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(54) **Title:** BILAYER ANTI-REFLECTIVE FILMS CONTAINING NANOPARTICLES IN BOTH LAYERS

(57) **Abstract:** The present invention relates to nanoparticles-containing stratified compositions for low refractive index compositions of utility as anti-reflective coatings for optical display substrates. The compositions comprise a high index refractive stratum and a low refractive index stratum on top of the high index stratum, and containing different nanoparticles in each stratum.

TITLE

Bilayer Anti-Reflective Films Containing Nanoparticles in Both Layers

FIELD OF INVENTION

5   The present invention relates to nanoparticles-containing stratified compositions for low refractive index compositions of utility as anti-reflective coatings for optical display substrates. The compositions comprise a high index refractive stratum containing nanoparticles and a low refractive index stratum containing nanoparticles on top of the high

10   index stratum.

BACKGROUND

Anti-reflective coatings are typically located on the outermost surface of optical displays, such as cathode ray tube displays (CRTs),

15   plasma display panels (PDPs), electroluminescence displays (ELDs), and liquid crystal displays (LCDs), to prevent contrast reduction or reduction of visibility due to reflection of ambient light by making use of optical interference. Refractive index of a material can be reduced by inclusion of fluorine and by decreasing the material density (e.g., voids), but both

20   approaches are accompanied by reductions in film strength (i.e., abrasion resistance). The inclusion of nanoparticles has also been used.

Another method that has been used to overcome these difficulties is to apply two or more antireflection coatings on a substrate, optionally containing nanoparticles, in which the combination of the two layers

25   together create an anti-reflective layer.   However, a two step process is complicated and cost-prohibitive for commercial use.

Thus, it is desirable in the industry to have an anti-reflective film with low reflectivity which can be applied with a low cost, single step coating process.

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SUMMARY

Briefly stated, and in accordance with one aspect of the present invention, there is provided article comprising:

(i) a substrate; and

5   (ii) a stratified anti-reflective coating on said substrate, said stratified anti-reflective coating comprising:

(iia) a high refractive index lower stratum located on said substrate comprising a low refractive index fluoropolymer binder and a plurality of high refractive index nanoparticles; and

10   (iib) a low refractive index upper stratum located on top of said high refractive index lower stratum comprising said low refractive index fluoropolymer binder and a plurality of low refractive index nanoparticles;

wherein the refractive index of the low refractive index upper

15   stratum is lower than the refractive index of the high refractive index lower stratum.

The high refractive index stratum that can have a refractive index of 1.41 or greater.

Pursuant to another aspect of the present invention, there is

20   provided process comprising:

(i)   forming a liquid mixture comprising a solvent having dissolved therein:

(i-a)   a fluoropolymer binder;

(i-b)   optionally, a multiolefinic crosslinker;

25   (i-c)   optionally, an oxysilane having at least one polymerizable functional group;

and wherein said solvent has suspended therein:

(i-d)   a plurality of high refractive index nanoparticles; and

(i-e)   a plurality of low refractive index nanoparticles;

30   (ii) coating said liquid mixture on a substrate to form a liquid mixture coating on said substrate;

(iii) removing solvent from said liquid mixture coating to form an uncured coating on said substrate; and

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(iv) curing said uncured coating thereby forming a stratified anti-reflective coating comprising:

        (iv-a) a high refractive index lower stratum located on said substrate comprising said fluoropolymer binder being cured and

5   said plurality of high refractive index nanoparticles; and

        (iv-b) a low refractive index upper stratum located on top of said high refractive index lower stratum comprising fluoropolymer binder being cured and said plurality of low refractive index nanoparticles;

10   wherein the refractive index of the low refractive index upper stratum is lower than the refractive index of the high refractive index lower stratum.

The coating can be formed on the substrate in a single coating

15   step.

DETAILED DESCRIPTION

The present invention discloses an article comprising a substrate having a stratified anti-reflective coating comprising:

20   (i) a substrate; and

(ii) a stratified anti-reflective coating on said substrate, said stratified anti-reflective coating comprising:

        (iia) a high refractive index stratum located on said substrate comprising a low refractive index fluoropolymer binder and a plurality of

25   high refractive index nanoparticles; and

        (iib) a low refractive index stratum located on top of said high refractive index stratum comprising said low refractive index fluoropolymer binder and a plurality of low refractive index nanoparticles.

For purposes of this application the term stratum means layer.

30   The appropriate choice of particles, binders, and thicknesses needed to achieve desirable anti-reflective properties can be determined using modeling equations, described in more detail *infra*.

Fluoropolymers suitable for use in forming the low refractive composition is described here in detail. For purposes of this application, fluoropolymers are obtained from fluorine-containing vinyl monomers including fluoroolefins (e.g., fluoroethylene, vinylidene fluoride,

5   tetrafluoroethylene, and hexafluoropropylene), partially or completely fluorinated alkyl ester derivatives of (meth)acrylic acid, and partially or completely fluorinated vinyl ethers. Hexafluoropropylene is a particularly preferred monomer from the standpoint of availability as well as the refractive index, solubility and transparency of the resultant

10   fluoropolymers. As the copolymerization ratio of the fluorine-containing vinyl monomer increases, the refractive index becomes smaller, and the polymer film strength can decrease. From this viewpoint, the fluorine-containing vinyl monomer is generally used to give a fluorine content of about 20% to about 70% by weight, preferably 30% to 50% by weight, in

15   the resulting cross-linkable polymer.

Fluoropolymers can contain a repeating unit having a (meth)acryloyl group in the side chain thereof. As the ratio of the (meth)acryloyl group-containing repeating unit increases, the film strength increases, but the refractive index also increases. An amount of the

20   (meth)acryloyl group-containing repeating unit of utility in the cross-linkable polymer is generally from about 5% to about 90% by weight, while varying depending on the fluorine-containing vinyl monomer combined therewith.

In addition to the fluorine-containing vinyl monomer unit and the

25   (meth)acryloyl group-containing unit, the cross-linkable polymer can contain one or more kinds of repeating units derived from other vinyl monomers for improving adhesion to a substrate, adjusting the glass transition temperature (Tg) that contributes to the film strength, and improving the solubility in a solvent, transparency, slip properties, antidust

30   and antifouling properties, and the like. The ratio of the other vinyl monomer units in the copolymer is generally from 0 to about 65 mol %.

Examples of useful other vinyl monomers include olefins (e.g., ethylene, propylene, isoprene, vinyl chloride, and vinylidene chloride), acrylic esters (e.g., methyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate,

and 2-hydroxyethyl acrylate), methacrylic esters (e.g., methyl methacrylate, ethyl methacrylate, butyl methacrylate, and 2-hydroxyethyl methacrylate), styrene derivatives (e.g., styrene, p-hydroxymethylstyrene, and p-methoxystyrene), vinyl ethers (e.g., methyl vinyl ether, ethyl vinyl

5   ether, cyclohexyl vinyl ether, hydroxyethyl vinyl ether, and hydroxybutyl vinyl ether), vinyl esters (e.g., vinyl acetate, vinyl propionate, and vinyl cinnamate), unsaturated carboxylic acids (eg., acrylic acid, methacrylic acid, crotonic acid, maleic acid, and itaconic acid), acrylamides (e.g., N,N-di methyl acrylamide, N-t-butylacrylamide, and N-cyclohexylacryl amide),

10   methacrylamides (e.g., N,N-dimethylmethacrylamide), and acrylonitrile.

       In one embodiment, the fluoropolymer is fluoroelastomer having at least one cure site selected from the group consisting of bromine, iodine and ethenyl. Fluoroelastomers suitable for use in forming the low refractive composition is described here in more detail. For purposes of

15   this application, a fluoroelastomer is a carbon-based polymer that contains at least about 65 weight% fluorine, preferably at least about 70 weight% fluorine, and is a substantially amorphous copolymer characterized by having carbon-carbon bonds in the copolymer backbone. Fluoroelastomer comprises repeating units arising from two or more types of monomers

20   and has cure sites allowing for crosslinking to form a three dimensional network. A first monomer type gives rise to straight fluoroelastomer chain segments with a tendency to crystallize. A second monomer type having a bulky group is incorporated into the fluoroelastomer chain at intervals to break up such crystallization tendency and produce a substantially

25   amorphous elastomer. Monomers of utility for straight chain segments are those without bulky substituents and include: vinylidene fluoride (VDF), $CH_2=CF_2$; tetrafluoroethylene (TFE), $CF_2=CF_2$; chlorotrifluoroethylene (CTFE), $CF_2=CFCl$; and ethylene (E), $CH_2=CH_2$. Monomers with bulky groups useful for disrupting crystallinity include hexafluoropropylene

30   (HFP), $CF_2=CFCF_3$; 1-hydropentafluoropropylene, $CHF=CFCF_3$; 2-hydropentafluoropropylene, $CF_2=CHCF3$; perfluoro(alkyl vinyl ether)s (e.g., perfluoro(methyl vinyl) ether (PMVE), $CF2=CFOCF_3$); and propylene (P), $CH_2=CHCH_3$. Fluoroelastomers are generally described by A. Moore

in Fluoroelastomers Handbook: The Definitive User's Guide and Databook, William Andrew Publishing, ISBN 0-8155-1517-0 (2006).

Fluoroelastomers according to the present invention can have at least one cure site selected from the group consisting of bromine, iodine 5 (halogen) and ethenyl. The cure sites can be located on, or on groups attached to, the fluoroelastomer backbone and in this instance arise from including cure site monomers in the polymerization to make the fluoroelastomer. Halogenated cure sites can also be located at fluoroelastomer chain ends and arise from the use of halogenated chain 10 transfer agents added in the polymerization to make the fluoroelastomer. The fluoroelastomer containing cure sites is subjected to reactive conditions, also referred to as curing (e.g., thermal or photochemical curing), that results in the formation of covalent bonds (i.e., crosslinks) between the fluoroelastomer and other reactive components in the 15 uncured composition. Cure site monomers leading to the formation of cure sites located on, or on groups attached to, the fluoroelastomer backbone generally include brominated alkenes and brominated unsaturated ethers (resulting in a bromine cure site), iodinated alkenes and iodinated unsaturated ethers (resulting in an iodine cure site), and 20 dienes containing at least one ethenyl functional group that it is not in conjugation with other carbon-carbon unsaturation (resulting in an ethenyl cure site). Additionally, or alternatively, iodine atoms, bromine atoms or mixtures thereof can be present at the fluoroelastomer chain ends as a result of the use of chain transfer agent during polymerization to make the 25 fluoroelastomer. Fluoroelastomers of utility generally contain from about 0.25 weight% to about 1 weight% of cure site, preferably about 0.35 weight% of cure site, based on the weight of monomers comprising the fluoroelastomer.

Fluoroelastomers containing bromine cure sites can be obtained by 30 copolymerizing brominated cure site monomers into the fluoroelastomer during polymerization to form the fluoroelastomer. Brominated cure site monomers have carbon-carbon unsaturation with bromine attached to the double bond or elsewhere in the molecule and can contain other elements including H, F and O. Examples of brominated cure site monomers

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include bromotrifluoroethylene, vinyl bromide, 1- bromo-2,2-difluoroethylene, perfluoroallyl bromide, 4-bromo-1,1,2-trifluorobutene, 4-bromo-3,3,4,4-tetrafluoro-1-butene, 4-bromo-1,1,3,3,4,4,-hexafluorobutene, 4-bromo-3-chloro-1,1,3,4,4-pentafluorobutene, 6-bromo-5,5,6,6-tetrafluorohexene, 4-bromoperfluoro-1-butene, and 3,3-difluoroallyl bromide. Further examples include brominated unsaturated ethers such as 2-bromo-perfluoroethyl perfluorovinyl ether and fluorinated compounds of the class $BrCF_2$(perfluoroalkylene)$OCF=CF_2$, such as $CF_2BrCF_2OCF=CF_2$, and fluorovinyl ethers of the class $ROCF=CFBr$ and $ROCBr=CF_2$, where R is a lower alkyl group or fluoroalkyl group, such as $CH_3OCF=CFBr$ and $CF3CH_2OCF=CFBr$.

Fluoroelastomers containing iodine cure sites can be obtained by copolymerizing iodinated cure site monomers into the fluoroelastomer during polymerization to form the fluoroelastomer. Iodinated cure site monomers have carbon-carbon unsaturation with iodine attached to the double bond or elsewhere in the molecule and can contain other elements including H, Br, F and O. Example iodinated cure site monomers include iodoethylene, iodotrifluoroethylene, 4-iodo-3,3,4,4-tetrafluoro-1-butene, 3-chloro-4-iodo-3,4,4-trifluorobutene, 2-iodo-1,1,2,2-tetrafluoro-1-(vinyloxy)ethane, 2-iodo-1-(perfluorovinyloxy)-1,1,2,2-tetrafluoroethylene, 1,1,2,3,3,3-hexafluoro-2- iodo-1-(perfluorovinyloxy)propane, 2-iodoethyl vinyl ether, and 3,3,4,5,5,5-hexafluoro-4-iodopentene. Further examples include olefins of the formula $CHR=CHZCH_2CHRI$, wherein each R is independently H or CH_3, and Z is a C1-C18 (per)fluoroalkylene radical, linear or branched, optionally containing one or more ether oxygen atoms, or a (per)fluoropolyoxyalkylene radical. Further examples of iodinated cure site monomers of utility are unsaturated ethers of the formula $I(CH_2CF_2CF_2)nOCF=CF_2$ and $ICH_2CF_2O[CF(CF_3)CF_2O]_nCF=CF_2$, wherein n=1-3.

Fluoroelastomers containing ethenyl cure sites can be obtained by copolymerizing ethenyl containing cure site monomers into the fluoroelastomer during polymerization to form the fluoroelastomer. Ethenyl cure site monomers have carbon-carbon unsaturation with ethenyl functionality that it is not in conjugation with other carbon-carbon

unsaturation. Thus, ethenyl cure sites can arise from non-conjugated dienes having at least two points of carbon-carbon unsaturation and optionally containing other elements including H, Br, F and O. One point of carbon-carbon unsaturation is incorporated (i.e., polymerizes) into the
5   fluoroelastomer backbone, the other is pendant to the fluoroelastomer backbone and is available for reactive curing (i.e., cross linking). Example ethenyl cure site monomers include non-conjugated dienes and trienes such as 1,4-pentadiene, 1,5-hexadiene, 1,7-octadiene, 8-methyl-4-ethylidene-1,7-octadiene and the like.
10   Preferred amongst the cure site monomers are bromotrifluoroethylene, 4-bromo-3,3,4,4-tetrafluoro-1-butene and 4-iodo-3,3,4,4-tetrafluoro-1-butene-1.

        In addition, or alternatively, to the aforementioned cure sites, halogen cure sites can be present at fluoroelastomer chain ends as the
15   result of the use of bromine and/or iodine (halogenated) chain transfer agents during polymerization of the fluoroelastomer. Such chain transfer agents include halogenated compounds that result in bound halogen at one or both ends of the polymer chains. Example chain transfer agents of utility include methylene iodide, 1,4-diiodoperfluoro-n-butane, 1,6-diiodo-
20   3,3,4,4-tetrafluorohexane, 1,3-diiodoperfluoropropane, 1,6-diiodoperfluoro-n-hexane, 1,3-diiodo-2-chloroperfluoropropane, 1,2-di(iododifluoromethyl)perfluorocyclobutane, monoiodoperfluoroethane, monoiodoperfluorobutane, 2-iodo-1-hydroperfluoroethane, 1-bromo-2-iodoperfluoroethane, 1-bromo-3-iodoperfluoropropane, and 1-iodo-2-
25   bromo-1,1-difluoroethane. Preferred are chain transfer agents containing both iodine and bromine.

        Fluoroelastomers containing cure sites can be prepared by polymerization of the appropriate monomer mixtures with the aid of a free radical initiator either in bulk, in solution in an inert solvent, in aqueous
30   emulsion or in aqueous suspension. The polymerizations may be carried out in continuous, batch, or in semi-batch processes. General polymerization processes of utility are discussed in the aforementioned Moore Fluoroelastomers Handbook. General fluoroelastomer preparative

processes are disclosed in U.S. Patent Numbers: 4,281,092; 3,682,872; 4,035,565; 5,824,755; 5,789,509; 3,051,677; and 2,968,649

Example fluoroelastomers containing cure sites include: copolymers of cure site monomer, vinylidene fluoride, hexafluoropropylene

5   and, optionally, tetrafluoroethylene; copolymers of cure site monomer, vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene and chlorotrifluoroethylene; copolymers of cure site monomer, vinylidene fluoride, perfluoro(alkyl vinyl ether) and, optionally, tetrafluoroethylene; copolymers of cure site monomer, tetrafluoroethylene, propylene and,

10   optionally, vinylidene fluoride; and copolymers of cure site monomer, tetrafluoroethylene and perfluoro(alkyl vinyl ether), preferably perfluoro(methyl vinyl ether). Fluoroelastomers containing vinylidene fluoride are preferred.

Fluoroelastomers comprising ethylene, tetrafluoroethylene,

15   perfluoro(alkyl vinyl ether) and a bromine-containing cure site monomer, such as those disclosed by Moore, in U.S. Patent No. 4,694,045, are of utility in the compositions of the present invention. Also of utility are copolymers of hexafluoropropylene, vinylidene fluoride, tetrafluoroethylene, and halogen cure site monomer such as the VITON®

20   GF-series fluoroelastomers, for example VITON® GF-200S, available from DuPont Performance Elastomers, DE, USA.

Another optional component of the uncured composition is at least one multiolefinic crosslinker. The term "multiolefinic" means herein that it contains at least two carbon-carbon double bonds that are not in

25   conjugation with one another. Multiolefinic crosslinker is present in the uncured composition in an amount of from about 1 to about 25 parts by weight per 100 parts by weight cross-linkable polymer (phr, parts per hundred), preferably from about 1 to about 10 phr. Multiolefinic crosslinkers of utility include those containing acrylic (e.g., acryloyloxy,

30   methacryloyloxy) and allylic functional groups.

A preferred multiolefinic crosslinker is non-fluorinated multiolefinic crosslinker. Herein, the term "non-fluorinated" means that it contains no covalently bonded fluorine atoms.

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Acrylic multiolefinic crosslinkers include those represented by the formula $R(OC(=O)CR'=CH_2)n$, wherein: R is linear or branched alkylene, linear or branched oxyalkylene, aromatic, aromatic ether, or heterocyclic; R' is H or CH_3; and n is an integer from 2 to 8. Representative polyols

5   from which acrylic multiolefinic crosslinkers can be prepared include: ethylene glycol, propylene glycol, triethylene glycol, trimethylolpropane, tris-(2-hydroxyethyl) isocyanurate, pentaerythritol, ditrimethylolpropane and dipentaerythritol . Representative acrylic multiolefinic crosslinkers include 1,3-butylene glycol di(meth)acrylate, 1,6-hexanediol

10 di(meth)acrylate, neopentyl glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, ethoxylated bisphenol A di(meth)acrylate, propoxylated bisphenol A di(meth)acrylate, alkoxylated cyclohexane dimethanol di(meth)acrylate, cyclohexane dimethanol di(meth)acrylate, trimethylolpropane tri(meth)acrylate,

15 ethoxylated trimethylolpropane tri(meth)acrylate, propoxylated trimethylolpropane tri(meth)acrylate, bistrimethylolpropane tetra(meth)acrylate, tris(2-hydroxy ethyl)isocyanurate tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, ethoxylated glycerol tri(meth)acrylate, propoxylated glycerol

20 tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, propoxylated pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, and combinations thereof. Herein, the designation "(meth)acrylate" is meant to encompass both acrylate and methacrylate.

25   Allylic multiolefinic crosslinkers include those represented by the formula $R(CH_2CR'=CH_2)n$, wherein R is linear or branched alkylene, linear or branched oxyalkylene, aromatic, aromatic ether, aromatic ester or heterocyclic; R' is H or CH_3; and n is an integer from 2 to 6. Representative allylic multiolefinic crosslinkers include 1,3,5-triallyl

30 isocyanurate, 1,3,5-triallyl cyanurate, and triallyl benzene-1,3,5-tricarboxylate.

          Another optional component of the uncured composition is at least one oxysilane. Oxysilanes of utility in forming the low refractive index composition according to the present invention are compounds

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comprising: i) an acryloyloxy or methacryloyloxy functional group, ii) an oxysilane functional group, and iii) a divalent organic radical connecting the acryloyloxy or methacryloyloxy functional group and the oxysilane functional group. Oxysilane includes those represented by the formula

5   $X-Y-SiR^1R^2R^3$. X represents an acryloyloxy ($CH_2=CHC(=O)O-$) or methacryloyloxy ($CH_2=C(CH_3)C(=O)O-$) functional group. Y represents a divalent organic radical covalently bonded to the acryloyloxy or methacryloyloxy functional group and the oxysilane functional group. Examples of Y radicals include substituted and unsubstituted alkylene

10 groups having 2 to 10 carbon atoms, and substituted or unsubstituted arylene groups having 6 to 20 carbon atoms. The alkylene and arylene groups optionally additionally have ether, ester, and amide linkages therein. Substituents include halogen, mercapto, carboxyl, alkyl and aryl. $SiR^1R^2R^3$ represents an oxysilane functional group containing three

15 substituents (R^{1-3}), one to all of which are capable of being displaced by (e.g., nucleophilic) substitution. For example, at least one of the R^{1-3} substituents are groups such as alkoxy, aryloxy or halogen and the substituting group comprises a group such as hydroxyl present on an oxysilane hydrolysis or condensation product, or equivalent reactive

20 functional group present on the substrate film surface. Representative $SiR^1R^2R^3$ oxysilane substitution includes where R^1 is C_1-C_{20} alkoxy, C_6-C_{20} aryloxy, or halogen, and R^2 and R^3 are independently selected from C_1-C_{20} alkoxy, C_6-C_{20} aryloxy, C_1-C_{20} alkyl, C_6-C_{20} aryl, C_7-C_{30} aralkyl, C_7-C_{30} alkaryl, halogen, and hydrogen. R^1 is preferably C_1-C_4 alkoxy, C_6-C_{10}

25 aryloxy or halogen . Example oxysilanes include: acryloxypropyltrimethoxysilane (APTMS, $H_2C=CHCO_2(CH_2)_3Si(OCH_3)_3$), acryloxypropyltriethoxysilane, acryloxypropylmethyldimethoxysilane, methacryloxypropyltrimethoxysilane, methacryloxypropyltriethoxysilane, and methacryloxypropylmethyldimethoxysilane. Preferred amongst the

30 oxysilanes is APTMS.

The oxysilane can be pre-hydrolyzed before use. Pre- hydrolysis means that at least one of the R^{1-3} substituents in the oxysilane has been replaced by hydroxyl. For example, $X-Y-SiR_2OH$, $X-Y-SiR(OH)_2$, and

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X–Y–Si(OH)$_3$. By oxysilane condensation product is meant a product formed by condensation reaction of one or more oxysilane and/or oxysilane hydrolysis products. For example, condensation products include: X-Y-Si(R^1)(R^2)OSi(R^1)(OH)-Y-X; X–Y–Si(R^1)(OH)OSi(R^1)(OH)-Y-
5   X; X-Y–Si(OH)$_2$OSi(R^1)(OH)-Y-X; X–Y–Si(R^1)(OH)OSi(R^1)(OSi(R^1)(OH)-Y-X)-Y-X; and X–Y–Si(R^1)(R^2)OSi(R^1)(OSi(R^1)(OH)-Y-X)-Y-X.

      Oxysilane hydrosylate and/or condensate is formed by contacting the oxysilane with from about 3 to about 9 moles of water per mole of hydrolyzable functional group bonded to the silicon of the oxysilane. The
10   hydrolysis of the oxysilane is considered complete after 24 hours at 25° C because less than 1wt % APTMS residual occurs after hydrolysis. In a preferred embodiment, oxysilane hydrosylate and/or condensate is formed by contacting the oxysilane with from about 4 to about 9 moles of water per mole of hydrolyzable functional group bonded to the silicon of the
15   oxysilane. In a more preferred embodiment, oxysilane hydrosylate and/or condensate is formed by contacting the oxysilane with from about 5 to about 7 moles of water per mole of hydrolyzable functional group bonded to the silicon of the oxysilane. The carbon-carbon double bond containing functional group attached to the oxysilane functional group are unaffected
20   by conditions used to form the oxysilane hydrosylate and/or condensate.

      The oxysilane hydrosylate and/or condensate is formed by contacting the oxysilane with water in the presence of a lower alkyl alcohol solvent. Representative lower alkyl alcohol solvents include aliphatic and alicyclic C$_1$-C$_5$ alcohols such as methanol, ethanol, n-propanol, iso-
25   propanol and cyclopentanol with ethanol being preferred.

      The oxysilane hydrosylate and/or condensate is formed by contacting the oxysilane with water in the presence of an organic acid that catalyzes hydrolysis of one, two or three of the oxysilane substituents R$^{1-3}$, and further may catalyze condensation of the resultant oxysilane
30   hydrosylates. The organic acids catalyze hydrolysis of oxysilane substituents such as alkoxy and aryloxy, and result in the formation of hydroxyl (silanol) groups in their place. Organic acids comprise the elements carbon, oxygen and hydrogen, optionally nitrogen and sulfur,

and contain at least one labile (acidic) proton. Example organic acids include carboxylic acids such as acetic acid, maleic acid, oxalic acid, and formic acid, as well as sulfonic acids such as methanesulfonic acid and toluene sulfonic acid. In one embodiment, the organic acids have a pKa of
5   at least about 4.7. A preferred organic acid is acetic acid.

In one embodiment, a concentration of from about 0.1 weight% to about 1 weight% organic acid in lower alkyl alcohol solvent is of utility for forming the oxysilane hydrosylate and/or condensate from the oxysilane. In one embodiment, a concentration of about 0.4 weight% organic acid in
10   lower alkyl alcohol solvent is of utility for forming the oxysilane hydrosylate and/or condensate from the oxysilane.

The conditions taught herein for the reaction of oxysilane and water in the presence of organic acid and lower alkyl alcohol result in less than about 1 mol% of unhydrolyzed oxysilane ($X-Y-SiR^1R^2R^3$) remaining in the
15   formed oxysilane hydrosylate and/or condensate.

In the embodiment where UV curing is used to cure the uncured composition, a mixture of acrylic multiolefinic crosslinker and allylic multiolefinic crosslinker is of utility. For example, a weight ratio mixture of from about 2:1 to about 1:2, preferably about 1:1, of acrylic to allylic
20   multiolefinic crosslinkers. The acrylic crosslinker is typically alkoxylated polyol polyacrylate, especially ethoxylated (3 mol) trimethylolpropane triacrylate, and the allylic crosslinker is typically 1,3,5-triallyl isocyanurate.

In one embodiment of uncured composition: the cross-linkable polymer is fluoroelastomer having at least one cure site selected from the
25   group consisting of bromine and iodine, especially iodine; the multiolefinic crosslinker is an allylic multiolefinic crosslinker, especially 1,3,5-triallyl isocyanurate; the uncured composition contains photoinitiator; the uncured composition contains polar aprotic organic solvent; and UV curing is used to cure the uncured composition.

30   Uncured compositions comprising a mixture of at least one reactive component that can be cured (e.g., cross-linkable polymer and multiolefinic cross linker) are cured to form compositions. The uncured compositions are preferably cured via a free radical mechanism. Free radicals may be generated by known methods such as by the thermal

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decomposition of organic peroxides, azo compounds, persulfates, redox initiators, and combinations thereof, optionally included in the uncured composition, or by radiation such as ultraviolet (UV) radiation, gamma radiation, or electron beam radiation, optionally in the presence of a

5   photoinitiator. The uncured compositions are preferably cured via irradiation with UV radiation.

When UV radiation initiation is used to cure the uncured composition, the uncured composition can include photoinitiator, generally between 1 and 10 phr, preferably between 5 and 10 phr of photo-initiator.

10 Photoinitiators may be used singly or in combinations of two or more. Free-radical photoinitiators of utility include, those generally useful to UV cure acrylate polymers. Example photoinitiators of utility include benzophenone and its derivatives; benzoin, alpha-methylbenzoin, alpha-phenylbenzoin, alpha-allylbenzoin, alpha-benzylbenzoin; benzoin ethers

15 such as benzyl dimethyl ketal (commercially available as Irgacure® 651 (Irgacure® products available from Ciba Specialty Chemicals Corporation, Tarrytown, NY, USA)), benzoin methyl ether, benzoin ethyl ether, benzoin n-butyl ether; acetophenone and its derivatives such as 2-hydroxy-2-methyl-1-phenyl-1-propanone (commercially available as Darocur® 1173

20 (Darocur ® products available from Ciba Specialty Chemicals Corporation, Tarrytown, NY, USA)) and 1-hydroxycyclohexyl phenyl ketone (commercially available as Irgacure® 184); 2-methyl-1-[4-methylthio)phenyl]-2-(4-morpholinyl)-1-propanone (commercially available as Irgacure® 907); alkyl benzoyl formates such as methylbenzoylformate

25 (commercially available as Darocur® MBF); 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone (commercially available as Irgacure® 369); aromatic ketones such as benzophenone and its derivatives and anthraquinone and its derivatives; onium salts such as diazonium salts, iodonium salts, sulfonium salts; titanium complexes such

30 as, for example, that which is commercially available as "CGI 784 DC", also from Ciba Specialty Chemicals Corporation; halomethylnitrobenzenes; and mono- and bis-acylphosphines such as those available from Ciba Specialty Chemicals Corporation under the trade designations Irgacure® 1700, Irgacure® 1800, Irgacure® 1850,

Irgacure® 819, Irgacure® 2005, Irgacure® 2010, Irgacure® 2020 and Darocur® 4265. Further, sensitizers such as 2- and 4-isopropyl thioxanthone, commercially available from Ciba Specialty Chemicals Corporation as Darocur® ITX, may be used in conjunction with the aforementioned photoinitiators.

Photoinitiators are typically activated by incident light having a wavelength between about 254 nm and about 450 nm. In a preferred embodiment, the uncured composition is cured by light from a high pressure mercury lamp having strong emissions around wavelengths 260 nm, 320 nm, 370 nm and 430 nm. In this embodiment, it is preferred to use a combination of at least one photoinitiator with relatively strong absorption at shorter wavelengths (i.e., 245-350 nm), and at least one photoinitiator with relatively strong absorption at longer wavelengths (i.e., 350-450 nm) to cure the present uncured compositions. Such a mixture of initiators results in the most efficient usage of energy emanating from the UV light source. Example photoinitiators with relatively strong absorption at shorter wavelengths include benzyl dimethyl ketal (Irgacure® 651) and methylbenzoyl formate (Darocur® MBF). Example photoinitiators with relatively strong absorption at longer wavelengths include 2- and 4-isopropyl thioxanthone (Darocur® ITX). An example of such mixture of photoinitiators is 10 parts by weight of a 2:1 weight ratio mixture of Irgacure® 651 and Darocur® MBF, to 1 part by weight of Darocur® ITX.

Thermal initiators may also be used together with photoinitiator when UV curing. Useful thermal initiators include, for example, azo, peroxide, persulfate and redox initiators.

UV curing of present uncured compositions can be carried out in the substantial absence of oxygen, which can negatively influence the performance of certain UV photoinitiators. To exclude oxygen, UV curing can be carried out under an atmosphere of inert gas such as nitrogen.

UV curing of present uncured compositions can be carried out at ambient temperature, but also can be carried out at an elevated temperature.

When thermal decomposition of organic peroxide is used to generate free radicals for curing the uncured composition, the uncured

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composition generally includes between 1 and 10 phr, preferably between 5 and 10 phr of organic peroxide. Useful free-radical thermal initiators include, for example, azo, peroxide, persulfate, and redox initiators, and combinations thereof. Organic peroxides are preferred, and example

5   organic peroxides include: 1,1-bis(t-butylperoxy)-3,5,5-trimethylcyclohexane; 1,1-bis(t-butylperoxy)cyclohexane; 2,2-bis(t-butylperoxy)octane; n-butyl-4, 4-bis(t-butylperoxy)valerate; 2,2-bis(t-butylperoxy)butane; 2,5-dimethylhexane-2,5-dihydroxyperoxide; di-t-butyl peroxide; t-butylcumyl peroxide; dicumyl peroxide; alpha,alpha'-bis(t-

10   butylperoxy-m-isopropyl)benzene; 2,5-dimethyl-2,5-di(t-butylperoxy)hexane; 2,5-dimethyl-2,5-di(t-butylperoxy)hexene-3; benzoyl peroxide; t-butylperoxybenzene; 2,5-dimethyl-2,5-di(benzoylperoxy)-hexane; t-butylperoxymaleic acid; and t-butylperoxyisopropylcarbonate. Preferred is benzoyl peroxide. Organic peroxides may be used singly or in

15   combinations of two or more.

One or more solvents can be included in the uncured composition to reduce the viscosity of the uncured composition in order to facilitate coating. The appropriate viscosity level of uncured composition containing solvent depends upon various factors such as the desired thickness of the

20   anti-reflective coating, application technique, and the substrate onto which the uncured composition is to be applied, and can be determined by one of ordinary skill in this field without undue experimentation. Generally, the amount of solvent in the uncured composition is about 10 weight% to about 60 weight%, preferably from about 20 weight% to about 40

25   weight%.

The solvent is selected such that it does not adversely affect the curing properties of the uncured composition or attack the optical display substrate. Additionally, solvent is chosen such that the addition of the solvent to the uncured composition does not result in flocculation of the

30   nanoparticles. Furthermore, the solvent should be selected such that it has an appropriate drying rate. That is, the solvent should not dry too slowly, which can undesirably delay the process of making an anti-reflective coating from the uncured composition. It should also not dry too quickly, which can cause defects such as pinholes or craters in the

resultant anti-reflective coating. Solvents of utility include polar aprotic organic solvents, and representative examples include aliphatic and alicyclic: ketones such as methyl ethyl ketone and methyl isobutyl ketone; esters such as propyl acetate; ethers such as di-n-butyl ether; and

5 combinations thereof. Preferred solvents include propyl acetate and methyl isobutyl ketone. Lower alkyl hydrocarbyl alcohols (e.g., methanol, ethanol, isopropanol, etc.) can be present in the solvent, but should comprise about 8% or less by weight of the solvent when the cross-linkable polymer is fluoroelastomer having at least one cure site selected

10 from the group consisting of bromine, iodine and ethenyl.

The solid nanoparticles of both strata can be any shape, including spherical and oblong, and are relatively uniform in size and remain substantially non-aggregated, as long as they can be used to satisfy the refractive index requirements of the bounding equations in the present

15 invention. They can be hollow, porous, or solid. The diameter of the particles are dependent on the relative refractive index of the particle and binder used, but in general should be small enough to avoid objectionable light scattering and be less than the thickness of the stratum. Typically the median diameter is less than about 100 nm, preferably less than 70 nm.

20 The concentration of the nanoparticles are dependent on the particle's refractive index of the particle and the binder, and is dependent on the solutions of the equations described *infra*.

The nanoparticles of both strata are typically inorganic oxides, such as but not limited to, for the lower strata, titanium oxide, aluminum oxide,

25 antimony oxide, zirconium oxide, indium tin oxide, antimony tin oxide, mixed titanium/tin/zirconium oxides, and binary, ternary, quaternary and higher order composite oxides of one or more cations selected from titanium, aluminum, antimony, zirconium, indium, tin, zinc, niobium and tantalum. For the upper strata, particles can also include oxides of

30 silicon, aluminum, titanium, zirconium, hollow (porous) nanosilicon oxide and solid nanosilicon oxide. More than one type of nanoparticle may be used in combination in a stratum.

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The particles become separated in the two strata by differences in size and/or surface functionality. The size and/or functionality needed for a particular system would depend on the specific fluoropolymer binder used.

For a fluoroelastomer binder system, a nanoparticle whose surface

5   is at least partially fluorinated or covered with coupling agents containing fluorocarbon functional groups can be present in the upper stratum; these particles can also be present, possibly to a lesser extent, in the lower stratum. If the surface of the nanoparticles is at least partially covered with acrylic or vinyl groups via coupling agents, then the nanoparticle

10   population will be primarily located in the lower stratum.

If both particle populations have similar surface chemistries, than some separation of particles can be achieved in the mean diameter of the nanoparticles intended for the upper stratum is more than twice the mean diameter of the nanoparticles intended for the lower stratum. In some

15   situations, the larger nanoparticles can be present in both strata; however, the smaller nanoparticle population will be primarily located in the lower stratum.

For example, if both particle populations have similar surface chemistry, some separation of two particles can also be achieved if the

20   mean diameter of the nanoparticles intended for the upper stratum is more than >2x the mean diameter of the nanoparticle intended for the lower stratum. For instance, the TiO_2 nanoparticles are in the lower stratum and possess a particle size of about 10- 20 nm. However, a larger nanoparticle with the same functionalization (e.g., 30-60 nm) and is solid nanosilicon

25   oxide is expected to begin segregating into the upper stratum.

Substrates suitable for the stratified anti-reflective coating described herein find use as display surfaces, optical lenses, windows, optical polarizers, optical filters, glossy prints and photographs, clear polymer films, and the like. Substrates may be either transparent, anti-smudge or

30   anti-glare and include acetylated cellulose (e.g., triacetyl cellulose (TAC)), polyester (e.g., polyethylene terephthalate (PET)), polycarbonate, polymethylmethacrylate (PMMA), polyacrylate, polyvinyl alcohol, polystyrene, glass, vinyl, nylon, and the like. Preferred substrates are TAC, PET, PMMA, and glass. The substrates optionally have a hardcoat

applied between the substrate and the anti-reflective coating, such as but not limited to an acrylate hardcoat. They can also have other layers such as an antistat layer applied on top of the hardcoat.

5   The refractive indices of the nanoparticles are not critical as long as they satisfy the equations as described herein, but typically the composite refractive index of the combination of particles in one stratum is 1.6. The nanoparticles can be surface functionalized with a variety of groups, such as but not limited to an acrylic functional group.

        In one embodiment, the one or both types of nanoparticles are
10   conductive or semiconductive, which would produce a coating with antistatic properties. Typical metal particles that can be used include indium tin oxide, antimony tin oxide, Sb_2O_3, SbO_2, In_2O_3, SnO_2, antimony zinc oxide, zinc oxide, aluminum zinc oxide, titanium oxide, tungsten oxide, molybdenum oxide, vanadium oxide and iron oxide.

15   One or both types of nanoparticles can be surface functionalized with an acrylic, allylic or vinyl functional group for particles in the lower stratum. An "acrylic functional group" for purposes herein means $CH_2=CH_2-C(O)O-$ with optional alkyl substitutions, such as methacrylic functionalities. Specifically, the acrylic functional group can be represented
20   by the formula X-Y-Si-, where the fragment can be covalent grafted to the surface of the nanoparticles using the reaction of surface with oxysilane of the type $X-Y-SiR^1R^2R^3$. X represents an acryloyloxy $(CH_2=CHC(=O)O-)$ or methacryloyloxy $(CH_2=C(CH_3)C(=O)O-)$ functional group. Y represents a divalent organic radical covalently bonded to the acryloyloxy or
25   methacryloyloxy functional group and the oxysilane functional group. Examples of Y radicals include substituted and unsubstituted alkylene groups having 2 to 10 carbon atoms, and substituted or unsubstituted arylene groups having 6 to 20 carbon atoms. The alkylene and arylene groups optionally additionally have ether, ester, or amide linkages therein.
30   Substituents include halogen, mercapto, carboxyl, alkyl and aryl. $SiR^1R^2R^3$ represents an oxysilane functional group containing three substituents (R^{1-3}), one or all of which are capable of being displaced by (e.g., nucleophilic) substitution. For example, at least one of the R^1, R^2, and R^3 substituents are groups such as alkoxy, aryloxy or halogen and the

substituting group comprises a group such as hydroxyl present on an oxysilane hydrolysis or condensation product, or equivalent reactive functional group present on the substrate film surface. Representative $SiR^1R^2R^3$ oxysilane substitution includes where R^1 is C_1-C_{20} alkoxy, C_6-C_{20} aryloxy, or halogen, and R^2 and R^3 are independently selected from C_1-C_{20} alkoxy, C_6-C_{20} aryloxy, C_1-C_{20} alkyl, C_6-C_{20} aryl, C_7-C_{30} aralkyl, C_7-C_{30} alkaryl, halogen, and hydrogen. R^1 is preferably C_1-C_4 alkoxy, C_6-C_{10} aryloxy or halogen . Example oxysilanes include: acryloxypropyltrimethoxysilane (APTMS, $H_2C=CHCO_2(CH_2)_3Si(OCH_3)_3$), acryloxypropyltriethoxysilane, acryloxypropylmethyldimethoxysilane, methacryloxypropyltrimethoxysilane, methacryloxypropyltriethoxysilane, and methacryloxypropylmethyldimethoxysilane.

A "vinyl functional group" for purposes herein means $CH_2=CH_2$- with optional alkyl substitutions. Specifically, the vinyl functional group can be represented by the formula X-Y-Si-, where the fragment can be covalent grafted to the surface of the nanoparticles using the reaction of surface hydroxyls oxysilanes of the type $X–Y–SiR^1R^2R^3$. X represents a vinyl $CH_2=CH_2$- functional group. Y represents a divalent organic radical covalently bonded to the vinyl functional group and the oxysilane functional group. Examples of Y radicals include substituted and unsubstituted alkylene groups having 2 to 10 carbon atoms, and substituted or unsubstituted arylene groups having 6 to 20 carbon atoms. The alkylene and arylene groups optionally additionally have ether, ester, or amide linkages therein. Substituents include halogen, mercapto, carboxyl, alkyl and aryl. $SiR^1R^2R^3$ represents an oxysilane functional group containing three substituents (R^{1-3}), one or all of which are capable of being displaced by (e.g., nucleophilic) substitution. For example, at least one of the R^1,R^2, and R^3 substituents are groups such as alkoxy, aryloxy or halogen and the substituting group comprises a group such as hydroxyl present on an oxysilane hydrolysis or condensation product, or equivalent reactive functional group present on the substrate film surface. Example oxysilanes include divinyltetramethyldisilazane, $H_2C=CHSi(OR)_3$, ($H_2C=CH-$ $Si(CH_3)_2NHSi(CH_3)_2CH=CH_2$, vinyltrimethoxysilane,

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vinyltriisopropoxysilane. Silazanes such as divinyltetramethyldisilazane can be used.

The surface functionalization can be done either subsequent to mixing with the polymeric binder or after mixing. Suitable surface functionalized particles can be obtained commercially, or synthesized in a variety of ways. A typical process involves the mixture of an inorganic dispersion with surface functionalization agents that react with surface groups on the nanoparticles, such as reactive –OH groups.

Suitable compositions that contain acrylic functional groups include those listed herein that are also used as acrylic multiolefinic crosslinkers. Other suitable compositions include those where the acrylic functionality is an oxysilane comprising: i) an acryloyloxy or methacryloyloxy functional group, ii) an oxysilane functional group, and iii) a divalent organic radical connecting the acryloyloxy or methacryloyloxy functional group and the oxysilane functional group. Oxysilane includes those represented by the formula $X–Y–SiR^1R^2R^3$. X represents an acryloyloxy ($CH_2=CHC(=O)O-$) or methacryloyloxy ($CH_2=C(CH_3)C(=O)O-$) functional group. Y represents a divalent organic radical covalently bonded to the acryloyloxy or methacryloyloxy functional group and the oxysilane functional group. Examples of Y radicals include substituted and unsubstituted alkylene groups having 2 to 10 carbon atoms, and substituted or unsubstituted arylene groups having 6 to 20 carbon atoms. The alkylene and arylene groups optionally additionally have ether, ester, and amide linkages therein. Substituents include halogen, mercapto, carboxyl, alkyl and aryl. $SiR^1R^2R^3$ represents an oxysilane functional group containing three substituents (R^{1-3}), one to all of which are capable of being displaced by (e.g., nucleophilic) substitution. For example, at least one of the R^{1-3} substituents are groups such as alkoxy, aryloxy or halogen and the substituting group comprises a group such as hydroxyl present on an oxysilane hydrolysis or condensation product, or equivalent reactive functional group present on the substrate film surface. Representative $SiR^1R^2R^3$ oxysilane substitution includes where R^1 is C_1-C_{20} alkoxy, C_6-C_{20} aryloxy, or halogen, and R^2 and R^3 are independently selected from C_1-C_{20} alkoxy, C_6-C_{20} aryloxy, C_1-C_{20} alkyl, C_6-C_{20} aryl, C_7-C_{30} aralkyl, C_7-C_{30}

alkaryl, halogen, and hydrogen. R^1 is preferably C_1-C_4 alkoxy, C_6-C_{10} aryloxy or halogen . Example oxysilanes include: acryloxypropyltrimethoxysilane (APTMS, $H_2C=CHCO_2(CH_2)_3Si(OCH_3)_3$), acryloxypropyltriethoxysilane, acryloxypropylmethyldimethoxysilane,

5   methacryloxypropyltrimethoxysilane, methacryloxypropyltriethoxysilane, and methacryloxypropylmethyldimethoxysilane. Preferred amongst the oxysilanes is APTMS.

The specular reflectance, also known as Rvis, was calculated using the TFCalc thin film design software, available from Software Spectra,

10   Portland, OR. This software performs calculations of the optical interference from multiple thin film layers. Materials are defined by the complex dispersion relations of their index of refraction. This allows for absorption from the bulk as well as reflection from the layer surfaces. The interference calculations required that both the intensity and phase of the

15   optical waves be treated for all possible paths and combined for calculations of the transmitted and the reflected beams. The normal angle of incidence was also accounted for in these calculations.

Three types of two stratum anti-reflective designs were used. These are known in the art as the "quarter quarter", the "w", and the "v"

20   designs. These are characterized by the optical thickness of each of the two stratums in each design. In all three cases one needs a high refractive index material, also called the "high index lower stratum" adjacent to the substrate and on top of that a low index material, also known as the "low index upper stratum". It was assumed that the

25   substrate consisted of an semi-infinitely thick TAC (tri acetal cellulose) layer (typically greater than 70 microns) with at least a 3 micron cross linked acrylic hard coat. In practice the hard coat is usually between 6 and 10 microns. The results reported are independent of the thickness of the hardcoat layer as long as it is at least several 3 microns thick. The

30   calculations depend on the index of refraction of the hard coat layer. A typical refractive index used for this layer is 1.53 at 550nm. Some commercial hardcoats have an index of refraction that is a function of the depth of the hard coat layer. In this case the index at the surface can be used for modeling purposes or the gradient can be used by creating a

series of thinner layers to simulate the gradient. The calculations used were relatively independent of which approach is taken.

The ideal optical thickness for the three designs considered are given in Table 1 below in units of quarter waves. These assume that 550 nm is the reference wavelength, so a quarter wave is (550/4) nm. Between the extremes of the bounding *equations*, in general, the optical thicknesses of the strata can vary by 25%; these films will still exhibit low reflectivities. In practice, the thicknesses can vary by about ±10%. The optical thickness is defined as n * d for a non absorbing stratum, where n is the index of refraction and d is the physical thickness.

Table 1

Design	Lower Stratum Optical Thickness	Upper Stratum Optical Thickness
quarter quarter	1	1
w	2	1
v	1.72	0.733

The potentially useful regions of index of refraction were explored for these three designs by varying both the index of the upper and lower stratums of the AR coatings. A preference was set in the TFcalc program to hold the optical thickness of the stratums constant when the index was varied. By doing this the physical thickness was automatically adjusted to compensate for the change in index to hold the optical thickness of each stratum constant. For each design the index was searched of refraction space for both stratums systematically while calculating the luminosity of the reflection in the xyY color space. Cap Y is the luminocity value in the TFcalc program. As used herein, % Rvis is 100 times cap Y.

While it is most useful to determine the parameters of the optimum anti-reflective stratum where the Rvis is minimized, it is also necessary to define the potentially useful space . It was selected that Rvis is less than 1.3%. Therefore, a procedure was followed that for each lower stratum refractive index the upper stratum index was varied away from the optimum value both upwards and downwards until Rvis increased

from the optimum reflectivity to a value of 1.3%. The upper and lower bounds of the refractive index of the upper stratum were then recorded for each lower stratum refractive index. The upper and lower bounds of the refractive index for the upper stratum were plotted as a function of the

5   lower stratum refractive index. The curves generated in these plots were fitted using least squares fitting techniques to generate empirical equations describing the range of useful values of index of refraction for each stratum of these three designs.

The simplified equations assume an Rvis of 1.3% and are

10   based on a substrate which includes an acrylic hardcoat layer (with a thickness > 2 microns) which is based on a triacetylcellulose. Other substrates (e.g. glass, hard coated PET) will be described with different equations which designate the limits of refractive indices for each of the designs.

15   From these equations, the real thickness can be calculated for each one of the designs that will have an Rvis of 1.3 %. In the equations below, HighIndex is the index of refraction for the lower stratum and LowIndex the index of refraction for the upper stratum. Note, that in all cases, the design space of this invention covers configurations where the

20   high refractive index stratum has a refractive index of 1.41 or greater. The low refractive index upper stratum could typically have a refractive index of 1.1 to 2.0, but for purposes of these equation has a range of 1.25 to 1.40, where the refractive index of the low refractive index stratum is lower than the refractive index of the high refractive index stratum.

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Quarter Quarter Design
Low index stratum varies from about 1.25 to about 1.46
LowIndex = 1.25 to 1.40

30   The corresponding boundary conditions for the refractive index of the high refractive index lower stratum for each value of the lower index upper stratum are shown by these equations. The high index lower bound is limited to a value of 1.41 or greater, and the configuration requires that

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the refractive index of the upper stratum is lower than the refractive index of the lower stratum.

HighIndex lower bound = [1.196849 * LowIndex] - 0.12526

HighIndex upper bound = [1.177721 * LowIndex] + 0.244887

W design

Low index stratum varies from about 1.25 to about 1.46

LowIndex = 1.25 to 1.46

The corresponding boundary conditions for the refractive index of the high refractive index lower stratum for each value of the low index upper stratum are shown by these equations. The high index lower bound is limited to a value of 1.41 or greater, and the configuration requires that the refractive index of the upper stratum is lower than the refractive index of the lower stratum.

HighIndex lower bound =

$[LowIndex^2 * 47.39975] - [121.43156 * LowIndex] + 78.88532$

HighIndex upper bound =

$[LowIndex^2 * (- 61.309701)] + [LowIndex * 160.269626] - 101.960123$

V design

The low index upper stratum varies from about 1.25 to about 1.60

LowIndex = 1.25 to 1.60

HighIndex = 1.41 or greater

The corresponding boundary conditions for the refractive index of the high refractive index lower stratum for each value of the low index upper stratum are shown by these equations. The high index lower bound is limited to a value of 1.41 or greater, and the configuration requires that the refractive index of the upper stratum is lower than the refractive index of the lower stratum.

HighIndex lower bound = [LowIndex * 1.778499] - 0.820833

HighIndex upper bound = [LowIndex * 1.55196] - 0.03609

Therefore, if the refractive index of the lower stratum is selected as having a range of 1.1 to 2.0, then the range of the refractive index of the upper stratum can be calculated using the various models:

Quarter Quarter Design

HighIndex lower bound = [1.196849 * (1.1 to - 2.0)] - 0.12526

HighIndex upper bound = [1.177721 * (1.1 to - 2.0)] + 0.244887

W design

HighIndex lower bound =

$[(1.1 \text{ -to } 2.0)^2 * 47.39975] - [121.43156 * (1.1 \text{ to } - 2.0) + 78.88532]$

HighIndex upper bound =

$[(1.1 \text{ to- } 2.0)^2 * (-61.309701)] + [(1.1 \text{ to- } 2.0) * 160.269626] - 101.960123$

V design

HighIndex lower bound = [(1.1 to- 2.0) * 1.778499] - 0.820833

HighIndex upper bound = [(1.1 to - 2.0) * 1.55196] - 0.03609

Between the extremes of the bounding questions, in general, the optical thicknesses of the strata can vary by 25%; these films will still exhibit low reflectivities.

The present invention also discloses a process for forming a stratified anti-reflective coating on a substrate comprising:

(i)   forming a liquid mixture comprising a solvent having dissolved therein:

(i-a)   a fluoropolymer binder;

(i-b)   optionally, a multiolefinic crosslinker;

(i-c)   optionally, an oxysilane having at least one polymerizable functional group;

and wherein said solvent has suspended therein:

(i-d)   a plurality of high refractive index nanoparticles; and

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(i-e) a plurality of low refractive index nanoparticles;

(ii) coating said liquid mixture on a substrate to form a liquid mixture coating on said substrate;

(iii) removing solvent from said liquid mixture coating to form an uncured coating on said substrate; and

(iv) curing said uncured coating thereby forming a stratified anti-reflective coating comprising:

(iv-a) a higher refractive index stratum located on said substrate comprising said fluoropolymer binder being cured and said plurality high refractive index nanoparticles; and

(iv-b) a lower refractive index stratum located on top of said high refractive index stratum comprising fluoropolymer binder being cured and said plurality low refractive index nanoparticles.

Fluoropolymer, fluoroelastomer, nanoparticles, oxysilane, multiolefinic crosslinker substrate and acrylic functional group are as defined supra.

The process includes a step of coating the liquid mixture on a substrate in a single coating step to form a liquid mixture coating on the substrate. Coating techniques useful for applying the uncured composition onto the substrate in a single coating step are those capable of forming a thin, uniform layer of liquid on a substrate, such as microgravure coating as described in US patent publication no. 2005/18733.

Suitable solvents include those listed above. The process includes a step of removing the solvent from the liquid mixture coating on the substrate to form an uncured coating on the substrate. The solvent can be removed by known methods, for example, heat, vacuum and a flow of inert gas in proximity to the coated liquid dispersion on the substrate.

Additives can be included in the coating formulation to lower the coefficient of friction (improve slip) and/or improve the leveling behavior of the film upon drying. These additives should be soluble in the solvents of the coating formulation, and can range in concentration from 0.01 to 3 wt % of the total coating formulation weight. Additives based on silicones or

polysiloxanes can be used. These can include, for instance, silicone oil, high molecular weight polydimethylsiloxanes, polyether modified silicones, and silicone glycol copolymer surfactants.

The present invention process includes a step of coating the liquid mixture on a substrate to form a liquid mixture coating. In one embodiment, the step of coating can be carried out in a single coating step. Coating techniques useful for applying the uncured composition onto the substrate in a single coating step are those capable of forming a thin, uniform layer of liquid on a substrate, such as microgravure coating, for example, as described in US patent publication no. 2005/18733.

The process of the present invention includes a step of removing the solvent from the liquid mixture coating to form an uncured coating on the substrate. The solvent can be removed by known methods, for example, heat, vacuum and a flow of inert gas in proximity to the coated liquid mixture.

The process includes a step of curing the uncured coating. As discussed previously herein, the uncured coating is preferably cured by a free radical mechanism. Free radicals may be generated by known methods such as by the thermal decomposition of an organic peroxide, optionally included in the uncured composition, or by radiation such as ultraviolet (UV) radiation, gamma radiation, or electron beam radiation. Present uncured compositions are preferably UV cured due to the relative low cost and speed of this curing technique when applied on industrial scale.

EXAMPLES

Abbreviations and Materials

APTMS: acryloxypropyltrimethoxysilane, available from Aldrich Chemicals, St. Louis, MO

Darocur® ITX: mixture of 2-isopropylthioxanthone and 4-
isopropylthioxanthone, photoinitiator available from Ciba Specialty
Chemicals, Tarrytown, NY, USA

5   Genocure® MBF: methlybenzoylformate, photoinitiator available from
Rahn USA Co., IL, USA

Irgacure® 651: 2, 2-dimethoxy-1, 2-diphenylethane-1-one, photoinitiator
available from Ciba Specialty Chemicals, Tarrytown, NY, USA

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MEK: methylethyl ketone

MIBK: methylisobutylketone

15   Nissan MEK-ST: silica colloid in methyl ethyl ketone, median diameter,
d50, of about 10-16 nm, 30-31 wt% silica, available from Nissan Chemical
America Co., Houston, TX, USA.

Sartomer SR533: triallyl isocyanurate crosslinker, Sartomer Company,
20   Inc., Exton, PA

Viton® GF200S: E. I. DuPont de Nemours, Inc., Wilmington, DE

Coating Method
25   A substrate film is coated with an uncured composition using a
Yasui-Seiki Co. Ltd., Tokyo, Japan, microgravure coating apparatus as
described in U.S. Pat. No. 4,791,881. The apparatus includes a doctor
blade and a Yasui-Seiki Co. gravure roll) having a roll diameter of 20 mm.
Coating is carried out using a gravure roll revolution of 6.0 rpm and a
30   transporting line speed of 0.5 m/min.
                The coated conditions were adjusted to yield a material with a
final coated thickness (dry film) of 194 nm.
                The coated substrate is cured using a UV exposure unit
supplied by Fusion UV Systems / Gaithersburg MD consisting of a LH-

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I6P1 UV source (200w/cm) coupled to a DRS Conveyer/UV Processor (15 cm wide) with controlled nitrogen inerting capability over a measured range of 10 to 1,000 ppm oxygen.

5   Lamp power and conveyer speed are set to give a film cure using a measured energy density of 500-600 millijoules/cm^2 (UV-A irradiation) at about 0.7 to 1.0 m/min transport rate. An EIT UV Power Puck® radiometer is used to measure the UV total energy in the UV-A band width.

         The "H" bulb used in the LH-I6P1 has the following typical

10   spectral output in the UV-B, UV-C and UV-V bands in addition to the UV-A mentioned above as shown in the table below.

"H" Bulb Spectral Performance at 2.5 m/min, 50% Power

Band	Range	Power	Energy	time (sec)	line speed	Exp Zone
	(nm)	(w/cm^2)	(J/cm^2)		(m/min)	(cm)
UV-C	250-260	0.107	0.079	0.7	2.5	3.1
UV-B	280-320	0.866	0.648	0.7	2.5	3.1
UV-A	320-390	0.891	0.667	0.7	2.5	3.1
UV-V	395-445	0.603	0.459	0.8	2.5	3.2

         The oxygen level in the unit is controlled using a nitrogen purge

15   to be at 350 ppm or less. The cured film is placed on a metal substrate preheated to 70°C before placing it on the cure conveyer belt.

Measurement of Specular Reflectance (Rvis)

         A 3.7 cm x 7.5 cm piece of substrate film coated with an anti-

20   reflective coating is prepared for measurement by adhering a strip of black PVC electrical tape (Nitto Denko, PVC Plastic tape #21) to the uncoated side of the film, in a manner that excludes trapped air bubbles, to frustrate the back surface reflections. The film is then held fixed and flat at normal to the spectrometer's optical path, with coated surface up. The reflected

25   light that is within about 2 degrees of normal incidence is captured and directed to on the stage of an infra-red extended range spectrometer (Filmetrics, model F50) using adhesive tape or a flat weight. The infra-red

spectrometer is calibrated between 400 nm and 1700 nm with a low reflectance standard of BK7 glass with its back surface roughened and blackened. The specular reflection is measured at normal incidence with an acceptance angle of about 2 degrees. The reflection spectrum is recorded in the range from 400 nm to 1700 nm with an interval of about 1 nm. A low noise spectrum is obtained by using a long detector integration time so that the instrument is at full range or saturated with about a 6% reflection. A further noise reduction is achieved by averaging 3 or more separate measurements of the spectrum. The reflectance reported from the recorded spectrum is the result of a color calculation of x, y, and Y where Y is reported as the specular reflectance (R_{VIS}). The color coordinate calculation is performed for a 10 degree standard observer with a type C light source.

EXAMPLE 1

32.8 volume % (fluorosilane treated) SiO2, 27.2 volume % TiO2, 3 volume % SiO2 in Viton

APTMS is prehydrolyzed by combining 6.697 g of APTMS with 41.136 g of ethanol (derived from combining 100 g of 95 volume % ethanol with 0.4 grams of glacial acetic acid). The mixture is allowed to stand for 24 hours at room temperature.

To 4.943 g of the prehydrolyzed APTMS is added 13.275 g of TiO_2 nanoparticles containing approximately 20.5 wt % TiO_2 in MIBK (Shokubai Kasei Kogyo Kabushiki Kaisha, Japan, ELCOM grade DU-1014TIV). The titanium oxide nanoparticles are approximately 20 nm in diameter by dynamic light scattering. The mixture is allowed to age for 24 hours at 50 °C prior to further use.

A solid nanosilicon oxide colloid is prefunctionalized with a urea fluorosilane according to the following procedure. 20 g of IPA-ST colloidal silica in isopropyl alcohol (Nissan Chemicals) was combined with 20 g of isopropyl alcohol. To this mixture, 1.302 g of the silane was added and the

entire mixture was heated for 3 hours, to reflux, under a nitrogen
atmosphere. Following this reflux procedure, approximately 20 g MIBK
(methyl isobutyl ketone) was added and the isopropyl alcohol was distilled
under vacuum. The final concentration of the silane treated colloid was 30

5   wt % in predominantly MIBK.

A second mixture is prepared by combining 7.198 g of the
prehydrolyzed APTMS with 12.691 g of silane treated colloid described
above.   This mixture is allowed to age for 24 hours, at 50 °C, prior to
further use.

10   A third mixture comprising fluoroelastomer was formed by
combining 12.00 g of a 10 wt% solution of Viton® GF200S in MIBK, 0.119
g Sartomer SR533, 0.071 g Irgacure® 907.

To the third mixture comprising fluoroelastomer was added
15.182 g of the first mixture (containing TiO_2 and hydrolyzed APTMS) and

15   8.287 g of the second mixture (containing silane treated SiO_2 and
hydrolyzed APTMS) to form the uncured composition.

The resultant uncured composition is then filtered through a
0.47 μ Teflon® PTFE membrane filter and is used for coating within two to
five hours of preparation.

20   A 40.6 cm by 10.2 cm strip of acrylate hard-coated triacetyl
cellulose film is coated with the uncured coating solution as described
above. An Rmin of about 0.2 % is obtained (Rvis = 0.3 %)

CLAIMS

What is claimed is:

1.   An article comprising :

    (i) a substrate; and

    (ii) a stratified anti-reflective coating on said substrate, said stratified anti-reflective coating comprising:

        (iia) a high refractive index lower stratum located on said substrate comprising a low refractive index fluoropolymer binder and a plurality of high refractive index nanoparticles; and

        (iib) a low refractive index upper stratum located on top of said high refractive index lower stratum comprising said low refractive index fluoropolymer binder and a plurality of low refractive index nanoparticles;

    wherein a refractive index of the low refractive index upper stratum is lower than a refractive index of the high refractive index lower stratum.

2.   The article of claim **1**, wherein the refractive index of the high refractive index lower stratum is 1.41 or greater.

3.   The article of claim **1**, wherein:

        the substrate is an acrylate hard-coated triacetyl cellulose;

        the low refractive index upper stratum has an optical thickness of a quarter wave at 550 nm and a refractive index value of LowIndex, ranging from about 1.25 to about 1.40;

        the high refractive index lower stratum has an optical thickness of a quarter wave at 550 nm and a refractive index value of HighIndex ranging from a lower bound calculated by

$$[1.196849 * \text{LowIndex}] - 0.12526$$

to an upper bound calculated by

$$[1.177721 * LowIndex] + 0.244887.$$

5   4.   The article of claim **1**, wherein:

the substrate is an acrylate hard-coated triacetyl cellulose;

the low refractive index upper stratum has an optical

thickness of a quarter wave at 550 nm and a refractive index value of

LowIndex ranging from about 1.25 to about 1.46;

10   and the high refractive index lower stratum has an optical

thickness of twice a quarter wave at 550 nm and a refractive index value of

HighIndex value ranging from a lower bound calculated by

$$[LowIndex^2 * 47.39975] - [121.43156 * LowIndex] + 78.88532$$

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to an upper bound calculated by

$$[LowIndex^2 * (-61.309701)] + [LowIndex * 160.269626] - 101.960123.$$

20   5.   The article of claim **1**, wherein the substrate is an acrylate

hard-coated triacetyl cellulose; the substrate is an acrylate hard-coated

triacetyl cellulose; the low refractive index upper stratum has an optical

thickness of 0.733 of a quarter wave at 550 nm and a refractive index

value of LowIndex ranging from about 1.25 to about 1.60;

25   and the high refractive index lower stratum has an optical thickness

of 1.72 of a quarter wave at 550 nm and a refractive index value of

HighIndex, ranging from a lower bound calculated by

$$[LowIndex * 1.778499] - 0.820833$$

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to an upper bound calculated by

$$[LowIndex * 1.778499] - 0.820833.$$

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6.   The article of claim **1**, wherein said high refractive index nanoparticles are comprised of inorganic oxides with at least one member selected from the group consisting of titanium oxide, aluminum oxide, antimony oxide, zirconium oxide, indium tin oxide, antimony tin oxide, mixed titanium/tin/zirconium oxides, and binary, ternary, quaternary and higher order composite oxides of one or more cations, said cations selected from the group consisting of titanium, aluminum, antimony, zirconium, indium, tin, zinc, niobium and tantalum combinations thereof;

and wherein said low refractive index nanoparticles are comprised of inorganic oxides with at least one member selected from the group consisting of titanium oxide, aluminum oxide, antimony oxide, zirconium oxide, indium tin oxide, antimony tin oxide, mixed titanium/tin/zirconium oxides, silicon oxides, hollow or solid nanosilicon oxide, and binary, ternary, quaternary and higher order composite oxides of one or more cations, said cations selected from the group consisting of titanium, aluminum, antimony, zirconium, indium, tin, zinc, niobium tantalum, and their combinations thereof.

7.   The article of claim **1**, wherein said stratified anti-reflective coating has anti-static properties.

8.   The article of claim **1**, wherein said stratified anti-reflective coating is formed on said substrate in a single coating step.

9.   The article of claim **1**, wherein said substrate comprises triacetyl cellulose, acetylated cellulose, polyethylene terephthalate, polycarbonate, polymethylmethacrylate, polyacrylate, polyvinyl alcohol, polystyrene, glass, vinyl, or nylon, and wherein the substrate, optionally, is treated with an acrylate hard-coat.

10. A process comprising:

(i) forming a liquid mixture comprising a solvent having dissolved therein:

(i-a) a fluoropolymer binder;

5 (i-b) optionally, a multiolefinic crosslinker;

(i-c) optionally, an oxysilane having at least one polymerizable functional group;

and wherein said solvent has suspended therein:

(i-d) a plurality of high refractive index nanoparticles; and

10 (i-e) a plurality of low refractive index nanoparticles;

(ii) coating said liquid mixture on a substrate to form a liquid mixture coating on said substrate;

(iii) removing the solvent from said liquid mixture coating to form an uncured coating on said substrate; and

15 (iv) curing said uncured coating thereby forming a stratified anti-reflective coating comprising:

(iv-a) a high refractive index lower stratum located on said substrate comprising a fluoropolymer binder being cured and said plurality of high refractive index nanoparticles; and

20 (iv-b) a low refractive index upper stratum located on top of said high refractive index lower stratum comprising a fluoropolymer binder being cured and said plurality of low refractive index nanoparticles;

wherein a refractive index of the low refractive index upper

25 stratum is lower than t a refractive index of the high refractive index lower stratum.

11. The process of claim **10**, wherein the refractive index of the high refractive index lower stratum is 1.41 or greater.

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12. The process of claim **10**, wherein:

the substrate is an acrylate hard-coated triacetyl cellulose;

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the low refractive index upper stratum has an optical thickness
of a quarter wave at 550 nm and a refractive index value of LowIndex,
ranging from about 1.25 to about 1.40;

the high refractive index lower stratum has an optical thickness

5   of a quarter wave at 550 nm and a refractive index value of HighIndex
ranging from a lower bound calculated by

$$[1.196849 * LowIndex] - 0.12526$$

10   to an upper bound calculated by

$$[1.177721 * LowIndex] + 0.244887.$$

        13. The process of claim **10**, wherein:

15   the substrate is an acrylate hard-coated triacetyl cellulose;

                the low refractive index upper stratum has an optical thickness
of a quarter wave at 550 nm and a refractive index value of LowIndex
ranging from about 1.25 to about 1.46;

                and the high refractive index lower stratum has an optical

20   thickness of twice a quarter wave at 550 nm and a refractive index value of
HighIndex ranging from a lower bound calculated by

$$[LowIndex^2 * 47.39975] - [121.43156 * LowIndex] + 78.88532$$

25   to an upper bound calculated by

$$[LowIndex^2 * (-61.309701)] + [LowIndex * 160.269626] - 101.960123.$$

        14. The process of claim **10**, wherein the substrate is an acrylate

30   hard-coated triacetyl cellulose;

                the substrate is an acrylate hard-coated triacetyl cellulose;

the low refractive index upper stratum has an optical thickness of 0.733 of a quarter wave at 550 nm and a refractive index value of LowIndex from about 1.25 to about 1.60;

and the high refractive index lower stratum has an optical
5   thickness of 1.72 of a quarter wave at 550 nm and a refractive index value of HighIndex ranging from a lower bound calculated by

$$[LowIndex * 1.778499] - 0.820833$$

10   to an upper bound calculated by

$$[LowIndex * 1.778499] - 0.820833.$$

15.   The process of claim **10**, wherein said high refractive index
15   nanoparticles are comprised of inorganic oxides with at least one member selected from the group consisting of titanium oxide, aluminum oxide, antimony oxide, zirconium oxide, indium tin oxide, antimony tin oxide, mixed titanium/tin/zirconium oxides, and binary, ternary, quaternary and higher order composite oxides of one or more cations; said cations
20   selected from the group consisting of titanium, aluminum, antimony, zirconium, indium, tin, zinc, niobium and tantalum, and their combinations thereof;

and wherein said low refractive index nanoparticles are comprised of inorganic oxides with at least one member selected from the
25   group consisting of titanium oxide, aluminum oxide, antimony oxide, zirconium oxide, indium tin oxide, antimony tin oxide, mixed titanium/tin/zirconium oxides, silicon oxides, hollow or solid nanosilicon oxide, and binary, ternary, quaternary and higher order composite oxides of one or more cations; said cations selected from the group consisting of
30   titanium, aluminum, antimony, zirconium, indium, tin, zinc, niobium tantalum, and their combinations thereof.

16.   The process of claim **10**, wherein said stratified anti-reflective coating has anti-static properties.

17.   The process of claim **10**, wherein said stratified anti-reflective coating is formed on said substrate in a single coating step.

18.   The process of claim **10**, wherein said substrate comprises triacetyl cellulose, acetylated cellulose, polyethylene terephthalate, polycarbonate, polymethylmethacrylate, polyacrylate, polyvinyl alcohol, polystyrene, glass, vinyl, or nylon, and wherein the substrate, optionally, is treated with an acrylate hard-coat.