-sensitive adhesives known in this technical field can be used as adhesive layers. The adhesive or pressure-sensitive adhesive is preferably an optically transparent adhesive or pressure-sensitive adhesive such as an optically transparent acrylic adhesive or pressure-sensitive adhesive. In the present disclosure, "optically transparent" means that the total light transmission rate in the visible light range (380 to 780 nm) is at least 90% and, as necessary, that total light transmission rate of light of other wavelength ranges (for example, the ultraviolet range) is also at least 90%. An adhesive layer may be formed by directly applying or extruding the adhesive and the pressure-sensitive adhesive onto the substrate, or an adhesive layer formed by applying the adhesive and the pressure-sensitive adhesive to a release liner may be laminated and transferred to the substrate.

A thickness of the adhesive layer including the adhesive or the pressure-sensitive adhesive is typically within the range of approximately 1 to 100  $\mu\text{m}$  (in several embodiments, from approximately 5 to 75  $\mu\text{m}$  or from approximately 10 to 50  $\mu\text{m}$ ). The adhesive or the pressure-sensitive adhesive may also contain the ultraviolet absorbent described above.

The anti-reflective hard coat and/or the adhesive layer may also be provided with a release liner known in this technical field as necessary. A material known in this technical field and prepared by performing silicon processing or the like on paper or a polymer film can be used as the release liner.

In some embodiments, the anti-reflective article may further contain a second substrate laminated on the dry-etched surface separately from the substrate supporting the anti-reflective hard coat layer. Such a second substrate may be laminated on the dry-etched surface via the adhesive layer described above, for example. The adhesive layer is preferably formed using an optically transparent adhesive or pressure-sensitive adhesive.

As examples using the anti-reflective article of the present disclosure, cross-sectional views of display units 30, 40, and 50 in which the second substrates are liquid crystal display panels 37, 47, and 57 are illustrated in FIGS. 4 to 6. In FIG. 4, hard coat layers 34 are disposed on both sides of a substrate 32, and a portion of a dry-etched surface 35 and the liquid crystal display panel 37 are adhered to one another via an optically transparent adhesive layer 36. In FIG. 4, a printing layer 38 is disposed on the outer periphery of the dry-etched surface 35 as a frame of the image display area of the liquid crystal display panel 37. The dry-etched surface 35 having minute surface roughness also has excellent printing characteristics with respect to the printing ink or the like used to form the printing layer 38. In FIG. 5, both hard coat layers 44 on both sides of a substrate 42 have dry-etched surfaces 45, and the anti-reflecting characteristics are thus further improved in comparison to FIG. 4. In FIG. 6, silane coupling treatment is further performed on a dry-etched surface 59 on the opposite side as the liquid crystal display panel 57 so as to provide the surfaces of the display unit with functionality such as smudge resistance, fog resistance, and the like.

The anti-reflective hard coat and the anti-reflective article of the present disclosure are suitable for applications such as liquid crystal displays, EL displays, LED displays, plasma displays, touch panels, lenses for cameras or the like, solar-powered panels (solar panels), and the like, for example. However, the anti-reflective hard coat and the anti-reflective article of the present disclosure are not limited to these applications and can be used for various applications requiring anti-reflective characteristics.

Various embodiments of the anti-reflective hard coat, article, and display are provided.

Embodiment 1 is an anti-reflective hard coat comprising a nanoparticle mixture and a binder, the anti-reflective hard coat having a dry-etched surface; the nanoparticles constituting from 40 to 95 mass% of an entire mass of the hard coat; from 10 to 50 mass% of the nanoparticles having an average particle size within a range of 2 to 200 nm; from 50 to 90 mass% of the nanoparticles having an average particle size within a range of 60 to 400 nm; a ratio of the average particle size of nanoparticles having an average particle size within the range of 60 to 400 nm to the average particle size of nanoparticles having an average particle size within the range of 2 to 200 nm being within a range of 2:1 to 200:1, wherein a particle size distribution of the nanoparticles is bimodal or multimodal.

Embodiment 2 is the anti-reflective hard coat of embodiment 1, wherein the nanoparticles are surface-modified nanoparticles.

Embodiment 3 is the anti-reflective hard coat of embodiment 1 or 2, wherein the dry etching is plasma etching.

Embodiment 4 is the anti-reflective hard coat of any one of embodiments 1 to 3, wherein the binder contains a fluorinated (meth)acrylic compound, a reaction product thereof, or a combination thereof.

Embodiment 5 is the anti-reflective hard coat of any one of embodiments 1 to 4, wherein silane coupling treatment is further performed on the dry-etched surface.

Embodiment 6 is an anti-reflective article comprising a substrate having a first surface; and a layer of an anti-reflective hard coat of any one of embodiments 1 to 5 disposed on the first surface of the substrate.

Embodiment 7 is the anti-reflective article of any one of embodiments 1 to 6, wherein the substrate further comprises a second surface and further comprises a layer of the anti-reflecting hard coat of one of embodiments 1 to 5 disposed on the second surface of the substrate.

Embodiment 8 is the anti-reflective article of any one of embodiments 1 to 7, wherein a second substrate is laminated on the dry-etched surface.

Embodiment 9 is the anti-reflective article of any one of embodiments 1 to 8, wherein the second substrate is laminated on the dry-etched surface via an optically transparent adhesive layer.

Embodiment 10 is a display unit comprising an anti-reflective article according to any of embodiments 1 to 9, wherein the second substrate is a liquid crystal display panel.

### **Examples**

In the following examples, specific embodiments of the present disclosure are illustrated, but the present invention is not limited to these embodiments. All "parts" and "percents" are based on mass

unless specified otherwise.

### Evaluation Methods

The characteristics of the anti-reflective hard coat of the present disclosure were evaluated in accordance with the following methods.

#### 1. Optical Characteristics

The transmission rate at a wavelength of 350 to 850 nm was measured using a UV-vis spectrophotometer (U-4100, acquired from the Hitachi High Technologies Corporation).

#### 2. Contact Angle

The water contact angle of the anti-reflective hard coat surface was measured by the Sessile Drop method using a contact angle meter (acquired from Kyowa Kaimen Kagaku Co., Ltd. under the product name "DROPMASER FACE"). The volume of liquid droplets was set to 4  $\mu$ L for static measurements. The value of the water contact angle was calculated from the average of five measurements. A surface with a water contact angle exceeding 100 degrees can prevent the deposition of dust or the like. On the other hand, a surface with a water contact angle of less than 20 degrees has high hydrophilicity, which makes it possible to prevent fogging due to water vapor condensation on the surface.

#### 3. Adhesive Force Tests

An optically transparent adhesive tape with a width of 25 mm (CEF0806, acquired from the 3M Company) was attached to the anti-reflective hard coat surface of each substrate using a 2.0 kg roller, and the adhesive force was measured at 25°C at a peeling angle of 90 degrees and a peel rate of 300 mm/minute.

Table 1: Reagents and Raw Materials

Trade designation	Chemical name or composition	Available from
SILQUEST A174	3-(Methacryloyloxy)propyltrimethoxy silane	Alfa Aesar, Ward Hill, Massachusetts
PROSTAB	4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxy; 5 mass%	Aldrich, Milwaukee, Wisconsin
NALCO 2329	SiO <sub>2</sub> sol; average particle size 75 nm	Nalco Company, Naperville, Illinois
NALCO 2327	SiO <sub>2</sub> sol; average particle size 20 nm	Nalco Company, Naperville, Illinois
MP-2040	SiO <sub>2</sub> sol; average particle size 190 nm	Nissan Chemical Industries, Ltd.

1-methoxy -2-propanol		Alfa Aesar, Ward Hill, Massachusetts
EBECRYL 4858	Urethane acrylate oligomer	Daicel-Cytec Company, Ltd.
SR340	2-Phenoxyethylmethacrylate	Sartomer Company
KAYARAD UX-5000	Urethane acrylate oligomer	Nippon Kayaku Co., Ltd.
LRGACURE 184	1-Hydroxy-cyclohexyl-phenyl-ketone	BASF AG
BYK-UV3500	Acrylate-containing polyether-modified silicone	BYK-Chemie GmbH
HFPO Urethane Acrylate	30 mass% of perfluoropolyethyl urethane acrylate, 4-4205-6329-2	3M Company
KY-1203	Fluorinated acrylic compound having siloxane units; 20 mass%	Shin-Etsu Chemical Co., Ltd.
EGC1720	Hydrophobic silane coupling agent	3M Company
L-21074	Hydrophilic (zwitter ion) silane coupling agent	3M Company

#### Preparation of Surface-Modified Silica Sol (Sol 1)

5 A surface-modified silica sol ("sol 1") was prepared as follows. First, 5.95 g of SILQUEST A174 and 0.5 g of PROSTAB was added to a mixture of 400 g of NALCO 2329 and 450 g of 1-methoxy-2-propanol in a glass vial and stirred at room temperature for 10 minutes. The glass vial was sealed and placed in an oven at 80°C for 16 hours. Water was removed from the resulting solution with a rotary evaporator until the solid content of the solution reached nearly 45 mass% at 60°C. Two-hundred g of 1-methoxy-2-propanol was added to the resulting solution, and the remaining water 10 was removed at 60°C using a rotary evaporator. The latter half of the steps were repeated twice so as to further remove water from the solution. Finally, the concentration of all of the SiO<sub>2</sub> nanoparticles was adjusted to 45 mass% by adding 1-methoxy-2-propanol, and an SiO<sub>2</sub> sol (hereafter called "sol 1") containing surface-modified SiO<sub>2</sub> nanoparticles having an average particle size of 75 nm was obtained.

#### 15 Preparation of Surface-Modified Silica Sol (Sol 2)

A surface-modified silica sol ("sol 2") was prepared as follows. Modification was performed with the same method as for sol 1 with the exception of using 400 g of NALCO 2327, 25.25 g of SILQUEST A174, and 0.5 g of PROSTAB, and an SiO<sub>2</sub> sol (hereafter called "sol 2") containing 45 mass% of surface-modified SiO<sub>2</sub> nanoparticles having an average particle size of 20 nm was obtained.

#### 20 Preparation of Surface-Modified Silica Sol (Sol 3)

A surface-modified silica sol ("sol 3") was prepared as follows. Modification was performed with the same method as for sol 1 with the exception of using 400 g of MP-2040, 4.74 g of SILQUEST A174, and 0.5 g of PROSTAB, and an SiO<sub>2</sub> sol (hereafter called "sol 3") containing 45 mass% of surface-modified SiO<sub>2</sub> nanoparticles having an average particle size of 190 nm was obtained.

5

#### Example 1

Sol 1 and sol 2 were mixed at a ratio of 65:35 (mass ratio), and the amount of 1-methoxy-2-propanol was adjusted to obtain a mixture containing a total of 46.65 mass% of surface-modified nanoparticles. A binder was prepared by mixing EBECRYL 4858, SR340, and IRGACURE 184 at a ratio of 90:10:8 (mass ratio). The mixture containing the surface-modified nanoparticles and the binder were mixed at a ratio of 75:25 (mass ratio). The resulting anti-reflective hard coat composition was applied to a glass sheet with a thickness of 2 mm (white sheet glass, acquired from Schott AG) using a #4 Meyer rod and dried for 10 minutes at 40°C. Next, the composition was irradiated for 5 minutes with ultraviolet rays having a wavelength of 253.7 nm in a nitrogen atmosphere using a 25 W UV lamp (bactericidal lamp G25T8, acquired from Sankyo Denki) (amount of irradiation: 268.43 mJ/cm<sup>2</sup>). The hard coat of Example 1 was formed on a glass sheet in this manner. The base pressure inside the chamber was then set to 10 mTorr using a PDC210 plasma treatment device (Yamato Scientific Co., Ltd.), and the hard coat surface was then subjected to plasma etching at 13.56 MHz, at a power of 200 W for 60 seconds at 25°C, and at an effective output of 28.7 J/cm<sup>2</sup>, while the pressure inside the chamber was maintained at 46 to 48 mTorr at an oxygen gas flow rate of 73 sccm, to prepare a sample for transmission rate measurements.

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#### Example 2

A sample for transmission rate measurements was prepared in the same manner as in Example 1 with the exception of setting the ratio of the mixture containing surface-modified nanoparticles to the binder to 69:31 (mass ratio).

25

#### Example 3

A sample for transmission rate measurements was prepared in the same manner as in Example 1 with the exception of setting the ratio of the mixture containing surface-modified nanoparticles to the binder to 65:35 (mass ratio).

30

#### Example 4

A sample for transmission rate measurements was prepared in the same manner as in Example 1 with the exception of using sol 3 instead of sol 1 and using a glass sheet with a thickness of 2 mm (float glass, acquired from Asahi Glass Co., Ltd.).

35

#### Comparative Examples 1 through 4

The samples for transmission rate measurements in Comparative Examples 1 to 4 were

respectively prepared with the same procedures as in Examples 1 to 4 with the exception that plasma etching was not performed on the hard coat surface.

The results of measuring the optical characteristics of the samples of Examples 1 to 4 and Comparative Examples 1 to 4 are shown in FIGS. 7 to 10.

#### Preparation of Hard Coat Precursor (HC-1)

First, 108.33 g of sol 1, 58.33 g of sol 2, and 25 g of Kayurad UX-5000 were mixed. Next, 2.0 g of IRGACURE 184 was added to the mixture as an optical polymerization initiator, and 0.01 g of BYK-UV3500 was added to the mixture as a leveling agent. The mixture was then adjusted so that the solid content was 50 mass% by adding 1-methoxy-2-propanol, and a hard coat precursor HC-1 was thus prepared.

#### Preparation of Hard Coat Precursors (HC-2 and HC-3)

Hard coat precursors HC-2 and HC-3 were prepared in the same manner as in HC-1 with the formulas described in Table 2. As anti-smudge agents, HFPO urethane acrylate was added to HC-2, and KY-1203 was added to HC-3.

The compositions of HC-1 to HC-3 are shown in Table 2.

Table 2

Hard Coat Precursor Composition (Compounding amounts are shown in grams)

Component		HC-1	HC-2	HC-3
Surface-modified silica nanoparticles	Sol 1 (Average particle size: 75 nm)	108.33	108.33	108.33
	Sol 2 (Average particle size: 20 nm)	53.33	58.33	58.33
Acrylic oligomer	KAYARAD UX-5000	25.00	25.00	25.00
Photoinitiator	IRGACURE 184	2.0	2.0	2.0
Anti-smudge agent	HFPO urethane acrylate	0.00	0.33	0.00
	KY-1203	0.00	0.00	2.50
Leveling agent	BYK-UV3500	0.01	0.01	0.01
Diluent	1-methoxy-2-propanol	8.34	8.21	6.84
	Solid content (%)	50.00	50.00	50.00

Example 5

A polycarbonate substrate (100 x 53 x 1 mm, obtained from Mitsubishi Gas Chemical Company, Inc. under the product name "Lupilon NF2000") was suspended from and fixed to the head of a dip coater and immersed in the hard coat precursor HC-1. After 30 seconds, the substrate was pulled up at a rate of 3.33 mm/sec. After the substrate was dried for 5 minutes at 60°C, the substrate was placed  
5 in a nitrogen-purged box with an oxygen concentration of 50 ppm. Next, the substrate was irradiated from both sides for 5 minutes with ultraviolet rays having a wavelength of 253.7 nm in a nitrogen atmosphere using a 25 W UV lamp (bactericidal lamp G25T8, acquired from Sankyo Denki) (amount of irradiation: 268.43 mJ/cm<sup>2</sup>). The base pressure inside the chamber was then set to 10 mTorr using a PDC210 plasma treatment device (Yamato Scientific Co., Ltd.), and the hard coat surface was then  
10 subjected to plasma etching at 13.56 MHz, at a power of 200 W for 60 seconds at 25°C, and at an effective output of 28.3 J/cm<sup>2</sup>, while the pressure inside the chamber was maintained at 46 to 48 mTorr at an oxygen gas flow rate of 73 sccm.

#### Example 6

15 The hard coat precursor HC-1 was applied and cured in the same manner as in Example 5. Plasma etching was performed on both sides of the sample under the same conditions as in Example 5.

#### Example 7

20 The hard coat precursor HC-1 was applied and cured in the same manner as in Example 5. Plasma etching was performed on both sides of the sample under the same conditions as in Example 5. After plasma etching, a hydrophobic silane coupling agent EGC1720 was applied to one surface and cured by heating for 30 minutes at 100°C.

#### Example 8

25 The hard coat precursor HC-1 was applied and cured in the same manner as in Example 5. Plasma etching was performed on both sides of the sample under the same conditions as in Example 5. After plasma etching, a hydrophilic silane coupling agent L-21074 was applied to one surface and cured by heating for 30 minutes at 100°C.

#### 30 Examples 9 and 10

The hard coat precursor HC-2 was applied and cured in the same manner as in Example 5. Plasma etching was performed on one side (Example 9) or both sides (Example 10) of the sample under the same conditions as in Example 5.

#### 35 Examples 11 and 12

The hard coat precursor HC-3 was applied and cured in the same manner as in Example 5. Plasma etching was performed on one side (Example 11) or both sides (Example 12) of the sample under the same conditions as in Example 5.



## Comparative Examples 5 through 8

An untreated polycarbonate substrate (100 x 53 x 1 mm, obtained from Mitsubishi Gas Chemical Company, Inc. under the product name "Lupilon NF2000") was used as Comparative Example 5, and a substrate in which plasma etching was not performed after the hard coat precursor was applied and cured in the same manner as in Examples 5, 9, and 11 was respectively used as Comparative Examples 6 to 8.

The results of evaluating these hard coats are shown in Table 3 and FIGS. 11 to 13.

Table 3: Surface Characteristics of the Plasma-Etched Anti-Reflective Hard Coats and the Untreated Hard Coats

Example	Hard coat	Plasma etching	Silane coupling treatment	Water contact angle (degrees)	Adhesive force (N/25 mm)
Comparative Example 5	-	-	-	89.1	-
Comparative Example 6	HC-1	-	-	86.8	8.5
Example 5	HC-1	One side	-	-	18
Example 7	HC-1	Both sides	Hydrophobicity	119.5	-
Example 8	HC-1	Both sides	Hydrophilicity	5.4	-
Comparative Example 7	HC-2	-	-	105.7	0.4
Example 9	HC-2	One side	-	-	19.2
Comparative example 8	HC-3	-	-	112.7	0.7
Example 11	HC-3	One side	-	-	18.9

As illustrated in FIGS. 7 to 13, the reflectivity of the hard coat surface decreases and the transmission rate of the hard coat increases due to plasma etching. In particular, hard coats that were plasma-etched on both sides demonstrated transmission rates approximately 5% higher than those that were not plasma-etched.

Table 3 shows the water contact angle and adhesive force before and after plasma etching. The hard coats that had anti-smudge agents and were not plasma-etched (Comparative Examples 7 and 8) demonstrated water contact angles exceeding 100 degrees. Example 7, which was subjected to hydrophobic silane coupling treatment, also demonstrated a water contact angle exceeding 100 degrees. On the other hand, the water contact angle of Example 8, which was subjected to hydrophilic silane coupling treatment, was less than 20 degrees. These results suggest that further subjecting the plasma-etched surface to silane coupling treatment makes it possible to provide the anti-reflective hard coat with smudge resistance or fog resistance.

The adhesive force of the optically transparent adhesive increased after plasma etching (Comparative Example 6 and Example 5, Comparative Example 7 and Example 9, and Comparative Example 8 and Example 11). These results suggest that the dry-etched surface of the anti-reflective hard coat of the present disclosure has excellent adhesiveness with the adhesive and printing suitability for printing ink or the like.

5

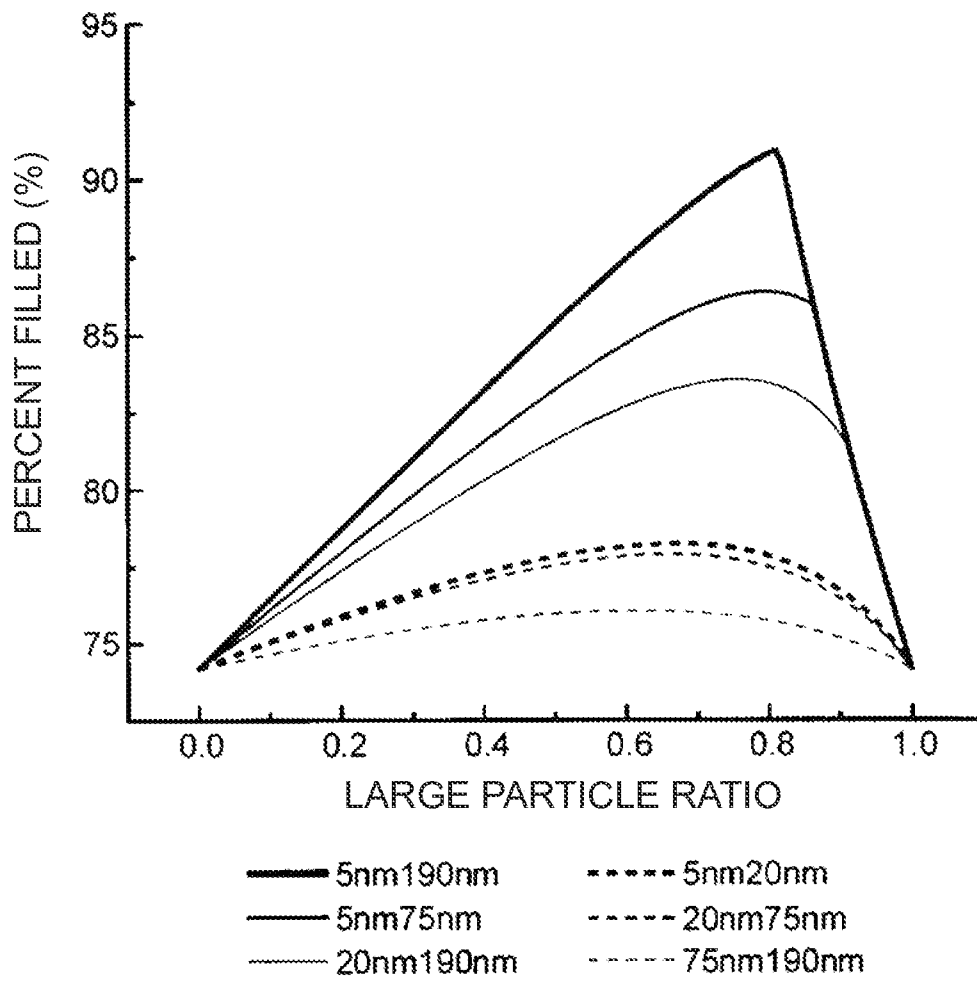
Explanation of Reference Numerals:

	10, 20	Anti-reflective articles
	12, 22	Substrates
10	14, 24	Hard coat layers
	15, 25	Dry-etched surfaces
	30, 40, 50	Liquid crystal displays
	32, 42, 52	Substrates
	34, 44, 54	Hard coat layers
15	35, 45, 55	Dry-etched surfaces
	36, 46, 56	Optically transparent adhesive layers
	37, 47, 57	Liquid crystal display panels
	38, 48, 58	Printing layers
	59	Dry-etched and silane coupling-treated surface

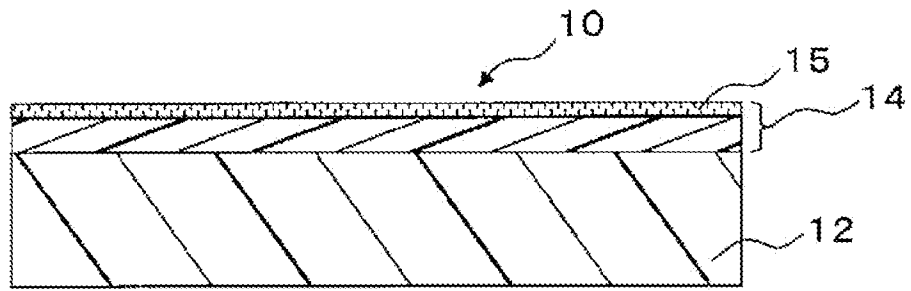
What is Claimed is:

1. An anti-reflective hard coat comprising a nanoparticle mixture and a binder, the anti-reflective hard coat having a dry-etched surface;  
5 the nanoparticles constituting from 40 to 95 mass% of an entire mass of the hard coat;  
from 10 to 50 mass% of the nanoparticles having an average particle size within a range of 2 to 200 nm;  
from 50 to 90 mass% of the nanoparticles having an average particle size within a range of 60 to 400 nm;  
10 a ratio of the average particle size of nanoparticles having an average particle size within the range of 60 to 400 nm to the average particle size of nanoparticles having an average particle size within the range of 2 to 200 nm being within a range of 2:1 to 200:1, wherein a particle size distribution of the nanoparticles is bimodal or multimodal.
- 15 2. The anti-reflective hard coat according to claim 1, wherein the nanoparticles are surface-modified nanoparticles.
3. The anti-reflective hard coat according to either claim 1 or 2, wherein the dry etching is plasma etching.  
20
4. The anti-reflective hard coat according to any one of claims 1 to 3, wherein the binder contains a fluorinated (meth)acrylic compound, a reaction product thereof, or a combination thereof.
5. The anti-reflective hard coat according to any one of claims 1 to 4, wherein silane coupling  
25 treatment is further performed on the dry-etched surface.
6. An anti-reflective article comprising a substrate having a first surface; and  
a layer of an anti-reflective hard coat according to any one of claims 1 to 5 disposed on the first surface of the substrate.  
30
7. The anti-reflective article according to claim 6, wherein the substrate further comprises a second surface and further comprises a layer of the anti-reflecting hard coat according to any one of claims 1 to 5 disposed on the second surface of the substrate.
- 35 8. The anti-reflective article according to either claim 6 or 7, wherein a second substrate is laminated on the dry-etched surface.
9. The anti-reflective article according to claim 8, wherein the second substrate is laminated on the dry-etched surface via an optically transparent adhesive layer.

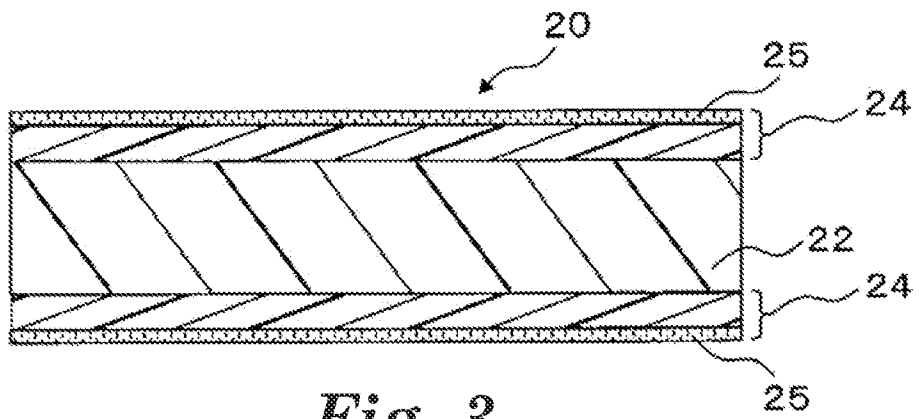
10. A display unit comprising an anti-reflective article according to either claim 8 or 9, wherein the second substrate is a liquid crystal display panel.



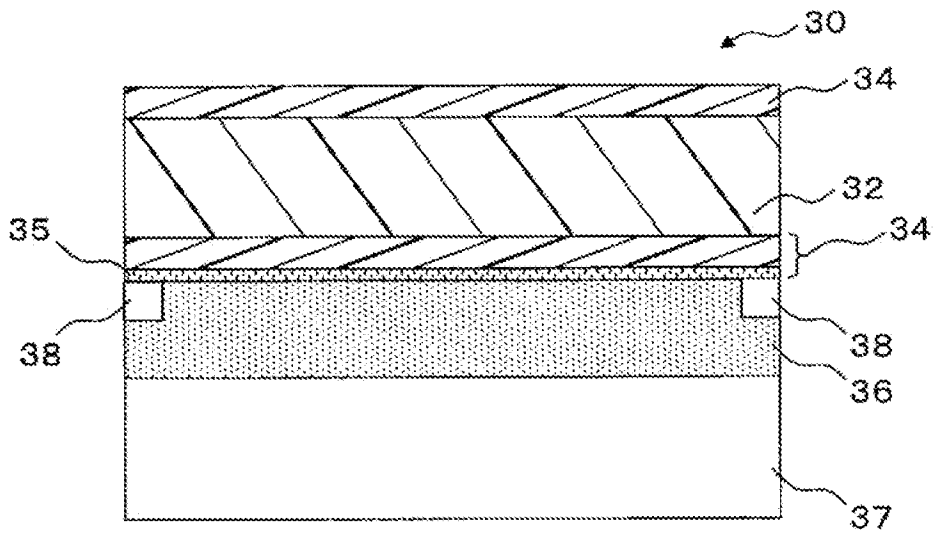
*Fig. 1*



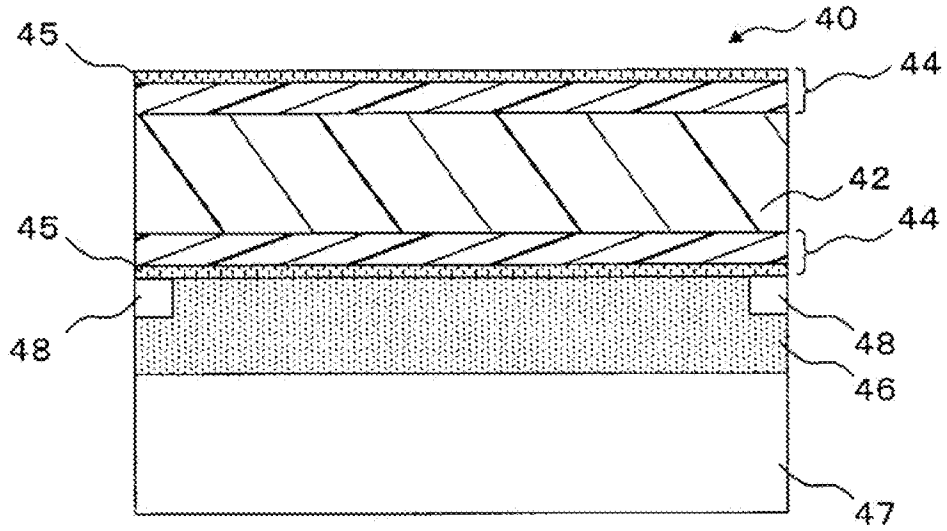
*Fig. 2*



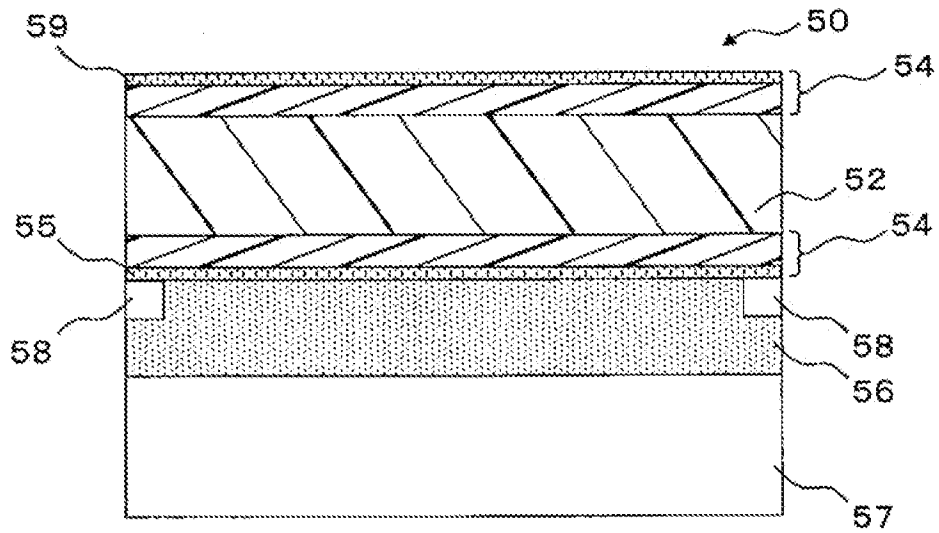
*Fig. 3*



*Fig. 4*



*Fig. 5*



*Fig. 6*

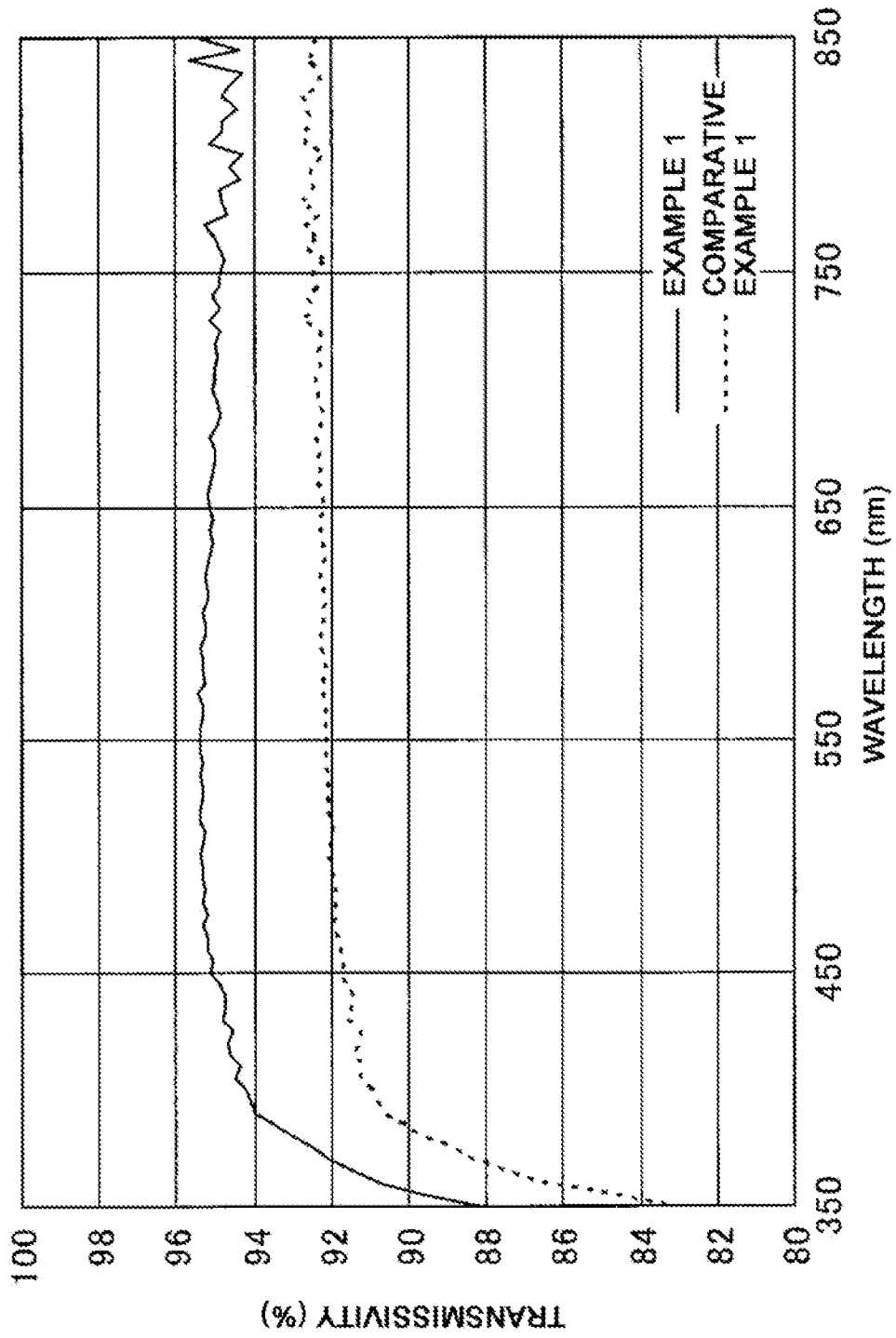


Fig. 7



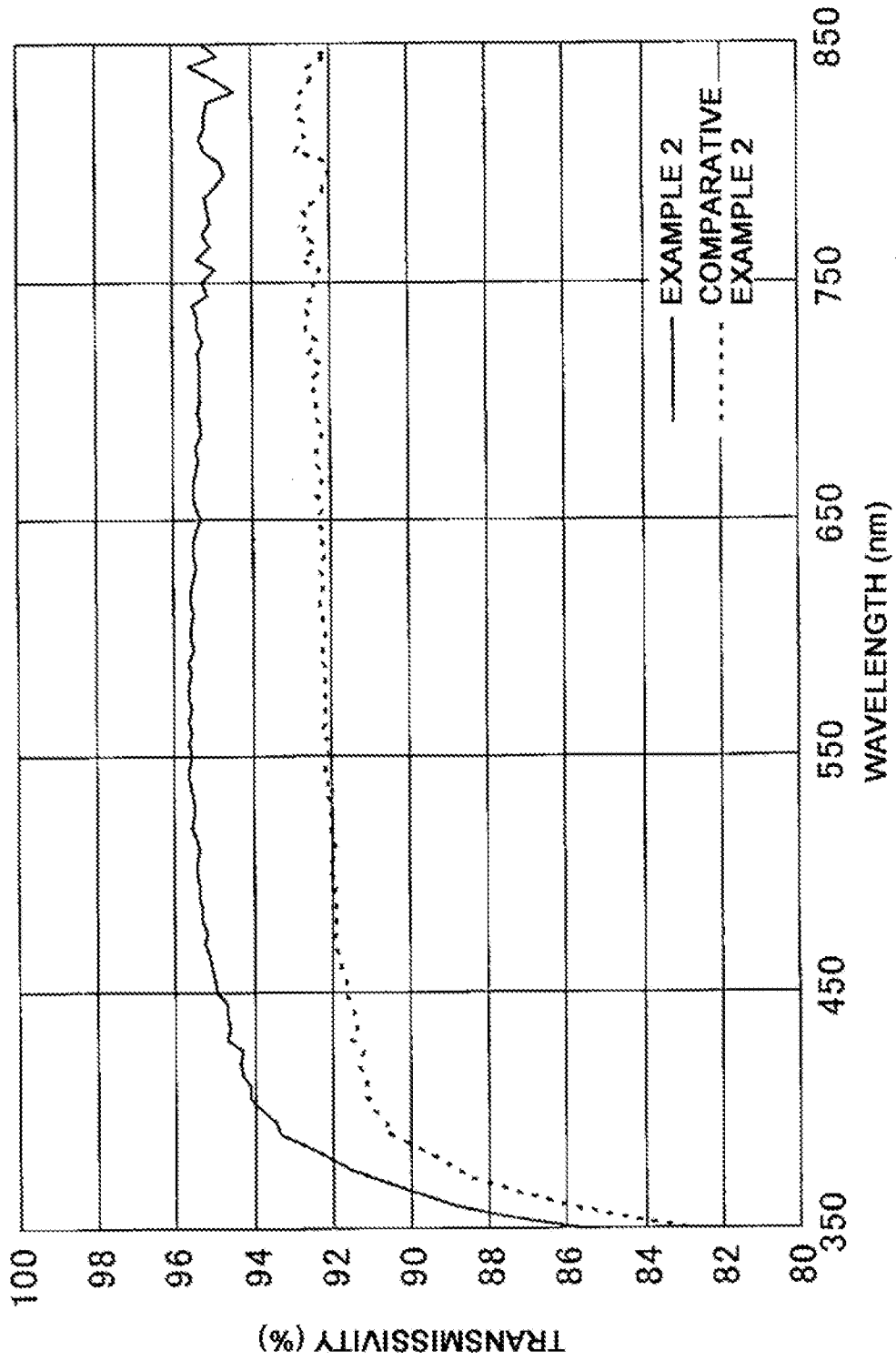
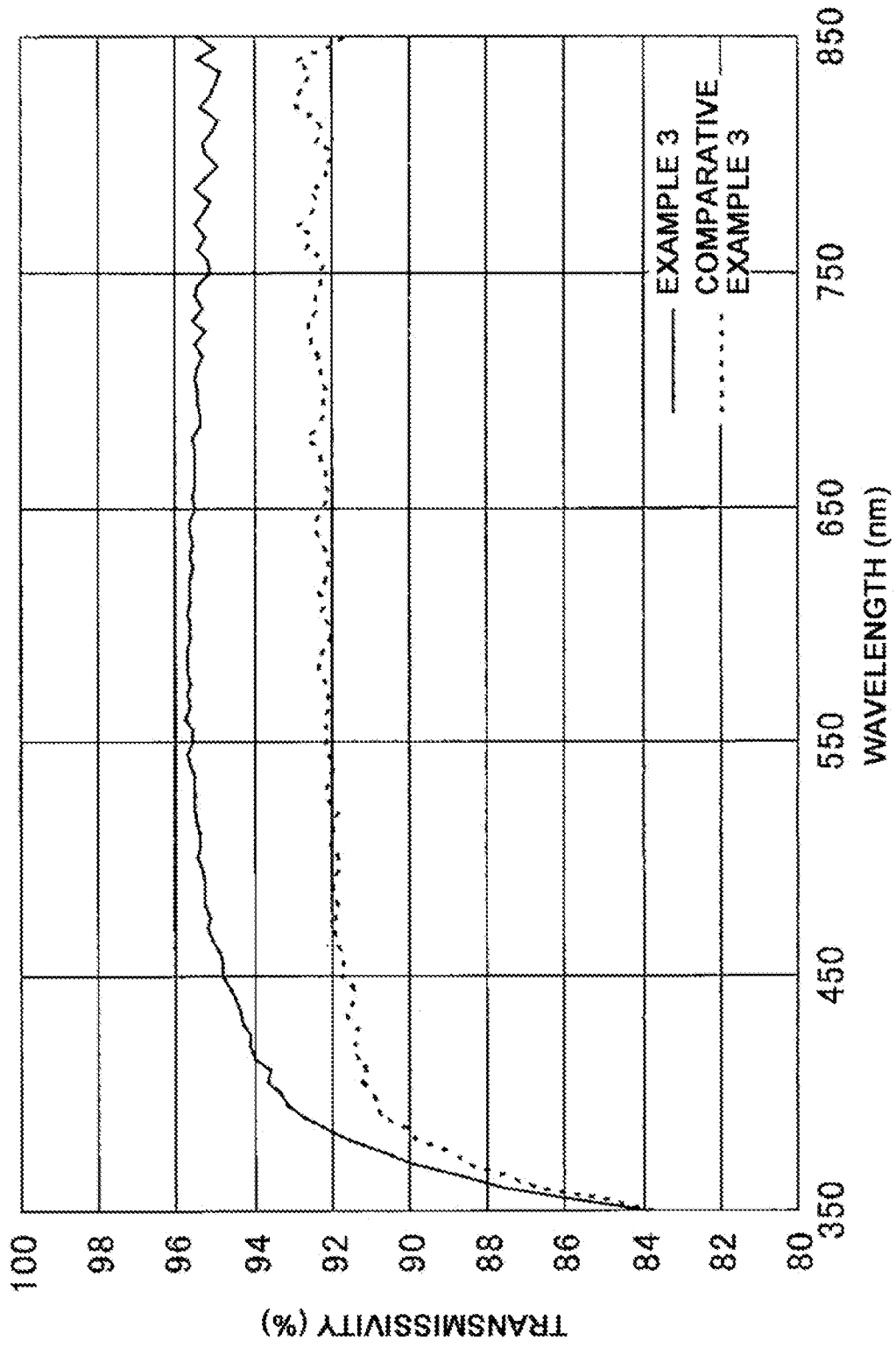
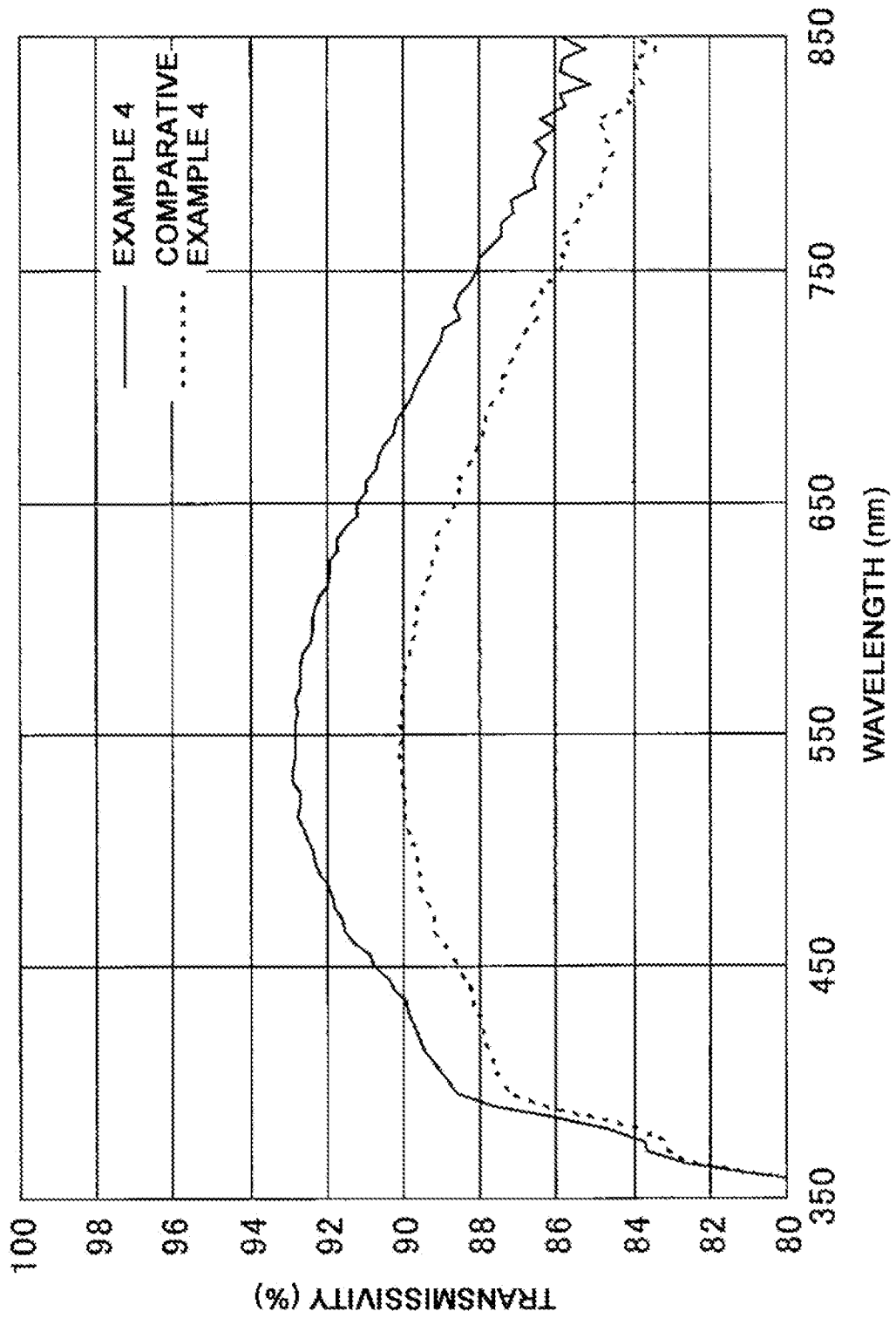


Fig. 8



*Fig. 9*



*Fig. 10*

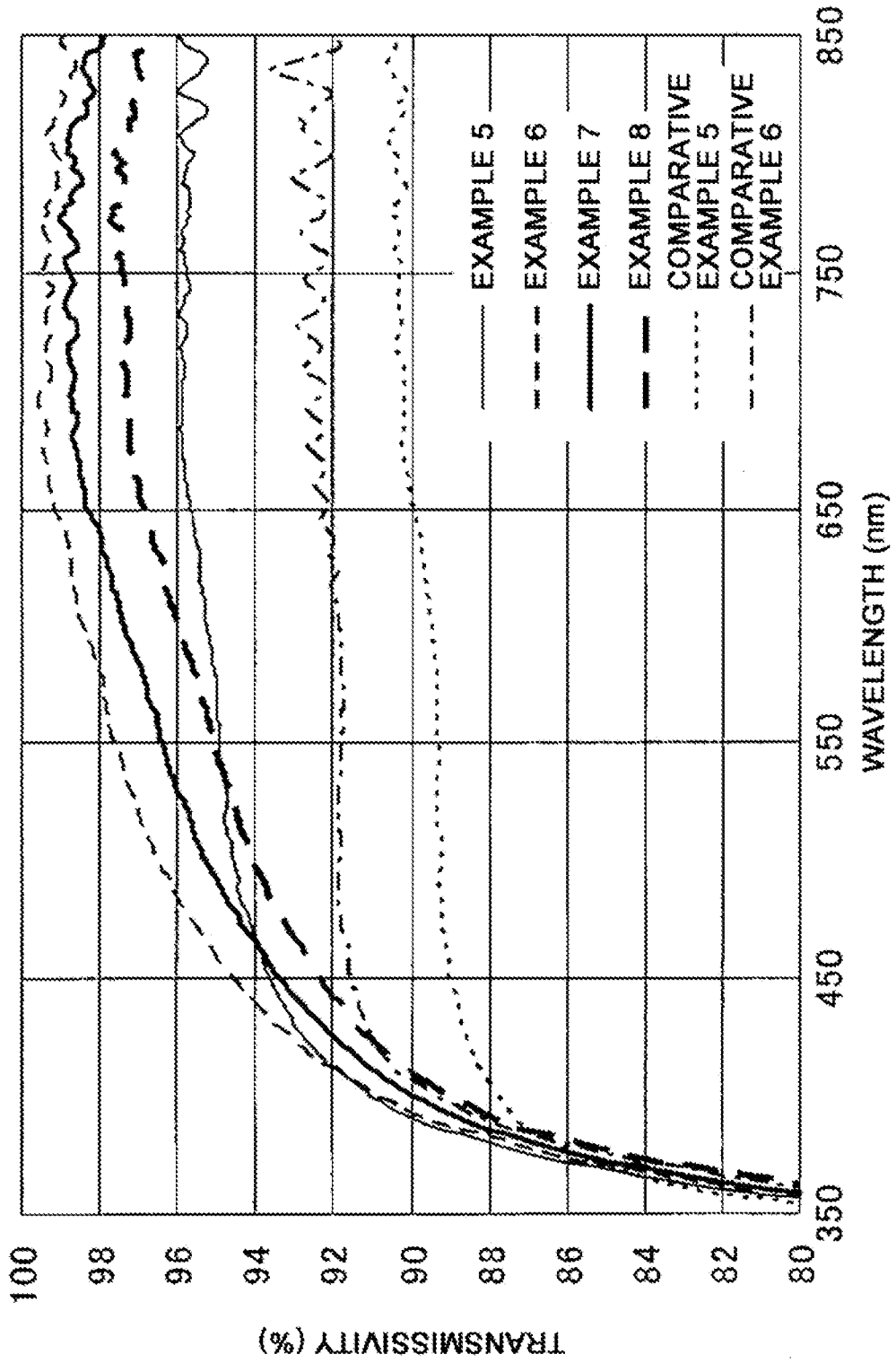


Fig. 11

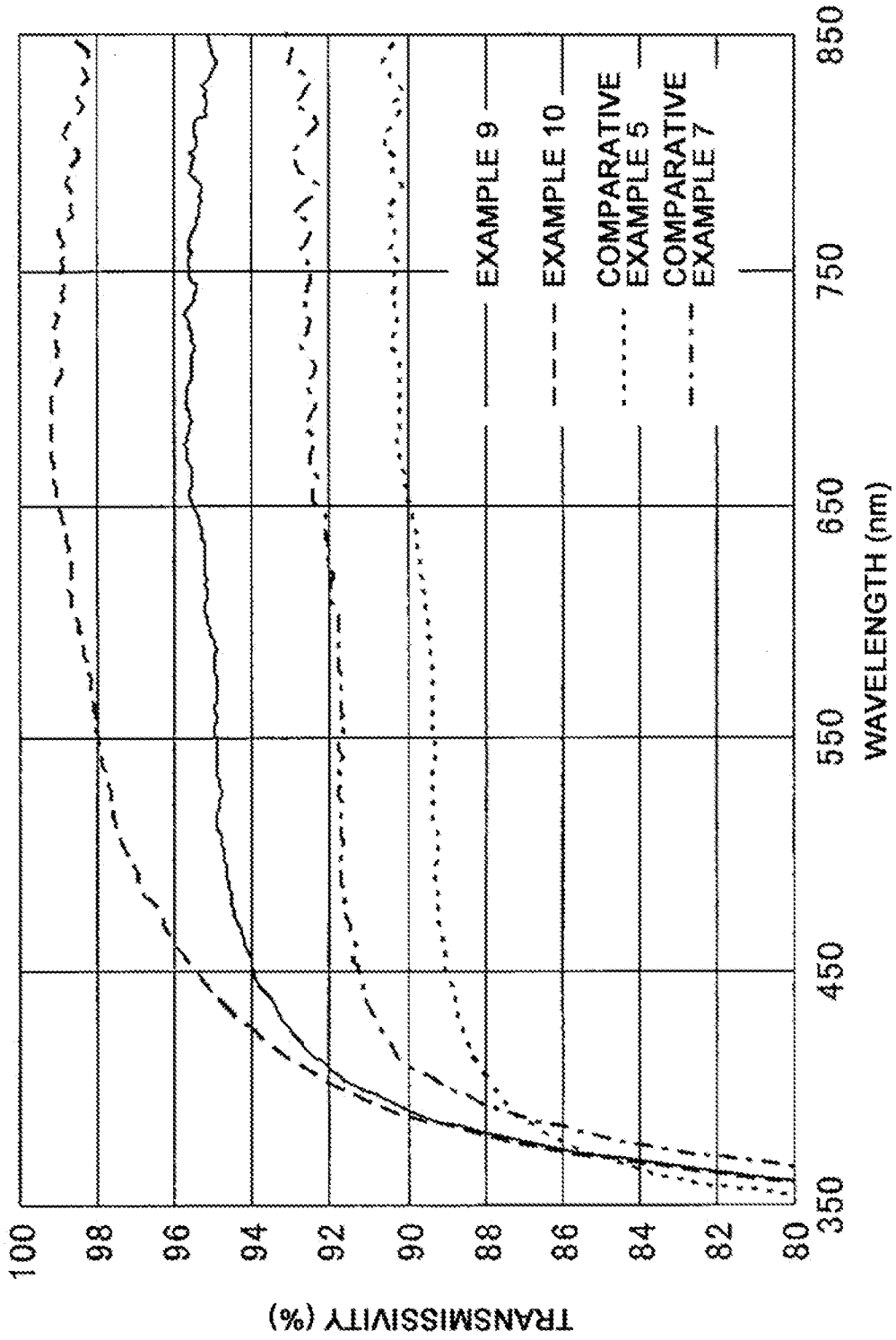


Fig. 12

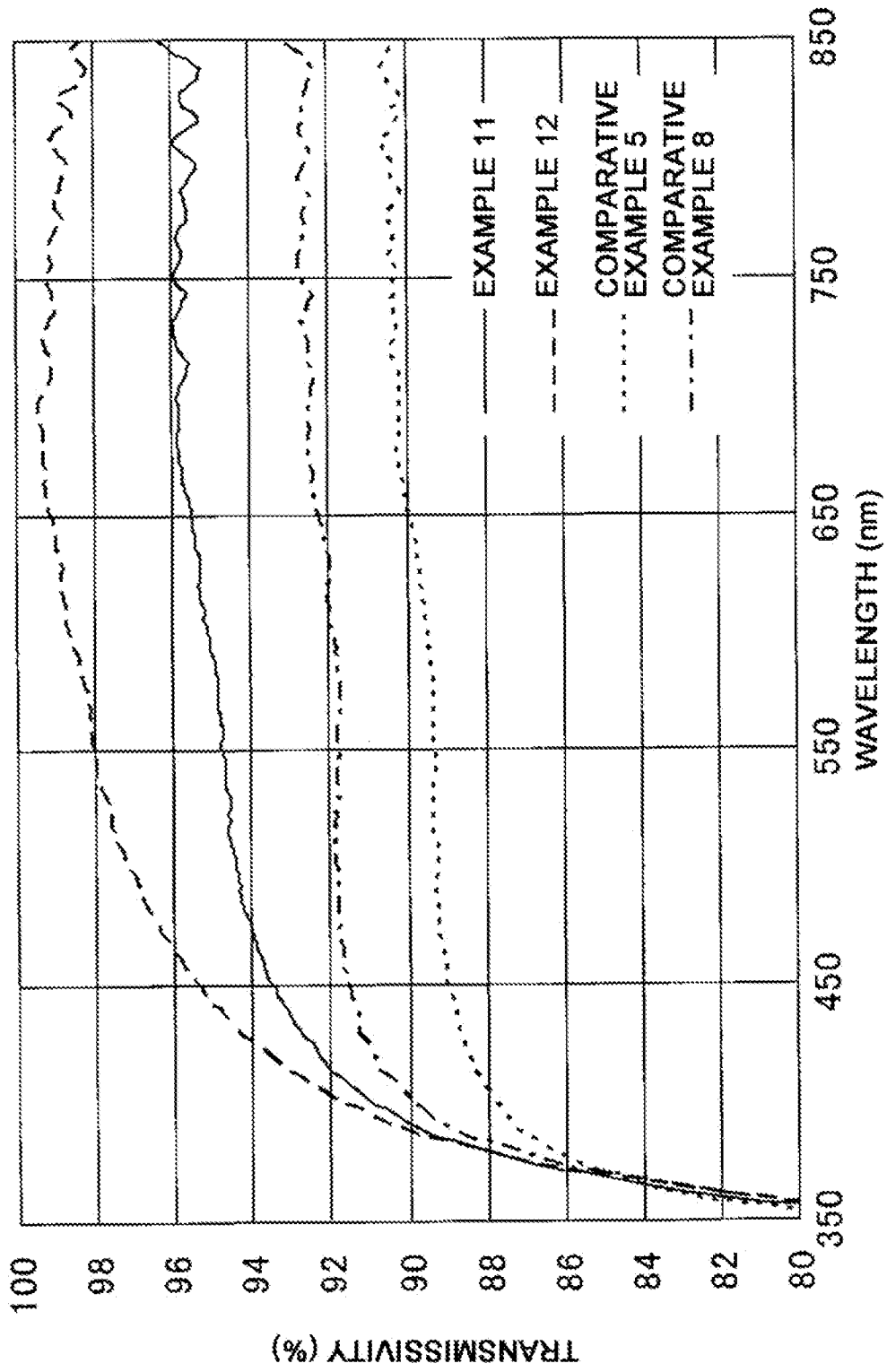


Fig. 13