

ANTI-SMUDGE HARD COAT AND ANTI-SMUDGE HARD COAT PRECURSORCross Reference To Related Application

This application claims priority to Japanese Patent Application JP 2012-170999, 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-smudge hard coat and an anti-smudge hard coat precursor.

Background

Hard coats are used to protect the surfaces of various hard materials and flexible materials. Hard coats are required to have excellent scratch resistance, impact resistance, and the like, as well as optical characteristics in the case of transparent materials. In addition, there is a strong demand for hard coat surfaces to be provided with anti-smudge properties.

Hard coat materials containing SiO₂ nanoparticles modified by a photo-curing silane coupling agent are described in U.S. Patent Nos. 5104929 and 7074463.

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.

The anti-smudge properties of a hard coat tend to deteriorate with the abrasion of the hard coat surface. Therefore, there is still a demand for further improvement in anti-smudge hard coat durability. Accordingly, an object of the present disclosure is to provide a hard coat and a hard coat precursor with excellent scratch resistance and durability of anti-smudge properties.

Summary

One embodiment of the present disclosure provides a hard coat including a nanoparticle mixture and a binder, 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; and the binder including a polyfunctional fluorinated (meth)acrylic compound, a reaction product thereof, or a combination thereof.

Another embodiment of the present disclosure provides a hard coat precursor including a nanoparticle mixture and a binder, the nanoparticles constituting from 40 to 95 mass% of a total mass of the nanoparticles and the binder; from 10 to 50 mass% of the nanoparticles having an average particle size within the range of 2 to 200 nm; from 50 to 90 mass% of the nanoparticles having 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 being within the range of 2:1 to 200:1; and the binder including a polyfunctional fluorinated (meth)acrylic compound.

The anti-smudge hard coat of the present disclosure filled with a high concentration of nanoparticles demonstrates both excellent scratch resistance and impact resistance while maintaining optical transparency. Additionally, since the binder contains a polyfunctional fluorinated (meth)acrylic compound, a reaction product thereof, or a combination thereof, it is possible to prevent the adhesion of fingerprints, grease, dust, smudges, and the like or to easily wash the hard coat in the event of such adhesion, and it is also possible to increase the durability of the anti-smudge properties. In addition, such an anti-smudge hard coat can be formed using the anti-smudge hard coat precursor of the present disclosure.

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 pattern diagram of an abrasion resistance test device used in the embodiments.

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".

The hard coat of one embodiment of the present disclosure contains a nanoparticle mixture and a binder, and the binder contains a polyfunctional fluorinated (meth)acrylic compound, a reaction product thereof, or a combination thereof.

Examples of representative binders contained in the 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 Kyoeisha 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 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. With the present disclosure, it is possible to form a hard coat with a relatively small amount of a binder.

The hard coat may be further cured with another curable monomer or 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, alkoxylated aliphatic diacrylate, alkoxylated cyclohexane dimethanol diacrylate, alkoxylated hexanediol diacrylate, alkoxylated neopentyl glycol diacrylate, caprolactone modified neopentyl glycol hydroxypivalate diacrylate, caprolactone modified neopentyl glycol hydroxypivalate diacrylate, cyclohexane dimethanol diacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, ethoxylated (10) bisphenol-A-diacrylate, ethoxylated (3) bisphenol-A-diacrylate, ethoxylated (30) bisphenol-A diacrylate, ethoxylated (4) bisphenol-A-diacrylate, hydroxypivalaldehyde modified trimethylol propane diacrylate, neopentyl glycol diacrylate, polyethylene glycol (200) diacrylate,

polyethylene glycol (400) diacrylate, polyethylene glycol (600) diacrylate, propoxylated 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, 5 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, 10 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. 15 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. 20 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 25 be used.

The nanoparticle mixture contained in the hard coat constitutes from approximately 40 to 95 mass% of the entire mass of the hard coat and, in several embodiments, constitutes from approximately 60 to 90 mass% or from approximately 70 to 85 mass% of the entire mass of the hard coat. The nanoparticle mixture contains from approximately 10 to 50 mass% of nanoparticles having an average 30 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 35 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 LaB₆ 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, SiO₂), 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, a hard coat having desired characteristics can be obtained by more accurately controlling the filling rate of nanoparticles in the 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 hard coat with a large amount of nanoparticles and thereby increase the hardness of the 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, a 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 hard coat is filled and to adjust the transparency and hardness of the resulting hard coat.

The thickness of the hard coat is typically within the range of approximately 80 nm to 30 μ m (in several embodiments, from approximately 200 nm to 20 μ m or from approximately 1 to 10 μ 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 a 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.

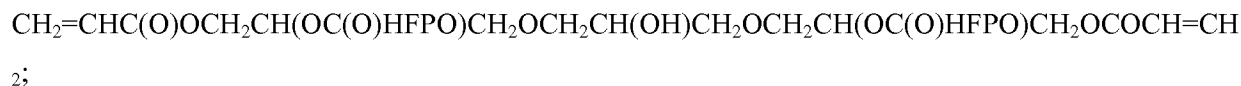
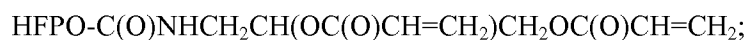
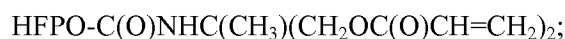
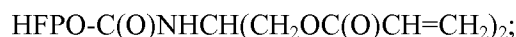
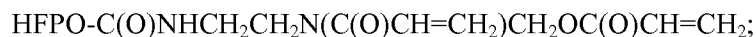
Representative examples of surface treating agents include compounds such as isooctyltrimethoxysilane, polyalkyleneoxide alkoxysilane (available from Momentive Specialty Chemicals, Inc. (Columbus, OH) under the product name "SILQUEST A1230", for example), N-(3-triethoxysilyl propyl) methoxyethoxy ethoxyethyl 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), β -carboxyethyl acrylate, 2-(2-methoxyethoxy)acetic acid, and methoxy phenyl acetic acid and mixtures thereof.

The binder of the anti-smudge hard coat of the present disclosure contains a polyfunctional fluorinated (meth)acrylic compound, a reaction product thereof, or a combination thereof, which provides the hard coat surface with anti-smudge properties and improves the ease of washing (for example, fingerprint prevention, oil resistance, dust prevention, and/or anti-smudge functions). 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, it may also be possible to increase scratch resistance by reducing the

coefficient of friction of the 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 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:



In the present disclosure, HFPO refers to a perfluoroether site expressed by $\text{F}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_n\text{CF}(\text{CF}_3)-$ (n is from 2 to 15) and a compound containing such a perfluoroether site.

The polyfunctional perfluoropolyether (meth)acrylate described above can be synthesized, for example, via a first step of reacting a poly(hexafluoropropylene oxide) ester such as HFPO-C(O)OCH_3 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 (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 $\text{HFPO-C(O)N(H)CH}_2\text{CH}_2\text{CH}_2\text{N(H)CH}_3$ and trimethylol propane triacrylate (TMPTA) and a poly(meth)acrylate.

A preferable polyfunctional fluorinated (meth)acrylic compound is one in which the

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 hard coat so as to improve the durability of the anti-smudge properties, and the perfluoroether site between (meth)acrylic groups migrates to the hard coat surface so as to 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 hard coat not only by the reaction 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: $-\text{CF}_2(\text{OCF}_2\text{CF}_2)_p(\text{OCF}_2)_q\text{OCF}_2-$ ($p/q=0.9$, $p+q \doteq 45$), and three acryloyloxy groups bond with each of these cyclic siloxanes via urethane groups, which is suited to the anti-smudge hard coat of the present disclosure.

When the polyfunctional fluorinated (meth)acrylic compound and reaction product thereof are considered a polyfunctional fluorinated (meth)acrylic compound accommodating the reaction product, the compound and reaction product are contained in the binder 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, for example.

The binder of the hard coat may further contain known additives such as an ultraviolet absorbent, a defogging agent, a leveling agent, an ultraviolet reflecting agent, an anti-static agent, or the like, or another chemical which provides a function of facilitating cleaning as necessary.

In some embodiments, the ultraviolet absorbent is contained in the binder of the hard coat. 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 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 hard coat containing the ultraviolet absorbent can achieve ultraviolet transmittance of less than 3%.

In some embodiments, a defogging agent is contained in the binder of the hard coat. 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 a hard coat contains the nanoparticle mixture described above, a binder containing a curable monomer and/or a curable oligomer and a polyfunctional fluorinated (meth)acrylic compound, a reaction initiator, and, if necessary a solvent such as methyl ethyl ketone (MEK), 1-methoxy-2-propanol (MP-OH), or the like, and the additives described above such as an ultraviolet absorbent, 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, and the binder contains a polyfunctional fluorinated (meth)acrylic compound.

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.

Examples of representative substrates to which the anti-smudge hard coat of the present disclosure is applied include films, plastics (polymer plates), sheet glass, and metal sheets. Films may be transparent or opaque. 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%, and "opaque" means that the total light transmission rate in the visible light range (380 to 780 nm) is less than 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. Plastics (polymer plates) may be transparent or opaque. 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. Metal sheets may be flexible or rigid. In the present disclosure, a "flexible metal sheet" refers to a metal sheet which does not undergo substantial irreversible changes and can receive mechanical stress such as bending or elongation, and a "rigid metal sheet" refers to a metal sheet which does not undergo substantial irreversible changes and cannot receive mechanical stress such as bending or elongation. A representative flexible metal sheet is one made from aluminum. Representative rigid metal sheets are sheets made from aluminum, nickel, nickel-chrome, and stainless steel.

A thickness of the film is within the range of approximately 5 to 500 μm (in several embodiments, from approximately 10 to 200 μm or from approximately 25 to 100 μm). 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 or metal sheet is within the range of approximately 5 to 500 μm 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 described above.

The hard coat can be applied to a plurality of surfaces of the substrate. In addition, a plurality of hard coat layers can be applied to 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 hard coat and the substrate. In particular, when the substrate contains a material with poor adhesiveness such as polypropylene, polyvinyl chloride, or the like, or when the substrate is a metal sheet, priming or a primer layer is particularly effective.

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.

5 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
10 copolymers, ethylene-vinyl acetate copolymers, chlorinated polyolefins such as chlorinated polyethylenes or chlorinated polypropylenes, and copolymers and derivatives thereof (for example, 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
15 film, it is advantageous for the primer to contain a chlorinated polypropylene or a modified chlorinated polypropylene.

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 μm (in
20 several embodiments, from approximately 0.5 to 5 μm).

The substrate may also have a printing layer, a coloring layer, a metal thin film layer, or the like with a desired pattern as necessary.

A product containing the hard coat of the present disclosure may also have an adhesive layer if necessary. The adhesive layer can be disposed on the surface of the substrate on the opposite side when
25 viewed from the hard coat, for example. 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. 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
30 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 μm (in several embodiments, from approximately 5 to 75 μm or from approximately 10 to 50 μm). The adhesive or the pressure-sensitive adhesive may also contain the ultraviolet absorbent described above.

35 The 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.

The anti-smudge hard coat of the present disclosure is useful, for example, in optical displays

(for example, cathode ray tube (CRT) and light-emitting diode (LED) displays), plastic cards, the lenses or main bodies of cameras, fans, doorknobs, faucet handles, mirrors, and household electronics such as vacuum cleaners, washing machines, and the like; personal digital assistants (PDAs), mobile telephones, liquid crystal display (LCD) panels, devices with touch sensor screens, detachable computer screens, or the like, and the main bodies of such devices, and the like. In addition, the anti-smudge hard coat of the present disclosure may also be useful, for example, in furniture, doors and windows, toilets and baths, interiors/exterior of vehicles, lenses (of cameras or glasses), or solar-powered panels (solar panels).

Various embodiments are provided that include a hard coat or a hard coat precursor.

Embodiment 1 is a hard coat comprising a nanoparticle mixture and a binder; 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; a particle size distribution of the nanoparticles being bimodal or multimodal; the binder comprising a polyfunctional fluorinated (meth)acrylic compound, a reaction product thereof, or a combination thereof; wherein the polyfunctional fluorinated (meth)acrylic compound comprises cyclic siloxane units.

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

Embodiment 3 is the hard coat of embodiment 1 or 2, wherein the polyfunctional fluorinated (meth)acrylic compound is a perfluoroether compound having two or more (meth)acrylic groups.

Embodiment 4 is the hard coat of any of the embodiments 1 to 3, wherein the polyfunctional fluorinated (meth)acrylic compound has 3 or more (meth)acrylic groups.

Embodiment 5 is the hard coat of any of the embodiments 1 to 4, wherein the nanoparticles are inorganic oxide nanoparticles, and the polyfunctional fluorinated (meth)acrylic compound comprises siloxane units.

Embodiment 6 is the hard coat of any of the embodiments 1 to 5, wherein the nanoparticles are silica nanoparticles.

Embodiment 7 is the hard coat of any of the embodiments 1 to 6, wherein the binder further comprises an ultraviolet absorbent.

Embodiment 8 is a hard coat precursor comprising a nanoparticle mixture and a binder; the nanoparticles constituting from 40 to 95 mass% of a total mass of the nanoparticles and the binder; 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; and the binder comprising a polyfunctional fluorinated (meth)acrylic compound; wherein the polyfunctional fluorinated (meth)acrylic compound comprises cyclic siloxane units.

EXAMPLES

5 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

10 The characteristics of the hard coat of the present disclosure were evaluated in accordance with the following methods. A hard coat was formed by applying a hard coat precursor to a substrate and irradiating the precursor with ultraviolet rays. The hard coat was evaluated while supported on the substrate.

15 1. Pencil Hardness

 The pencil hardness of the surface of the hard coat formed on the substrate was determined using a 750 g weight in accordance with JIS K5600-5-4 (1999).

20 2. Optical Characteristics

 The haze of the hard coat was measured using an NDH-5000W haze meter (acquired from Nippon Denshoku Industries Co., Ltd.) in accordance with JIS K 7136 (2000).

25 3. Contact Angle

 The water contact angle of the 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 "DROPMAS-TER FACE"). The volume of liquid droplets was set to 4 μ L for static measurements. The value of the water contact angle was calculated from the average of five measurements.

30 4. Ink Repellency Test

 The external appearance was observed visually after drawing a single straight line on the hard coat using a permanent marker (Maki (black), acquired from the Zebra Co., Ltd.). Samples which repelled ink and did not form a line were assessed as good, and samples which did not repel ink and formed a line were assessed as poor.

35 5. Abrasion Resistance Test

 The scratch resistance of the hard coat was evaluated by measuring the optical characteristics and the water contact angle after abrasion resistance testing. In a fabric abrasion resistance test, a JIS test fabric (acquired from the Japanese Industrial Standards Committee) with a width of 32 mm was used

under a load of 500 g, and in a steel wool abrasion resistance test, a 32 mm square piece of #0000 steel wool was used under a load of 1 kg. The hard coat surface was subjected to 200 cycles of abrasion at a speed of 60 cycles/minute of 85 mm strokes. FIG. 2 illustrates a schematic diagram of an abrasion resistance test device 60 (IMC-157C rubbing tester, acquired from Imoto Machinery Co., Ltd.). Here, a sample 10 is fixed to the top of a stage 61, and the load of a weight 63 is applied to the fabric or the steel wool 64 via a stylus 62 so as to rub the surface of the sample by moving the stage 61 back and forth. The abrasion resistance test simulates scratching that occurs with wiping and washing.

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 ₂ sol; average particle size 75 nm	Nalco Company, Naperville, Illinois
NALCO 2327	SiO ₂ sol; average particle size 20 nm	Nalco Company, Naperville, Illinois
1-methoxy -2-propynol		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.
IRGACURE 2959	1-[4-(2-Hydroxyethoxy)-phenyl]2-hydroxy-2-methyl-1-propane-1-on	BASF AG
BYK-UV3500	Acrylate containing polyether-modified silicone	BYK-Chemie GmbH
HFPO Urethane Acrylate	Perfluoropolyether urethane acrylate 30 mass% solution, 4-4205-6329-2	3M Company
KY-1203	Fluorinated acrylic compound having siloxane units; 20 mass%	Shin-Etsu Chemical Co., Ltd.

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.

10 Two-hundred g of 1-methoxy-2-propanol was added to the resulting solution, and the remaining water 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 SiO₂ nanoparticles was adjusted to 45 mass% by adding 1-methoxy-2-propanol, and an SiO₂ sol (hereafter called "sol 1") containing surface-modified SiO₂ nanoparticles having an average particle size of 75 nm was obtained.

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
5 SILQUEST A174, and 0.5 g of PROSTAB, and an SiO₂ sol (hereafter called "sol 2") containing 45 mass% of surface-modified SiO₂ nanoparticles having an average particle size of 20 nm was obtained.

Preparation of Hard Coat Precursor (HC-1)

First, 11.34 g of sol 1, 5.88 g of sol 2, 2.25 g of EBECRYL 4858, and 0.25 g of SR340 were
10 mixed. Next, 0.20 of IRGACURE 2959 was added to the mixture as an optical polymerization initiator, and 0.001 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.

15 Preparation of Hard Coat Precursor (HC-2)

First, 11.34 g of sol 1, 5.88 g of sol 2, 2.25 g of EBECRYL 4858, and 0.25 g of SR340 were mixed. Next, 0.17 g of HFPO urethane acrylate was added to the mixture as an anti-smudge agent, 0.1
20 g of IRGACURE 2959 was added to the mixture as an optical polymerization initiator, and 0.001 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-2 was thus prepared. HFPO urethane acrylate is a monofunctional fluorinated (meth)acrylic compound.

Preparation of Hard Coat Precursors (HC-3 to HC-8)

Hard coat precursors HC-3 to HC-8 were prepared in the same manner as HC-2 with the
25 formulas described in Table 2. KAYARAD UX-5000 was used as an acrylate oligomer in HC-6 to HC-8, and KY-1203 was used as a polyfunctional (meth)acrylic compound (anti-smudge agent) in HC-4, HC-5, and HC-8. The compositions of HC-1 to HC-8 are shown in Table 2.

Table 2

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

Component		HC - 1	HC - 2	HC - 3	HC - 4	HC - 5	HC - 6	HC - 7	HC - 8
Surface-modified silica nanoparticles	Sol 1 (Average particle size: 75 nm)	11.34	11.34	11.34	11.34	11.34	11.34	11.34	11.34
	Sol 2 (Average particle size: 20 nm)	5.88	5.88	5.88	5.88	5.88	5.88	5.88	5.88
Acrylic oligomer/monomer	EBECRYL 4858	2.25	2.25	2.25	2.25	2.25	0.00	0.00	0.00
	KAYARAD UX – 5000	0.00	0.00	0.00	0.00	0.00	2.25	2.25	2.25
	SR340	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Photoinitiator	IRGACURE 2959	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Anti-smudge agent	HFPO urethane acrylate	0.00	0.03	0.17	0.00	0.00	0.00	0.03	0.00
	KY-1203	0.00	0.00	0.00	0.05	0.25	0.00	0.00	0.25
Leveling agent	BYK-UV3500	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Diluent	1-methoxy-2-propanol	0.28	0.25	0.16	0.24	0.17	0.28	0.26	0.17
	Solid content (%)	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0

Example 1

A PMMA substrate (Acrylite L-001, 100 x 53 x 2 mm, acquired from Mitsubishi Rayon Co., Ltd.) was fixed to the top of a stainless steel table equipped with a level. Hard coat precursor HC-4 was applied to the PMMA substrate using a #16 Meyer rod and dried for 5 minutes at 60°C. Next, the coating surface was irradiated with ultraviolet rays ten times (irradiance: approximately 1400 mJ/²) at a line rate of 13 m/minute, in a nitrogen atmosphere, using an H-valve (DRS model) made by Fusion UV System Inc. The thickness of the hard coat was approximately 10 μm. In this manner, the hard coat of Example 1 was formed on the PMMA substrate.

Examples 2 and 3 and Comparative Examples 1 to 5

Hard coats were formed on PMMA substrates in the same manner as in Example 1 using hard coat precursors HC-1 to HC-3 and HC-5 to HC-8. The results of evaluating these hard coats are shown in Tables 3 and 4.

Table 3
Fabric Abrasion Resistance Tests

Example	Hard Coat	Anti-smudge agent	Pencil hardness	Original		After fabric abrasion resistance test	
				Water contact angle (degrees)	Ink repellency	Water contact angle (degrees)	Ink repellency
Example 1	HC - 4	KY - 1203	8H	101.5	Favorable	89.7	Favorable
Example 2	HC - 5	KY - 1203	8H	106.0	Favorable	100.0	Favorable
Comparative Example 1	HC - 1	none	8H	73.3	Unfavorable	68.6	Unfavorable
Comparative Example 2	HC - 2	HFPO	8H	108.8	Favorable	103.7	Favorable
Comparative Example 3	HC - 3	HFPO	8H	113.5	Favorable	70.1	Unfavorable

Table 4

Fabric Abrasion Resistance Tests and Steel Wool Abrasion Resistance Tests

Example	Hard Coat	Anti-smudge agent	Pencil hardness	Original			After fabric abrasion resistance test		Fabric abrasion resistance tests and steel wool abrasion resistance tests			
				Haze (%)	Water contact angle (degrees)	Ink repellency	Water contact angle (degrees)	Ink repellency	Haze (%)	Δ Haze (%)	Water contact angle (degrees)	Ink repellency
Example 3	HC - 8	KY - 1203	8H	0.34	107.9	Favorable	104.7	Favorable	0.36	0.02	93.9	Favorable
Comparative Example 4	HC - 6	none	8H	0.30	81.5	Unfavorable	80.1	Unfavorable	0.41	0.11	78.2	Unfavorable
Comparative Example 5	HC - 7	HFPO	8H	0.42	111.0	Favorable	106.3	Favorable	0.50	0.08	51.5	Unfavorable

As shown in Table 3, the hard coats containing fluorinated (meth)acrylic compounds as anti-smudge agents (Examples 1 and 2: KY-1203, Comparative Examples 2 and 3: HFPO urethane acrylate) demonstrated a pencil hardness of 8 H equivalent to that of a hard coat not containing a fluorinated (meth)acrylic compound (Comparative Example 1). The addition of an appropriate amount of a fluorinated (meth)acrylic compound did not affect the pencil hardness of the hard coat. The water contact angle increased when a fluorinated (meth)acrylic compound was added. HC-4 (Example 1) and HC-5 (Example 2) demonstrated favorable ink repellency even after fabric abrasion resistance tests. On the other hand, the ink repellency became poor after fabric abrasion resistance tests on HC-3 (Comparative Example 3), in which the amount of HFPO urethane acrylate used as an anti-smudge agent was increased.

Table 4 shows the results of performing steel wool abrasion resistance tests in addition to fabric abrasion resistance tests. The water contact angle and the ink repellency were compared before and after the fabric abrasion resistance tests, and the water contact angle, the ink repellency, and the optical characteristics were compared before and after the steel wool abrasion resistance tests. HC-7 (Comparative Example 5) and HC-8 (Example 3) demonstrated water contact angles exceeding 100 degrees as well as favorable ink repellency both at the beginning and after fabric abrasion resistance tests. The hard coat of Example 2 containing UX-5000, a polyfunctional acrylate having a plurality of acrylate groups, as a urethane acrylate oligomer had higher scratch resistance than the hard coat of Example 3 containing EBECRYL 4858.

The steel wool abrasion resistance improved as a result of the addition of a fluorinated (meth)acrylic compound. The changes in the haze values (Δ haze) of HC-7 (Comparative Example 5) and HC-8 (Example 3) after steel wool abrasion resistance tests were less than 0.1%. The coefficient of friction of the hard coat surface decreased and the steel wool abrasion resistance of the hard coat improved due to the fluorinated (meth)acrylic compound. In particular, HC-8 (Example 8 containing KY-1203) had excellent scratch resistance and demonstrated high durability with regard to anti-smudge properties. The ink repellency of HC-8 did not change even after steel wool abrasion resistance tests. The hard coats containing polyfunctional fluorinated (meth)acrylic compounds having siloxane units demonstrated higher anti-smudge durability than those containing monofunctional fluorinated (meth)acrylic compounds.

Parts list:

- 60 Abrasion resistance test device
- 61 Stage
- 62 stylus
- 63 Weight
- 64 Fabric or steel wool

What is Claimed is:

1. A hard coat comprising a nanoparticle mixture and a binder;
the nanoparticles constituting from 40 to 95 mass% of an entire mass of the hard coat;
5 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
10 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;
a particle size distribution of the nanoparticles being bimodal or multimodal;
the binder comprising a polyfunctional fluorinated (meth)acrylic compound, a reaction product
15 thereof, or a combination thereof; wherein the polyfunctional fluorinated (meth)acrylic compound comprises cyclic siloxane units.
2. The hard coat according to claim 1, wherein the nanoparticles are surface-modified nanoparticles.
20
3. The hard coat according to claim 1 or 2, wherein the polyfunctional fluorinated (meth)acrylic compound is a perfluoroether compound having two or more (meth)acrylic groups.
4. The hard coat according to one of claims 1 to 3, wherein the polyfunctional fluorinated
25 (meth)acrylic compound has 3 or more (meth)acrylic groups.
5. The hard coat according to one of claims 1 to 4, wherein the nanoparticles are inorganic oxide nanoparticles, and the polyfunctional fluorinated (meth)acrylic compound comprises siloxane units.
- 30 6. The hard coat according to claim 5, wherein the nanoparticles are silica nanoparticles.
7. The hard coat according to one of claims 1 to 6, wherein the binder further comprises an ultraviolet absorbent.
- 35 8. A hard coat precursor comprising a nanoparticle mixture and a binder;
the nanoparticles constituting from 40 to 95 mass% of a total mass of the nanoparticles and the binder;
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; and

the binder comprising a polyfunctional fluorinated (meth)acrylic compound; wherein the polyfunctional fluorinated (meth)acrylic compound comprises cyclic siloxane units.