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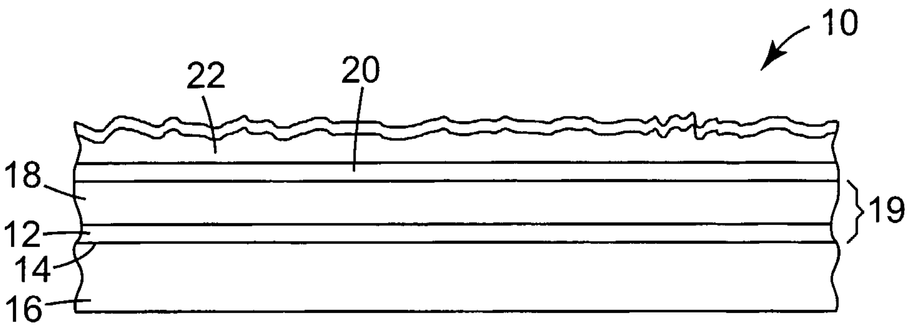
[Continued on next page]

(54) **Title:** DURABLE HIGH INDEX NANOCOMPOSITES FOR AR COATINGS



(57) Abstract: The present invention includes ultraviolet curable compositions preferably containing discrete, crystalline zirconia nanoparticles with reactive, or copolymerizable, surface modification, in a polymerizable monomer/oligomer resin mixture. It is believed that copolymerizable surface modification provides a functional group that enables the functionalized particle to co-polmerize with the reactive monomers, oligomers, and crosslinkers in the formulation. Relative to surface modifation of the nanoparticles, acrylate functionality is preferred over methacrylate functionality. On the other hand, methacrylate functionality is preferred over non-reactive, or nonpolymerizable, functionality. As the nanocomposite cures, the resultant network is heavily crosslinked by selection of raw materials with substantial acrylate functionality.

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DURABLE HIGH INDEX NANOCOMPOSITES FOR AR COATINGS

Background Of The Invention

The development of films or coatings as protective films for display devices such as a CRT screen is well documented in the art. These include antireflective coatings, hardcoats, optical coatings, and the like. Nevertheless, there continues to be a need for further improvement in the development of polymerizable high index materials for optical applications. Exemplary applications include antireflective coatings and hardcoat materials. Many polymerizable films have a refractive index of 1.5 or less. Because of the optical advantages, however, an increase of the refractive index to 1.6 or more would be a desirable improvement, in the development of the very thin coatings (about 85 nm) required for high optical layers for in anti-reflection applications. Furthermore, there is a need for durable, inexpensive, and yet high quality antireflective coatings that exhibit a relatively low reflectance, that is less than 1%.

Another concern is that after application to a useful substrate, many formulations that consist of a mixture of resins, monomers, oligomers, and photoinitiators dewet (or bead up) when the mixture solution is dried of solvent, prior to the UV curing step. As a result, there are portions of the substrate that are not covered with the requisite thickness of the high index layer and other portions that are thicker than desired.

Summary Of The Invention

The above-referenced concerns are resolved by the development of new ultraviolet curable compositions preferably containing discrete, crystalline zirconia nanoparticles with reactive, or copolymerizable, surface modification, in a polymerizable monomer/oligomer resin mixture. It is believed that copolymerizable surface modification provides a functional group that enables the functionalized particle to co-polmerize with the reactive monomers, oligomers, and crosslinkers in the formulation.

Relative to surface modifying nanoparticles, acrylate functionality is preferred over methacrylate functionality. On the other hand, methacrylate functionality is preferred over non-reactive, or nonpolymerizable, functionality. As the nanocomposite cures, the resultant network is heavily crosslinked by selection of raw materials with substantial acrylate functionality.

Mixtures of nanoparticles of different sizes have been found to be advantageous to the invention. In particular, mixtures containing a majority of nanoparticles ranging in size from 10-30nm along with a minority of nanoparticles ranging in size from about 80-150nm, result in highly transparent and durable compositions.

Brief Description Of The Drawings

FIG. 1 illustrates a coating construction containing an optical coating, in accordance with the present invention.

FIG. 2 illustrates a typical display device in accordance with the present invention.

Detailed Description

The present invention includes a composition containing a polymerizable monomer/oligomer resin mixture. The resin mixture is provided at about 30 to 70 wt% of the total composition. Resins with multifunctionality are preferred. Acrylate functionality is preferred over methacrylate functionality. Methacrylate functionality is preferred over nonreactive functionality. Resins of the present invention may be selected from the group including resins having mono acrylate, diacrylate, triacrylates, and multifunctional (>3) acrylates such as tetraacrylate, and pentaacrylate functionality. Other resins may be selected from the group including resins possessing aromatic and halogen functionality (bromine being particularly preferred) to raise the refractive index. Particular resins of the present invention include pentaerythritol tri and tetraacrylate mixture, dipentaerythritol pentaacrylate, diacrylate of epoxidized bisphenol A, diacrylate of epoxidized brominated bisphenol A, and phenoxyethyl acrylate.

Useful crosslinking agents include, for example, poly (meth)acryl monomers selected from the group consisting of (a) di(meth)acryl containing compounds 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 neopentylglycol hydroxypivalate diacrylate, caprolactone modified neopentylglycol hydroxypivalate diacrylate, cyclohexanedimethanol 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 trimethylolpropane diacrylate, neopentyl glycol diacrylate, polyethylene glycol (200) diacrylate, polyethylene glycol (400) diacrylate, polyethylene glycol (600) diacrylate, propoxylated neopentyl glycol diacrylate, tetraethylene glycol diacrylate, tricyclodecanedimethanol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate; (b) tri(meth)acryl containing compounds such as glycerol triacrylate, trimethylolpropane triacrylate, ethoxylated triacrylates (e.g., ethoxylated (3) trimethylolpropane triacrylate, ethoxylated (6) trimethylolpropane triacrylate, ethoxylated (9) trimethylolpropane triacrylate, ethoxylated (20) trimethylolpropane triacrylate), pentaerythritol triacrylate, propoxylated triacrylates (e.g., propoxylated (3) glyceryl triacrylate, propoxylated (5.5) glyceryl triacrylate, propoxylated (3) trimethylolpropane triacrylate, propoxylated (6) trimethylolpropane triacrylate), trimethylolpropane triacrylate, tris(2-hydroxyethyl)isocyanurate triacrylate; (c) higher functionality (meth)acryl containing compounds such as ditrimethylolpropane tetraacrylate, dipentaerythritol pentaacrylate, ethoxylated (4) pentaerythritol tetraacrylate, pentaerythritol tetraacrylate, caprolactone modified dipentaerythritol hexaacrylate; (d) oligomeric (meth)acryl compounds such as, for example, urethane acrylates, polyester acrylates, epoxy acrylates; polyacrylamide analogues of the foregoing; and combinations thereof. Such compounds are widely available from vendors such as, for example, Sartomer Company, Exton, PA; UCB Chemicals Corporation, Smyrna, GA; and Aldrich Chemical Company, Milwaukee, WI. Additional useful (meth)acrylate materials include hydantoin moiety-containing poly(meth)acrylates, for example, as described in U.S. 4,262,072 (Wendling et al.).

A preferred crosslinking agent comprises at least three (meth)acrylate functional groups. Preferred commercially available crosslinking agents include those available from Sartomer Company, Exton, PA such as trimethylolpropane triacrylate (TMPTA) available under the trade designation "SR351", pentaerythritol tri/tetraacrylate (PETA) available under the trade designation "SR444" or "SR295" and dipentraerythritol pentaacrylate available under the trade designation “SR399”. Further, mixtures of multifunctional and lower functional acrylates, such as a mixture of PETA and phenoxyethyl acrylate (PEA) may also be utilized.

Surface modified colloidal nanoparticles are present in the polymerized structure in an amount effective to enhance the abrasion resistance and/or refractive index of the coating. The surface modified colloidal nanoparticles described herein may have a variety of desirable attributes, including for example: nanoparticle compatibility with resin systems such that the nanoparticles form stable dispersions within the resin systems; surface modification to provide reactivity of the nanoparticle with the resin system thereby making the composite more abrasion resistant; and surface modified nanoparticles added to resin systems thereby providing a low impact on the stability of the uncured composition viscosity. A combination of surface modifications can be used to manipulate the uncured and cured properties of the composition. Appropriately surface modified nanoparticles can improve optical and physical properties of the composition such as, for example, improved resin mechanical strength, minimized viscosity changes while increasing solid volume loading in the resin system and maintaining optical clarity while increasing solid volume loading in the resin system.

The surface modified colloidal nanoparticles can be oxide particles having a particle size or associated particle size of greater than 1 nm and less than 200 nm. Their measurements can be based on transmission electron miscroscopy (TEM). The nanoparticles can include metal oxides such as, for example, alumina, tin oxides, antimony oxides, silica, zirconia, titania, mixtures thereof, or mixed oxides thereof. Surface modified colloidal nanoparticles can be substantially fully condensed.

Silica nanoparticles may have a particle size from 5 to 150. Silica nanoparticles may be present in the durable article or optical element in an amount from 10 to 60 wt%, or 10 to 40 wt%. Silicas for use in the materials of the invention are commercially available from Nalco Chemical Co. (Naperville, Ill.) under the product designation NALCO COLLOIDAL SILICAS. For example, silicas include NALCO products 1040, 1042, 1050, 1060, 2327 and 2329.

Zirconia nanoparticles will typically exhibit a particle size from 5-150 nm, or 5 to 75 nm, or 5 to 25 nm, or 5-15 nm. Zirconia nanoparticles can be present in the coating in an amount from 10 to 70 wt%, or 30 to 50 wt%. Zirconias for use in materials of the invention are commercially available from Nalco Chemical Co. (Naperville, Ill.) under the product designation NALCO OOSSOO8, Buhler (Uzweil, Switzerland) under the product designation WO or WOS. 3M Company produces zirconia internally as described in copending U.S. Patent Application Serial No. 11/027426, filed December 30, 2004.

Titania, antimony oxides, alumina, tin oxides, and/or mixed metal oxide nanoparticles can have a particle size or associated particle size from 5 to 50 nm, or 5 to 15 nm, or 10 nm. Titania, antimony oxides, alumina, tin oxides, and/or mixed metal oxide nanoparticles are anticipated to be useful in the durable article or optical element in an amount from 10 to 70 wt%, or 30 to 50 wt%. Mixed metal oxide for use in materials of the invention are commercially available from Catalysts & Chemical Industries Corp., (Kawasaki, Japan) under the product designation Optolake 3.

U.S. Patent No. 6,800,378 further describes other inorganic oxide particles useful as nanoparticles, and, aqueous, organic, and mixed sols that may be employed when surface modifying the nanoparticles of the present invention. Mixed oxides containing more than one type of inorganic atom are also employed as described in U.S. Patent Application No. US2003/0165680. Accordingly, in some embodiments, Ti/Sb mixed oxide nanoparticles may be combined with additional nanoparticles having a different elemental composition (e.g., silica, zirconia, alumina, titania, antimony pentoxide). Desirably, such additional nanoparticles, if present, have an average particle size comparable to that of the Ti/Sb mixed oxide nanoparticles. Such nanoparticles may be commercially obtained, for example, from Nalco Chemical Co. (Naperville, Ill.) or Nyacol Nano Technologies, Inc. (Ashland, Mass.). Exemplary additional nanoparticles are also described in U.S. Pat. Nos. 5,037,579; and 6,261,700.

Surface-treating the nano-sized particles can provide a stable dispersion in the polymeric resin. Preferably, the surface-treatment stabilizes the nanoparticles so that the particles will be well dispersed in the polymerizable resin and results in a substantially homogeneous composition. Furthermore, the nanoparticles can be modified over at least a portion of its surface with a surface treatment agent so that the stabilized particle can copolymerize or react with the polymerizable resin during curing.

The nanoparticles of the present invention are preferably treated with a surface treatment agent. In general a surface treatment agent has a first end that will attach to the particle surface (covalently, ionically or through strong physisorption) and a second end that imparts compatibility of the particle with the resin and/or reacts with resin 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 metal oxide surface. Silanes are preferred for silica and other siliceous fillers. Silanes and carboxylic acids are preferred for metal oxides such as zirconia. The surface modification can be done either subsequent to mixing with the monomers or after mixing. When silanes are employed, reaction of the silanes with the particle or nanoparticle surface is preferred prior to incorporation into the resin. The required amount of surface modifier is dependant upon several factors such as particle size, particle type, modifier molecular weight, and modifier type. In general, it is preferred that about a monolayer of modifier be attached to the surface of the particle. The attachment procedure or reaction conditions required also depend on the surface modifier used. When employing silanes, surface treatment at elevated temperatures under acidic or basic conditions for about 1-24 hours is preferred. Surface treatment agents such as carboxylic acids do not usually require elevated temperatures or extended time.

Representative embodiments of surface treatment agents suitable for the durable compositions include compounds such as, for example, isooctyl trimethoxy-silane, N-(3-triethoxysilylpropyl) methoxyethoxyethoxyethyl carbamate (PEG3TES), Silquest A1230, N-(3- triethoxysilylpropyl) methoxyethoxyethoxyethyl carbamate (PEG2TES), 3-(methacryloyloxy)propyltrimethoxysilane, 3-(Acryloxypropyl)trimethoxysilane, 3-(methacryloyloxy)propyltriethoxysilane, 3-(methacryloyloxy) propylmethyldimethoxysilane, 3-(acryloyloxypropyl)methyldimethoxysilane, 3-(methacryloyloxy)propyldimethylethoxysilane, 3-(methacryloyloxy) propyldimethylethoxysilane, vinyldimethylethoxysilane, phenyltrimethoxysilane, n-octyltrimethoxysilane, dodecyltrimethoxysilane, octadecyltrimethoxysilane, propyltrimethoxysilane, hexyltrimethoxysilane, vinylmethyldiacetoxysilane, vinylmethyldiethoxysilane, vinyltriacetoxysilane, vinyltriethoxysilane, vinyltriisopropoxysilane, vinyltrimethoxysilane, vinyltriphenoxysilane, vinyltri-t-butoxysilane, vinyltris-isobutoxysilane, vinyltriisopropenoxysilane, vinyltris(2-methoxyethoxy)silane, styrylethyltrimethoxysilane, mercaptopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, acrylic acid, methacrylic acid, oleic acid, stearic acid, dodecanoic acid, 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MEEAA), beta-carboxyethylacrylate, 2-(2-methoxyethoxy)acetic acid, methoxyphenyl acetic acid, and mixtures thereof.

The surface modification of the particles in the colloidal dispersion can be accomplished in a variety of ways. The process involves the mixture of an inorganic dispersion with surface modifying agents. Optionally, a co-solvent can be added at this point, such as for example, 1-methoxy-2-propanol, ethanol, isopropanol, ethylene glycol, N,N-dimethylacetamide and 1-methyl-2-pyrrolidinone. The co-solvent can enhance the solubility of the surface modifying agents as well as the surface modified particles. The mixture comprising the inorganic sol and surface modifying agents is subsequently reacted at room or an elevated temperature, with or without mixing. In a preferred method, the mixture can be reacted at about 85 degree C for about 24 hours, resulting in the surface modified sol. In a preferred method, where metal oxides are surface modified the surface treatment of the metal oxide can preferably involve the adsorption of acidic molecules to the particle surface. The surface modification of the metal oxide may take place at room temperature.

The surface modification of ZrO_2 with silanes can be accomplished under acidic conditions or basic conditions. In one preferred case the silanes are preferably heated under acid conditions for a suitable period of time. At which time the dispersion is combined with aqueous ammonia (or other base). This method allows removal of the acid counter ion from the ZrO_2 surface as well as reaction with the silane. In a preferred method the particles are precipitated from the dispersion and separated from the liquid phase and redispersed in a solvent.

The surface modified particles can then be incorporated into the curable resin in various methods. In a preferred aspect, a solvent exchange procedure is utilized whereby the resin is added to the surface modified sol, followed by removal of the water and co-solvent (if used) via evaporation, thus leaving the particles dispersed in the polymerizable resin. The evaporation step can be accomplished for example, via distillation, rotary evaporation or oven drying.

In another aspect, the surface modified particles can be extracted into a water immiscible solvent followed by solvent exchange, if so desired.

Alternatively, another method for incorporating the surface modified nanoparticles in the polymerizable resin involves the drying of the modified particles into a powder, followed by the addition of the resin material into which the particles are dispersed. The drying step in this method can be accomplished by conventional means suitable for the system, such as, for example, oven drying or spray drying.

A combination of surface modifying agents can be useful, wherein at least one of the agents has a functional group co-polymerizable with a hardenable resin. For example, the polymerizing group can be ethylenically unsaturated or a cyclic function subject to ring opening polymerization. An ethylenically unsaturated polymerizing group can be, for example, an acrylate or methacrylate, or vinyl group.

Compositions of the present invention may also be characterized as nanocomposites. Nanocomposites are defined as a polymer matrix that contains well-dispersed nanoparticles. Nanoparticles are defined as particles that are smaller than 200 nanometers and often smaller than 100nm. U.S. Patent No. 5,385,776 exemplifies the current understanding of nanocomposites incorporated within polyamides. A nanoparticle is generally an inorganic particle such as a metal, metal oxide, metal nitride, metal carbide or metal chloride. In accordance with the present invention, the use of high index nanoparticles increases the refractive index of compositions incorporating the same. Preferred nanoparticles include crystalline zirconia, although other high index nanoparticles such as zirconia, silica, titania, antimony, mixtures of metal oxides, mixed metal oxides, and mixtures thereof are acceptable. Crystalline zirconia is preferred over amorphous zirconia due to the greater refractive index of compositions containing crystalline zirconia. The zirconia may optionally contain yttrium in an amount of about 0.1 to 8.0% with regard to the total amount of oxide. Functionalized silica nanoparticles may be added to the zirconia based compositions for added reinforcement and abrasion resistance of the finished coating. Example of useful silica particles are those available from Nalco Chemical Company of Naperville, Illinois. Examples of useful zirconia are those described in U.S. Patent No. 6,376,590, and examples of titania are described in U.S. Patent No. 6,432,526. Zirconia particles may be supplied by NALCO, 3M Company, and BUHLER. Zirconia is typically employed at about 30-70 wt%, with the combination of high refractive index and durability observed when provided at about 50-70 wt%. With lower amounts of zirconia in this preferred range (50-70 wt-%) greater durability was observed as determined by laboratory analysis. Accordingly, 50 wt% of zirconia is most preferred. Silica nanoparticles may be provided at about 0 to 20 wt% with 10 wt% preferred. All weight percents are given relative to the total compositional weight. In the invention, resins are present in 30-70 wt% and nanoparticles are present in 30-70 wt%. The neat formulation method only permits formulation with at most 50 wt% particles, whereas the dilute mixing method permits formulating with unlimited % particles. Therefore, for examples where >50 wt% nanoparticles are employed, the dilute mixing method was utilized.

In further accordance with the present invention, a relatively small percentage of relatively larger particles, but still less than one micron in size, may be included in the present compositions. Because the percentage is low, the use of larger particles of relatively high or low index is included.

The present invention may be distinguished from matte particles. The use of matte coatings as optical films is well known in the display industry. A matte appearance provides enhanced viewing for the reader by lowering glare through the use of relatively larger particles, 1-10 micrometers, that provide "scattered reflection". This sort of product can be prepared without any AR function at all. However, the antiglare (AG) character provided by these larger particles may be added to an antireflection (AR) construction by incorporation of the large (1-10 micron) particles either in the hardcoat layer or in the high index layer as described by Fuji, U.S. Patent No. 6,693,746.

Surface modification of the nanoparticles relates to the reaction of specific molecules on the surface of particles, and is useful in achieving good dispersion or solubility within the polymer matrix, improved coating transparency, and improved coating durability. Accordingly, the nanoparticles are preferably treated with surface modifying agents such as carboxylic acids, silanes and/or dispersants to help compatibilize them with the polymer matrix. U.S. Patent No. 6,329,058 exemplifies typical surface modifiers. In essence, it is believed that surface modification prevents particle agglomeration thereby facilitating particle dispersion within the monomers and resins, and therefore enhancing the transparency of the coating formulation. Furthermore, the mixtures of the present invention contain high index nanoparticles thereby resulting in films or coatings less likely to dewet when dried out of solvent, thus enabling the formation of very thin but uniform coatings that may then by UV cured to form uniform high refractive index layers. Surface modification is also necessary for transparency and assist in easy particle dispersion in the monomers, solvents, and resins. Surface modifier molecules exhibit a functionality that can covalently bond or adsorb to the particle surface. For example, carboxylic acid or silane functionality can covalently bond or adsorb to particle surface and examples of these modifiers include methoxyethoxyethoxyacetic acid

(MEEAA) and Silquest A-1230™. The use of surface modifiers with high refractive index is also preferred and includes naphthyl acetic acid and trimethoxy phenyl silane.

The nanoparticles of the present invention may also be surface modified by reactive or copolymerizable surface modifiers. Reactive surface modification means that surface modifiers are employed that include functional groups that facilitate polymerization in addition to functionality that can either adsorb or covalently bond with the particle surface.

When a coating of the present invention is polymerized (or cured), it forms a nanocomposite having particles covalently linked to the polymer matrix thus enhancing the durability of the cured coating. Examples of such modifiers are acrylic acid, methacrylic acid, and silanes with a radical polymerizable group, such as the trimethoxysilylpropylmethacrylate, preferred acrylate silane, and silica. When employing mixtures of nanoparticles, a combination of benefits may be realized. For example, surface modified zirconia may be added to raise the refractive index, while surface modified silica may be added to further enhance durability.

Compositions of the present invention may further contain any of the well known Type I and Type II UV photoinitiators, such as the substituted acetophenones, benzoins, phosphine oxides, benzophenone/amine combinations, and other photoinitiator classes well known to those in the art. Exemplary photoinitiators include Irgacure™ 819, Darocure™ 1173, or TPO supplied for example by Ciba Specialty Chemicals of Tarrytown, New York, and TPO-L supplied for example by BASF. It is believed that radical photoinitiators cleave in the presence of ultraviolet light to form radicals that initiate the polymerization of the acrylate and methacrylate functional groups in the formulation to form the crosslinked nanocomposite. Known types and classes of radical photoinitiators may be employed as described in, "Chemistry and Technology of UV & EB Formulation For Coatings, Inks, & Paints" of Volume 3 of Photoinitiators for Free Radical Cationic Polymerization, published by SITA Technology Ltd., Gardiner House, Broomhill Road, LONDON SW18184JQ ENGLAND.

Specific photoinitiators which are useful in the compositions of the invention include onium salts as described in U.S. Patent No. 5,545,676. Onium salts have been found to be useful as coinitiators in high speed visible light curing of free radically polymerizable systems. Photoinitiators are typically employed from about 0.05 wt% to about 10 wt%, and more preferably at about 1 to 4 wt%.

The refractive index of the composite is a function of the ZrO_2 loading and the index of the resin. Refractive indices can be calculated employing known densities, refractive indices of the particles or resins, and weight ratios using a volume average method. For example for a two component system weight percents are converted to volume percentages and the net refractive index is the sum of (volume fraction 1 times index 1) + (volume fraction 2 times index 2).

The durability is a function of the particle loading, particle size, particle size distribution, the surface treatment, film surface roughness, the resin system crosslinking, and the surface treatment reactivity with the curing resin matrix. It has been shown that surface modification using materials that react into the matrix give much better durability than nonreactive surface treatments. A preferred surface treatment agent is 3-(acryloxypropyl)trimethoxy silane.

The compositions need to provide a high refractive index layer that is very thin (less about 110nm) and are desirably durable. It is also preferred that they can be processed by fluid coating techniques and hardened rapidly at temperatures low enough to not destroy polymer films substrates such as PET. Compositions have been found that meet these requirements. The compositions have been effectively solvent coated and cured on polymeric films. Reproducible coating thickness of below 100 nm have been obtained.

It has been found that surface roughness on a very small scale gives an increase in durability without affecting the optical quality. This roughness may be obtained by incorporating a small amount of larger particles into the composition. This can be accomplished, for instance, by using ZrO_2 with a broad particle size distribution or deliberate introduction of a small fraction of larger particles. The surface roughness may also develop due to certain drying or curing conditions. The surface topography can be measured by Atomic Force Microscopy (AFM). AFM measurements show various amounts of roughness for different compositions. The AFM reveals "peaks" that rise up out of the surface as much as 120 nm high in some samples. These peaks may serve to keep the source of abrasion away from the cured surface. The surface of the UV cured films of the invention have been studied by AFM (atomic force microscopy). The "10 pt mean" is the mean value of the highest 10 points observed in a 10 um by 10 um square on the surface of the film. The films with the higher 10 pt mean values have a rougher surface and performed better (with the preferred nanoparticle surface modification) in the cheesecloth abrasion test.

The instrument used for this analysis was a Digital Instruments Dimension 5000 SPM. The probes used were Olympus OTESPA single crystal silicon levers with a force constant of ~40N/M. The mode of operation was tapping-mode™, the scan size was 10 micrometers on a side (10 x 10 μm imaged area), the scan speed was 1.02 Hz, the imaging setpoint ratio was 75% of the original amplitude signal in space (A_0) (A_{sp}/A_0=1.5/2/0). The data was fit to a plane to correct for sample tilt. The Rz (10 point mean) was measured on the 10 μm datasets (where Rz is the average of the ten greatest peak-to-valley separations on the sample;

$$\frac{1}{n}[(H_1 + H_2 \ldots H_n) - (L_1 + L_2 + \ldots L_n)]$$

where Hn are the ten highest points in the dataset and Ln are the ten lowest points.

Ten micron by ten micron squares were measured with the AFM and the mean value of the 10 highest peaks was then recorded. The rougher films all employ bigger particles, in the form of the broader distribution zirconia (zirconia sol 1 and zirconia sol 2) or the bimodal distribution containing primarily smaller zirconia and larger silica, in the dimensions and weight percents characterized herein. With regard to the "10 point peak mean", at least 30nm is desired for preferred durability or suitable roughness, but no greater than 1000nm. It has been found that roughness is not the only factor that contributes to good performance or optimum durability. The particulates are preferably treated with acrylate silanes rather than methacrylate silanes, although both may be employed in the present invention. Furthermore, it has been found that compositions containing 70 wt% or more zirconia (or total inorganic particles) exhibit a relative reduced durability.

Coatings made in accordance with the present invention exhibit a 10 point mean roughness value of at least 30 nanometers and as high as 120 nanometers, as examined using Atomic Force Microscopy on a typical 10 x 10 micrometer area. Preferably, the roughness is 60-120 nm.

One method for obtaining the rough surface is incorporation of a minority of larger particles into the formulation. This can be done by using a nanoparticle with a broader particle size distribution. Alternatively a rough surface may be obtained by deliberately adding a minority of larger sized particles into a formulation with smaller particles.

Particle size and particle size distribution were determined by Photon Correlation Spectroscopy (PCS). The volume-average particle size was determined by Photon Correlation Spectroscopy (PCS) using a Malvern Series 4700 particle size analyzer (available from Malvern Instruments Inc., Southborough, MA). Dilute zirconia sol samples were filtered through a 0.2 μm filter using syringe-applied pressure into a glass cuvette that was then covered. Prior to starting data acquisition the temperature of the sample chamber was allowed to equilibrate at 25 °C. The supplied software was used to do a CONTIN analysis with an angle of 90 degrees. CONTIN is a widely used mathematical method for analyzing general inverse transformation problems that is further described in S.W. Provencher, Comput. Phys. Commun., 27, 229 (1982). The analysis was performed using 24 data bins. The following values were used in the calculations: refractive index of water equal to 1.333, viscosity of water equal to 0.890 centipoise, and refractive index of the zirconia particles equal to 1.9.

Two particle size measurements were calculated based on the PCS data. The intensity-average particle size, reported in nanometers, was equal to the size of a particle corresponding to the mean value of the scattered light intensity distribution. The scattered light intensity was proportional to the sixth power of the particle diameter. The volume-average particle size, also reported in nanometers, was derived from a volume distribution that was calculated from the scattered light intensity distribution taking into account both the refractive index of the zirconia particles and the refractive index of the dispersing medium (i.e., water). The volume-average particle size was equal to the particle size corresponding to the mean of the volume distribution. The intensity-average particle size was divided by the volume-average particle size to provide a ratio that is indicative of the particle size distribution.

Relative to size distribution, it is believed that grinding zirconia particles produces a broad spectrum of relatively smaller particles with a reduced quantity of relatively larger particles dispersed therein.

The size and size distribution can be measured by photon correlation spectroscopy. The polydispersity term above is a measure of the distribution of different size particles. As polydispersity values become smaller, the closer the actual distribution is to the ideal case where all the particles are identical in size (i.e. they are monodisperse). In accordance with the present invention, it is desirable to have a distribution of relatively larger and smaller particles. Accordingly, a polydispersity value ranging from 0.4 to 0.8, and more preferably about 0.6 to 0.7, is desired to provide the protrusion of larger particles that is believed to lead to greater durability. The volume mean and Z average means are values the instrument predicts would match the light scattering data. In the analysis of the particle sizes, the Z average substantially emphasizes those particles that are on the high end of the distribution. Accordingly, a Z average mean ranging from about 20 to 80, and more preferably about 60 to 65, is desired. On the other hand, the volume mean typically measures about 3.5 to about 20. What is most important is that the compositions of the present invention contain larger particles mixed with smaller particles. The Intensity (I) mean is the calculated mean of particle size that deflects the light. As large particles are far more likely to encounter the light than small ones, the intensity mean, like the Z average mean, emphasizes those particles that are very large. As shown in the table relative to Malvern PCS Measurements, an intensity mean of about 25 to 150, and more preferably 90 to 105, reflects useful batches of nanoparticles with respect to larger particles. In this patent application, the large particles are believed to be those that protrude from the surface of the film. Accordingly, the exact quantity of very large particles is not assessed, and the presence of this population is described by the polydispersity, Z average mean, I average, and the ratio of I average to the Volume average. The ratio of I average to the Volume average typically ranges from about 1.5 to about 18, wherein a preferred value is about 14.28.

Bimodal particle distribution

In the mixtures of ZrO_2 with silica that provide a bimodal particle distribution the fraction of particles that are large is equal to (wt-% large particles) / (total wt-% particles). The fraction of large particles is preferably at least 5% and more preferably at least 10% . The fraction of large particle is typically less than 40 wt-% and preferably ranges up to 35%. Other relatively larger particles may include zirconia for example.

The majority of nanoparticles are sized to have a Volume mean average of 10-30 nanometers. "Majority" is defined to be over 50% by weight of the nanoparticles, and more preferably from about 67 to 90% by weight. A minority of nanoparticles are sized to have an average cross-sectional diameter of about 80-150 nanometers. "Minority" is defined to be less than 50% by weight of the nanoparticles, and more preferably from about 33 to 10% by weight. To illustrate, Example 51 has 40 wt% ZrO_2 and 20 wt% silica with the weight percents relative to the total compositional weight. Therefore, the % of large particles as a % of all of the particles is 20/60 or about 33.3%. Accordingly, in yet a further aspect of the invention, a composition as described above and further containing a particle distribution as described immediately above is believed to give superior durability while retaining refractive indices greater than 1.60.

Other additives may included in the present compositions. For example, UV sensitizers, oxygen scavengers, and other components useful in free radical curing may be employed as known in the art.

Films made in accordance with the present invention may be layered, laminated, or otherwise coupled to other films or display devices in accordance with the present invention. U.S. Patent No. 6,800,378 describes a process of bonding layers of film together and also of bonding the antireflective film, for example, upon a display device. The same process may be employed in accordance with the present invention. Known techniques of preparing multilayer films may be employed to include spin coating, knife coating, and the like.

In yet another aspect of the invention, the optical films described above are included within an antireflective film construction. As shown in FIG. 1, an antireflective coating 10 contains a substrate 12 (e.g. formed from PET or polycarbonate), or any other material recognized for its utility as a substrate in antireflective films. An adhesive 14 may be provided on both sides of the substrate 12 whereby the substrate 12 is coupled to a display device 16 and also to a juxtaposed layer outwardly oriented from the substrate 12. In accordance with the present invention, a hardcoat layer 18 is coupled to and layered over substrate 12 thereby forming an outwardly oriented layer in physical contact with substrate 12. An optical layer 20 having a relatively high refractive index of at least 1.6, formed as described above, is next coupled to and layered over hardcoat layer 18. If desired, the construct 10 may include other layers typically used in antireflective film such as a relatively lower refractive index layer 22, or an anti-smudge layer (not shown) as known in the art.

The substrate 12 may comprise or consist of any of a wide variety of non-polymeric materials, such as glass, or various thermoplastic and crosslinked polymeric materials, such as polyethylene terephthalate (PET), (e.g. bisphenol A) polycarbonate, cellulose acetate, poly(methyl methacrylate), polyolefins such as biaxially oriented polypropylene which are commonly used in various optical devices. The substrate may also comprises or consist of polyamides, polyimides, phenolic resins, polystyrene, styrene-acrylonitrile copolymers, epoxies, and the like. In addition, the substrate 16 may comprise a hybrid material, having both organic and inorganic components.
Typically the substrate will be chosen based in part on the desired optical and mechanical properties for the intended use. Such mechanical properties typically will include flexibility, dimensional stability and impact resistance. The substrate thickness typically also will depend on the intended use. For most applications, substrate thicknesses of less than about 0.5 mm are preferred, and more preferably about 0.02 to about 0.2 mm. Self-supporting polymeric films are preferred. The polymeric material can be formed into a film using conventional filmmaking techniques such as by extrusion and optional uniaxial or biaxial orientation of the extruded film. The substrate can be treated to improve adhesion between the substrate and the hardcoat layer, e.g., chemical treatment, corona treatment such as air or nitrogen corona, plasma, flame, or actinic radiation. If desired, an optional tie layer or primer can be applied to the substrate and/or hardcoat layer to increase the interlayer adhesion.

Various light transmissive optical film are known including but not limited to, multilayer optical films, microstructured films such as retroreflective sheeting and brightness enhancing films, (e.g. reflective or absorbing) polarizing films, diffusive films, as well as (e.g. biaxial) retarder films and compensator films such as described in U.S. Patent Application Publication No. 2004-0184150, January 29, 2004.

As described is U.S. Patent Application 2003/0217806, multilayer optical films, i.e., films that provide desirable transmission and/or reflection properties at least partially by an arrangement of microlayers of differing refractive index. The microlayers have different refractive index characteristics so that some light is reflected at interfaces between adjacent microlayers. The microlayers are sufficiently thin so that light reflected at a plurality of the interfaces undergoes constructive or destructive interference in order to give the film body the desired reflective or transmissive properties. For optical films designed to reflect light at ultraviolet, visible, or near-infrared wavelengths, each microlayer generally has an optical thickness (i.e., a physical thickness multiplied by refractive index) of less than about 1 μm. However, thicker layers can also be included, such as skin layers at the outer surfaces of the film, or protective boundary layers disposed within the film that separate packets of microlayers. Multilayer optical film bodies can also comprise one or more thick adhesive layers to bond two or more sheets of multilayer optical film in a laminate.

The reflective and transmissive properties of multilayer optical film body are a function of the refractive indices of the respective microlayers. Each microlayer can be characterized at least at localized positions in the film by in-plane refractive indices n_x, n_y, and a refractive index n_z associated with a thickness axis of the film. These indices represent the refractive index of the subject material for light polarized along mutually orthogonal x-, y-, and z-axes. In practice, the refractive indices are controlled by judicious materials selection and processing conditions. Films can be made by co-extrusion of typically tens or hundreds of layers of two alternating polymers A, B, followed by optionally passing the multilayer extrudate through one or more multiplication die, and then stretching or otherwise orienting the extrudate to form a final film. The resulting film is composed of typically tens or hundreds of individual microlayers whose thicknesses and refractive indices are tailored to provide one or more reflection bands in desired region(s) of the spectrum, such as in the visible or near infrared. In order to achieve high reflectivities with a reasonable number of layers, adjacent microlayers preferably exhibit a difference in refractive index (δ n_x) for light polarized along the x-axis of at least 0.05. If the high reflectivity is desired for two orthogonal polarizations, then the adjacent microlayers also preferably exhibit a difference in refractive index (δ n_y) for light polarized along the y-axis of at least 0.05. Otherwise, the refractive index difference can be less than 0.05 and preferably about 0 to produce a multilayer stack that reflects normally incident light of one polarization state and transmits normally incident light of an orthogonal polarization state. If desired, the refractive index difference (δ n_z) between adjacent microlayers for light polarized along the z-axis can also be tailored to achieve desirable reflectivity properties for the p-polarization component of obliquely incident light.

Exemplary materials that can be used in the fabrication of polymeric multilayer optical film can be found in PCT Publication WO 99/36248 (Neavin et al.). Desirably, at least one of the materials is a polymer with a stress optical coefficient having a large absolute value. In other words, the polymer preferably develops a large birefringence (at least about 0.05, more preferably at least about 0.1 or even 0.2) when stretched. Depending on the application of the multilayer film, the birefringence can be developed between two orthogonal directions in the plane of the film, between one or more in-plane directions and the direction perpendicular to the film plane, or a combination of these. In special cases where isotropic refractive indices between unstretched polymer layers are widely separated, the preference for large birefringence in at least one of the polymers can be relaxed, although birefringence is still often desirable. Such special cases may arise in the selection of polymers for mirror films and for polarizer films formed using a biaxial process, which draws the film in two orthogonal in-plane directions. Further, the polymer desirably is capable of maintaining birefringence after stretching, so that the desired optical properties are imparted to the finished film. A second polymer can be chosen for other layers of the multilayer film so that in the finished film the refractive index of the second polymer, in at least one direction, differs significantly from the index of refraction of the first polymer in the same direction. For convenience, the films can be fabricated using only two distinct polymer materials, and interleaving those materials during the extrusion process to produce alternating layers A, B, A, B, etc. Interleaving only two distinct polymer materials is not required, however. Instead, each layer of a multilayer optical film can be composed of a unique material or blend not found elsewhere in the film. Preferably, polymers being coextruded have the same or similar melt temperatures.

Exemplary two-polymer combinations that provide both adequate refractive index differences and adequate inter-layer adhesion include: (1) for polarizing multilayer optical film made using a process with predominantly uniaxial stretching, PEN/coPEN, PET/coPET, PEN/sPS, PET/sPS, PEN/Eastar,.TM. and PET/Eastar,.TM. where "PEN" refers to polyethylene naphthalate, "coPEN" refers to a copolymer or blend based upon naphthalene dicarboxylic acid, "PET" refers to polyethylene terephthalate, "coPET" refers to a copolymer or blend based upon terephthalic acid, "sPS" refers to syndiotactic polystyrene and its derivatives, and Eastar™ is a polyester or copolyester (believed to comprise cyclohexanedimethylene diol units and terephthalate units) commercially available from Eastman Chemical Co.; (2) for polarizing multilayer optical film made by manipulating the process conditions of a biaxial stretching process, PEN/coPEN, PEN/PET, PEN/PBT, PEN/PETG and PEN/PETcoPBT, where "PBT" refers to polybutylene terephthalate, "PETG" refers to a copolymer of PET employing a second glycol (usually cyclohexanedimethanol), and "PETcoPBT" refers to a copolyester of terephthalic acid or an ester thereof with a mixture of ethylene glycol and 1,4-butanediol; (3) for mirror films (including colored mirror films), PEN/PMMA, coPEN/PMMA, PET/PMMA, PEN/Ecdel™, PET/Ecdel™, PEN/sPS, PET/sPS, PEN/coPET, PEN/PETG, and PEN/THV™, where "PMMA" refers to polymethyl methacrylate, Ecdel™ is a thermoplastic polyester or copolyester (believed to comprise cyclohexanedicarboxylate units, polytetramethylene ether glycol units, and cyclohexanedimethanol units) commercially available from Eastman Chemical Co., and THV™ is a fluoropolymer commercially available from 3M Company.

Further details of suitable multilayer optical films and related constructions can be found in U.S. Pat. No. 5,882,774 (Jonza et al.), and PCT Publications WO 95/17303 (Ouderkirk et al.) and WO 99/39224 (Ouderkirk et al.). Polymeric multilayer optical films and film bodies can comprise additional layers and coatings selected for their optical, mechanical, and/or chemical properties. See U.S. Pat. No. 6,368,699 (Gilbert et al.). The polymeric films and film bodies can also comprise inorganic layers, such as metal or metal oxide coatings or layers.

The term “low refractive index” layer typically has a refractive index of less than about 1.5, and more preferably less than about 1.45, and most preferably less than about 1.42. The minimum refractive index of the low index layer is typically at least about 1.35. The term “high refractive index”, for the purposes of the present invention, shall generally mean a material, when applied as a layer to a substrate, forms a coating layer having a refractive index of greater than about 1.6. The maximum refractive index of the high index layer is typically no greater than about 1.75. The difference in refractive index between the high index layer and low index layer is typically at least 0.15 and more typically 0.2 or greater.

The low index layer 22 may be formed as known in the art. U.S. Patent No. 6,723,423 exemplifies the known understanding of forming a low refractive index layer, although not by way of limitation. An exemplary low index layer may be formed from low refractive index fluoropolymer compositions and derived from an interpenetrating polymer network or semi-interpenetrating polymer network which includes a reactive fluoroplastic and/or a fluoroelastomer (i.e. the functional fluoropolymer phase) blended with multi-functional acrylates (i.e. the acrylate phase) such as trimethylolpropane triacrylate (TMPTA) and optionally additional fluorinated mono-functional acrylates or multi-functional fluorinated acrylates which can be coated and cured by ultraviolet light or by thermal means. The presence of an acrylate crosslinker provides a composition with both low refractive index and improved adhesion to high index polymer substrates such as polyethylene terephthalate ("PET") or hard coated PET films. The low index coating mixture preferably describes a reactive high molecular weight fluoropolymer(s) that can participate in the crosslinking reactions between the monomeric multi-functional acrylates. This enhances the crosslinkability of the fluoropolymer phase to the forming polyacrylate phase and produces a co-crosslinked, interpenetrating or semi-interpenetrating polymer network with enhanced interfacial contact between the high index layer and the low index layer and thereby improves durability and low refractive index.

Various optional permanent and removable grade adhesive compositions 14 may be coated on the opposite side of the substrate 12 (i.e. to that of the hardcoat 18) so the article 10 can be easily mounted to a display surface. Typically, the adhesive 14, substrate 12, and hard coating layer 18 are prepackaged as a film 19 having a release layer (not shown) attached to the adhesive 14. The release layer is then removed and the adhesive layer 14 coupled to a housing or other area of the display 16 to form the optical display 16.

Suitable optional adhesive compositions 14 include (e.g. hydrogenated) block copolymers such as those commercially available from Kraton Polymers, Westhollow, TX under the trade designation "Kraton G-1657", as well as other (e.g. similar) thermoplastic rubbers. Other exemplary adhesives include acrylic-based, urethane-based, silicone-based and epoxy-based adhesives. Preferred adhesives are of sufficient optical quality and light stability such that the adhesive does not yellow with time or upon weather exposure so as to degrade the viewing quality of the optical display. The adhesive can be applied using a variety of known coating techniques such as transfer coating, knife coating, spin coating, die coating and the like. Exemplary adhesives are described in U.S. Patent Application Publication No. 2003/0012936. Several of such adhesives are commercially available from 3M Company, St. Paul, MN under the trade designations 8141, 8142, and 8161. The substrate layer 12 may consist of any of a wide variety of non-polymeric materials, such as glass, or polymeric materials, such as polyethylene terephthalate (PET), bisphenol A polycarbonate, cellulose triacetate, poly(methyl methacrylate), and biaxially oriented polypropylene which are commonly used in various optical devices.

The antireflection materials are particularly useful for optical displays ("displays"). The antireflection material functions to decrease glare and decrease transmission loss while improving durability and optical clarity.

Such displays include multi-character and especially multi-line multi-character displays such as liquid crystal displays ("LCDs"), plasma displays, front and rear projection displays, cathode ray tubes ("CRTs"), signage, as well as single-character or binary displays such as light emitting tubes ("LEDs"), signal lamps and switches. The light transmissive (i.e. exposed surface) substrate of such display panels may be referred to as a "lens." The invention is particularly useful for displays having a viewing surface that is susceptible to damage.

The coating composition, and reactive product thereof, as well as the protective articles of the invention, can be employed in a variety of portable and non-portable information display articles. These articles include, but are not limited by, PDAs, LCD-TV's (both edge-lit and direct-lit), cell phones (including combination PDA/cell phones), touch sensitive screens, wrist watches, car navigation systems, global positioning systems, depth finders, calculators, electronic books, CD and DVD players, projection televisions screens, computer monitors, notebook computer displays, instrument gauges, instrument panel covers, signage such as graphic displays and the like. These devices can have planar viewing faces, or non-planar viewing faces such as slightly curved faces.

The coating composition or coated film, can be employed on a variety of other articles as well such as for example camera lenses, eyeglass lenses, binocular lenses, mirrors, retroreflective sheeting, automobile windows, building windows, train windows, boat windows, aircraft windows, vehicle headlamps and taillights, display cases, eyeglasses, road pavement markers (e.g. raised) and pavement marking tapes, overhead projectors, stereo cabinet doors, stereo covers, watch covers, as well as optical and magneto-optical recording disks, and the like.

The invention is further illustrated, but not thereby limited, by the Examples given below.

Raw Materials and Suppliers

The table given below lists the various tradenames mentioned herein, and the respective chemical and respective supplier for each tradename.

Material	Chemical Name	Vendor or source
SR295	Mixture of pentaerythritol tri and tetraacrylate	Sartomer
CN120Z	Acrylated bisphenol A	Sartomer
SR339	Phenoxyethyl acrylate	Sartomer
SR399	Dipentaerythritol pentaacrylate	
MEEAA	Methoxyethoxyethoxyacetic acid	Sigma-Aldrich
ASi	3-(acryloxypropyl)trimethoxysilane	Gelest
A1230	Nonionic silane	OSI Specialties, a Crompton Corp.
AA	Acrylic Acid	Sigma-Aldrich
Dowanol[PM]	1-Methoxy-2-Propanol	Sigma-Aldrich
A174	(3-Methacryloxy)propyltrimethoxysilane	OSI Specialties, a Crompton Corp.
Darocure 1173	2-Hydroxy-2-methyl-1-phenyl-2-propan-1-one	Ciba Specialty Chemicals
Irgacure 819		Ciba Specialty Chemicals
Lucirin TPO-L		BASF
ZrO_2 Sol 1	Buhler ZrO_2 Sol WO lot 1	Buhler, Uzweil, Switzerland
ZrO_2 Sol 2	Buhler ZrO_2 sol WO lot 2	Buhler, Uzweil, Switzerland
ZrO_2 Sol 3	Buhler ZrO_2 Sol WOS (lot 3)	Buhler, Uzweil, Switzerland
ZrO_2 Sol 4	Nalco ZrO_2 Sol	Nalco Chemical

		Company
ZrO_2 Sol 5	Several batches were used in this application all made similarly according to copending application serial no. 11/027426, filed December 30, 2004	3M
Silica Sol 1	Nalco SiO_2 Sol (110 nm) XC3A0265AO	Nalco Chemical Company
Prostab 5198	Inhibitor	Ciba Specialty Chemicals
RDX51027	Diacrylate of brominated bisphenol A	Surface Specialties, Smyrna, GA.

Particle size determination

The particle size and particle size distribution for ZrO2 Sol 1, sol 2, sol 3, and sol 5 were measured via photon correlation spectroscopy. Appropriate lots of nanoparticles were examined with a Malvern PCS Autosizer 4700 (from Malvern Instruments Ltd, Malvern, UK) with a laser wavelength of 488nm, temperature 25.0C, cell type ZET5110, and detector angle of 90deg. For the ZrO2 dispersions, an appropriate amount was diluted in water, and measured with settings of Dispersant R.I. 1.33 and sample R.I. 1.90. The measurements were performed on 5 samples of each sol, each sample measurement was measured 20 times and the average values are reported for each sol.

For the analysis of the data by CUMULANTS analysis, a monomodal (or Gaussian) distribution is presumed. A Z average mean or (intensity mean size) is calculated (and is proportional to d^6 where d=particle diameter) and the polydispersity is a measure of the breadth of the distribution. Larger polydispersities imply bigger distributions and therefore some larger particles.

For the analysis of the data by CONTIN, which is a multimodal method, particles are not presumed to be monomodal, and values of Intensity average (I-ave) and volume average (V-ave) are calculated. As the Intensity average is proportional to d^6, whereas volume average is proportional to d^3, the Intensity average gives higher weight to larger particles. Therefore the larger the ratio of I-ave/V-ave, the bigger the distribution. The table below presents the analysis results from both the CUMULANTS and CONTIN analysis.

The particle size of SiO_2 sol 1 was not measured. The manufacturer reports a size of 110nm with a narrow size distribution

Malvern PCS Measurements						
ZrO_2	Dispersant RI=1.33	Sample RI=1.90				
Sample	Z Ave Mean (nm)	Polydispersity	Intensity Mean (nm)	Volume Mean (nm)	Analysis mode	I ave /V ave
ZrO_2 sol 3	35.7	0.442	57.4	13.3	Contin	4.31
ZrO_2 sol 2	54.0	0.645	118.0	8.5	Contin	13.8
ZrO_2 sol 4	70.5	0.655	144.3	10.1	Contin	14.28
ZrO_2 sol5	27.4	0.223	34.4	17.3	Contin	1.98

Data for ZrO_2 sol 5 is representative data from one of the batches used.

EXAMPLE 1:

General Approach to Formulation Preparation:

Neat Preparation: One or more commercially available resins with various levels of functionality such as mono acrylate, diacrylate, tetraacrylate, and pentaacrylate functionality, were mixed in amber jars. Some resins possessed aromatic and halogen functionality (bromine is especially preferred) to raise the refractive index. Surface modified nanoparticles (prepared separately) were added in the solvent, along with a photoinitiator, and then the solvent was removed by rotary evaporation. This process yields a neat, viscous mixture of particles in resins. This material can then be combined with coating solvents, photoinitiators, and other adjuvants.

Solution Mixing: Nanoparticles were surface modified and transferred into a solvent. Resins were mixed in a separate container with solvent. Resin solution and nanoparticles solutions are then mixed in desired proportions. The process is not encumbered by viscosity. Typical solvents include methyl ethyl ketone (MEK), acetone, toluene, and ethyl acetate. The loading of all solids within the solvent, including the particles, modifiers, resins, monomers, photoinitiators, is about 2 to 20 wt-%, with the solvent comprising the remainder of the weight. With the solution mixing approach, nanoparticles may be added between 0-100% of the solids, and resins may be added between 0-100 wt-% of the solids, as there is no viscosity constraint. For the purposes of the overall invention, the useful loading of the nanoparticles is 30-70 wt-% of the solids and the useful loading of the resins is 30-70 wt-% of the solids.

EXAMPLE 2:

Surface Modification of Zirconia Nanoparticles:

1. Preparation of Silane-modified Zirconia Nanoparticle Dispersion

400.0 grams of ZrO_2 Sol 4 and 26.57 grams of MEEAA were charged to a 1 L round bottom flask. The water and acetic acid were removed via rotary evaporation at 80°C. The powder thus obtained was redispersed in 398 grams of D.I. water. 416.56 grams of the particles dispersed in water was charged to a 2L beaker. While stirring the particle dispersion, 800 grams of 1-methoxy-2-propanol, 45.0 grams of Silane A-174™, and 29.21 grams of Silquest A-1230™ were slowly added to the beaker. This mixture was then poured into two quart-sized jars, sealed and heated to 90°C for three hours. The contents of the jars were removed and concentrated via rotary evaporation to 40.43 wt% zirconia. 1268.0 grams of deionized water and 42.0 grams concentrated aqueous ammonia (29% ammonia) were charged to a 4L beaker.

The concentrated dispersion was added slowly to the beaker while stirring. The white precipitate thus obtained was isolated via vacuum filtration and washed with additional deionized water. The damp solids were dispersed in methylethylketone (MEK). The resultant silane modified zirconia dispersion contained 14.89% zirconia and was employed in making the formulations described in Examples 29, 30, and 34.

2. Preparation of Silane-modified Zirconia Nanoparticle Dispersion

400.0 grams of ZrO_2 Sol 4 and 26.57 grams of MEEAA were charged to a one liter round bottom flask. The water and acetic acid were removed via rotary evaporation. The powder thus obtained was redispersed in 302.82 grams of deionized water and charged to a two liter beaker to which was added while stirring 800 grams 1-methoxy-2-propanol, 41.19 grams of (trimethoxysilyl)propyl acrylate, 29.34 grams of Silquest™A-1230 and 0.5 grams of a 2% solution of Prostab™5198 in water. This mixture was stirred thirty minutes at room temperature then poured into 1L (quart) jars, sealed and heated to 90°C for 3.0 hours. The contents of the jars were removed and concentrated via rotary evaporation. 1242 grams of deionized water and 42 grams of concentrated aqueous ammonia (29%

ammonia) were charged to a 4L beaker. The concentrated dispersion was added slowly to the beaker with stirring. The white precipitate thus obtained was isolated via vacuum filtration and washed with additional deionized water. The damp solids were dispersed in acetone. The resultant silane modified zirconia dispersion contained 16.2% zirconia. Zirconia dispersions were all filtered to less than one micron. This material was formulated by the dilute solution method to make example 33.

3. ZrO_2 Sol 5 75/25 3-(acryloxypropyl)trimethoxy silane/A1230

Dialysis: ZrO_2 sol 5 (1,085g 44.53wt% solids) was charged to 5 dialysis bags (Spectra/Por Molecularporous Membrane tubing MWCO 12-14,000) and dialyzed in 8 lt of DI water. The water was replenished after 30 min and after 12hr. The sol was isolated (1291.2g, 35.64% solids) and used for the silane treatment.

The dialyzed ZrO_2 sol (320.19g, 35.63% solids, 32.25% ZrO_2) was charged to a 1 qt jar. DI water (150g) was charged with stirring. Methoxypropanol (443g), 3-(acryloxypropyl) trimethoxy silane (26.92g) and A1230 (18.23g) were charged to a 1lt beaker with stirring. The methoxypropanol mixture was then charged to the ZrO_2 sol with stirring. The jar was sealed and heated to 90°C for 4hr 40min. After heating the mixture was concentrated to 405 g via rotary evaporation. DI water (1290g) and concentrated NH_3 (29.5g, 29 wt-%) were charged to a 4 l beaker. The above concentrated sol was added to this with minimal stirring. A white precipitate was obtained. The precipitate was isolated as a damp filter cake via vacuum filtration. The damp solids (360g) were dispersed in methoxypropanol (1400g). The mixture was stirred for about 48 h. The mixture was then concentrated (265.29g) via rotary evaporation. Methoxypropanol (248g) was added and the mixture concentrated (273.29 g) via rotary evaporation. Methoxypropanol was charged (221g) and the mixture was concentrated via rotary evaporation. The final product 282.29g was isolated at 45.24% solids. The mixture was filtered thru a 1 micron filter. This material was used in examples 48-52.

4. ZrO_2 Sol 3 75/25 3-(acryloxypropyl)trimethoxy silane/A1230

The ZrO_2 sol 3 (400.7g, 23.03 % ZrO_2) was charged to a 1 qt jar. Methoxypropanol (400g), 3-(acryloxypropyl) trimethoxy silane (18.82g) and A1230 (12.66g) were charged to a 1l beaker with stirring. The methoxypropanol mixture was then charged to the ZrO2 sol with stirring. The jar was sealed and heated to 90°C for 5.5hr. After heating the mixture (759g) was stripped to 230.7g via rotary evaporation.

DI water (700g) and concentrated NH_3 (17.15g, 29 wt-%) were charged to a 4l beaker. The above concentrated sol was added to this with minimal stirring. A white precipitate was obtained. The precipitate was isolated as a damp filter cake via vacuum filtration. The damp solids (215g) were dispersed in methoxypropanol (853g). The mixture was then concentrated (226g) via rotary evaporation. Methoxypropanol (200g) was added and the mixture concentrated (188.78g) via rotary evaporation. Methoxypropanol was charged (195g) and the mixture was concentrated (251.2g) via rotary evaporation. Methoxypropanol (130g) was charged and the mixture concentrated via rotary evaporation. The final product 244.28 was isolated at 39.9 % solids. The mixture was filtered thru a 1 micron filter. This material was used in examples 44-47.

5. ZrO_2 Sol 5 75/25 3-(acryloxypropyl)trimethoxy silane/A1230

The ZrO_2 sol 5(280.12g, 40.05 wt-% solids, 36.02% ZrO_2) was charged to a 1 qt jar. DI water (150g) was charged with stirring. Methoxypropanol (456g), 3-(acryloxypropyl) trimethoxy silane (26.26g) and A1230 (17.75) were charged to a 1lt beaker with stirring. The methoxypropanol mixture was then charged to the ZrO_2 sol with stirring. The jar was sealed and heated to 90°C for 4hr. After heating the mixture was stripped to 359.4g via rotary evaporation. DI water (1287g) and concentrated NH_3 (28.34, 29 wt-%) were charged to a 4 l beaker. The above concentrated sol was added to this with minimal stirring. A white precipitate was obtained. The precipitate was isolated as a damp filter cake via vacuum filtration. The damp solids (336g) were dispersed in methoxypropanol (800g). The mixture was then concentrated (296.9g) via rotary evaporation. Methoxypropanol (200g) was added and the mixture concentrated (280.7g) via rotary evaporation. Methoxypropanol was charged (200g) and the mixture was concentrated via rotary evaporation. The final product 258.6g was isolated at 49.56% solids. The mixture was filtered with a 1 um filter. This material was used in example 40.

6. ZrO_2 Sol 5 3-(methacryloxypropyl)))trimethoxysilane

Dialysis ZrO_2 Sol 5 (207.4g) was charged to a dialysis bag and dialyzed in 3500g of DI water for 6 hr. (sigma diagnostics tubing MWCO > 1200 was used. The sol was isolated (34.03% solids) and used for the silane treatment.

The dialyzed ZrO_2 sol (80g, 34.03 wt-% solids, 30.8 % ZrO_2) was charged to a 16oz jar. DI water (80g) was charged with stirring. Methoxypropanol (160g), 3-(methacryloxypropyl) trimethoxy silane (8.59g) were charged to a 500ml beaker with stirring. The methoxypropanol mixture was then charged to the ZrO_2 sol with stirring. The jar was sealed and heated to 90° C for 3 hr 15 min. After heating the mixture was stripped to 170g via rotary evaporation and a white slurry was obtained. DI water (258g) and concentrated NH_3 (5.7g, 29 wt-%) were charged to a 1 l beaker. The above concentrated sol was added to this with minimal stirring. The solids were isolated as a damp filter cake via vacuum filtration. The damp solids (82g) were dispersed in methoxypropanol (200g). The mixture was then concentrated (97g) via rotary evaporation. Methoxypropanol (204g) was added and the mixture concentrated (85.5g) via rotary evaporation. Methoxypropanol was charged (205g) and the mixture was concentrated via rotary evaporation. The final product 91.46g was isolated at 27.4% solids. The mixture was filtered with a 1 um filter. This material was used in example 32.

7. ZrO_2 Sol 5 75/25 3-(acryloxypropyl)trimethoxy silane

The ZrO_2 sol 5(71.77g, 42.14 % solids, 37.92% ZrO_2) was charged to a 16oz jar. DI water (61.47g) was charged with stirring. Methoxypropanol (135.2g), 3-(acryloxypropyl) trimethoxy silane (7.87g) and A1230 (5.3g) were charged to a 500ml beaker with stirring. The methoxypropanol mixture was then charged to the ZrO_2 sol with stirring. The jar was sealed and heated to 90°C for 3 hr 30 min. After heating the mixture was stripped to 97g via rotary evaporation and a white slurry was obtained. DI water (386g) and concentrated NH_3 (8.5g, 29 wt-%) were charged to a 1l beaker. The above concentrated sol was added to this with minimal stirring. The solids were isolated as a damp filter cake via vacuum filtration. The damp solids (85.7g) were dispersed in methoxypropanol (~150g). The mixture was then concentrated (110g) via rotary evaporation. Methoxypropanol (100g) was added and the mixture concentrated (106.8g) via rotary evaporation. Methoxypropanol (100g) was added and the mixture concentrated (109.46g) via rotary evaporation. Methoxypropanol was charged (100g) and the mixture was concentrated via rotary evaporation. The final product 91.02g was isolated at 39.2% solids. The mixture was filtered with a 1 um filter. This material was used in example 41.

8. SiO_2 Sol 1 75/25 3-(acryloxypropyl)trimethoxy silane/A1230

Silica sol 1(110 nm) (327g, 39.63% silica) was charged to a 1 qt jar. Methoxypropanol (351g), 3-(Acryloxypropyl)trimethoxysilane (2.65g), and A1230 (1.7g) were charged to a 1 l beaker. The mixture was then charged to the silica sol with stirring. The mixture was heated to 90°C for 16.5 hr. The mixture (299.53g) was concentrated (153g) via rotary evaporation. Methoxypropanol (194g) was charged and the mixture concentrated (161.9g) via rotary evaporation. Methoxypropanol (190g) was charged and the mixture concentrated via rotary evaporation. The final product 157.5g was isolated at 37.65% solids.

9. ZrO_2 Sol 1 75/25 3-(acryloxypropyl)trimethoxysilane/A1230

The ZrO_2 sol 1 (100.24 g, 18.01 % ZrO_2) was charged to a 16 oz jar. Methoxypropanol (101g), 3-(acryloxypropyl) trimethoxy silane (3.65g) and A1230 (2.47g) were charged to a 500ml beaker with stirring. The methoxypropanol mixture was then charged to the ZrO_2 sol with stirring. The jar was sealed and heated to 90°C for 4hr. After heating the mixture was stripped to 52g via rotary evaporation.

DI water (175g) and concentrated NH_3 (3.4g, 29 wt-%) were charged to a 500ml beaker. The above concentrated sol was added to this with minimal stirring. A white precipitate was obtained. The precipitate was isolated as a damp filter cake via vacuum filtration. The damp solids (43g) were dispersed in acetone (57g). $MgSO_4$ was added to the mixture and allowed to stand for about 30 min. The mixture was then filtered with fluted filter paper follow by 1 micron filter. The final product was isolated at 15.8 % solids. This material was used in examples 36 and 37.

10. ZrO_2 Sol 1 75/25 (3-(methacryloxypropyl))trimethoxysilane/A1230

The ZrO_2 sol 1 (100g, 29.46 % ZrO_2) was charged to a 16 oz jar. Methoxypropanol (100g), 3-(methacryloxypropyl) trimethoxy silane (6.14) and A1230 (4.26) were charged to a 500ml beaker with stirring. The methoxypropanol mixture was then charged to the ZrO2 sol with stirring. The jar was sealed and heated to 90°C for 5 hr. After heating the mixture was stripped to 52g via rotary evaporation. DI water (179g) and concentrated NH_3 (5.5g, 29 wt-%) were charged to a 500ml beaker. The above concentrated sol was added to this with minimal stirring. A white precipitate was obtained. The precipitate was isolated as a damp filter cake via vacuum filtration. The damp solids (83.5g) were dispersed in acetone (66.5g). $MgSO_4$ was added to the mixture and allowed to stand for about 20 minutes. The mixture was then filtered with fluted filter paper follow by 1 micron filter. The final product was isolated at 12.9 wt-% solids. This material was used in example 31 and 35.

11. ZrO_2 Sol 5 75/25 (3-acryloxypropyl)trimethoxysilane/A1230

The ZrO_2 sol 5(100g, 21.47 % ZrO_2) was charged to a 16 oz jar. Methoxypropanol (100g), 3-(acryloxypropyl) trimethoxy silane (5.59g) and A1230 (3.75g) were charged to a 500ml beaker with stirring. The methoxypropanol mixture was then charged to the ZrO_2 sol with stirring. The jar was sealed and heated to 90°C for 3hr. After heating the mixture was stripped to 130.62g via rotary evaporation. DI water (143g) and concentrated NH_3 (4.5g, 29 wt-%) were charged to a 500ml beaker. The above concentrated sol was added to this with minimal stirring. A white precipitate was obtained. The precipitate was isolated as a damp filter cake via vacuum filtration. The damp solids (65.65g) were dispersed in acetone (79g). $MgSO_4$ was added to the mixture and allowed to stand. The mixture was then filtered with fluted filter paper follow by 1 micron filter. The final product was isolated at 16.9 % solids. This material was used in example 38.

12. ZrO_2 Sol 2 75/25 (3-Acryloxypropyl)trimethoxysilane/A1230)

The ZrO_2 sol 2 (300.2g, 27.12 % ZrO_2) was charged to a 16 oz jar. Methoxypropanol (300.57g), (3-Acryloxypropyl trimethoxy silane (16.55g) and A1230 (11.22g) were charged to a 500ml beaker with stirring. The methoxypropanol mixture was then charged to the ZrO_2 sol with stirring. The ZrO_2 sol 2 (400.1g, 27.12 % ZrO_2) was charged to a 16 oz jar. Methoxypropanol (401g), (3-Acryloxypropyl trimethoxy silane (21.91g) and A1230 (14.98g) were charged to a 500ml beaker with stirring. The methoxypropanol mixture was then charged to the ZrO_2 sol with stirring. The jar was sealed and heated to 90°C for 4hr. After heating the mixture from the two jars was combined and concentrated to 507.77g via rotary evaporation. DI water (1400g) and Concentrated NH_3 (34g, 29 wt-%) were charged to a 2000ml beaker. The above concentrated sol was added to this with minimal stirring. A white precipitate was obtained. The precipitate was isolated as a damp filter cake via vacuum filtration. The damp solids (515g) were dispersed in acetone (300g). This was stirred overnight $MgSO_4$ (226g) was added and the mixture allowed to stand for about 30 min while being cooled in an ice bath. The mixture was then filtered with fluted filter paper follow by 1 micron filter and acetone (175g) was added. The final product was isolated at 25 wt-% solids. This material was used in examples 39, 42 and 43.

Preparation of a Dilute Formulation

Dilute formulations were prepared by providing a surface modified nanoparticle sol in a solvent, adding additional monomers/resins, additional solvents, and photoinitiators to afford the compositions described in the forthcoming tables.

Preparation of Coated Films:

The substrate was a polyester film which had been previously coated with a hardcoat. The hardcoat contains functionalized silica particles and multifunctional acrylate monomers, monomers, and photoinitiators. In this case, the hardcoat was essentially formed as described in Example 3 of U.S. Patent No. 6,299,799.

The coating process/line speed for the curing conditions as measured by EIT POWERPUCK™, were as follows:

% Solids=5 wt% solids/95 wt% solvent

Line Speed=10 fpm, solvents dried-out on line

Bulb=D provided by Fusion Systems "D" or "H" bulb, which provides UV radiation.

Nitrogen inerting was employed

UV Energy and power were measured with a POWERPUCK™ from EIT, Inc. (Sterling, VA), for the UVA, UVB, UVC, and UVV regions of the ultraviolet spectrum, and the following were recorded.

This information gives the energy (J/cm^2) and power (W/cm^2) that the coating solution experienced as it was being UV polymerized. All our examples are cured at the same speed, therefore these values apply throughout the application. Essentially this implies that whenever a coating of the invention is UV polymerized at this speed, with this type of light, these conditions (N_2 inerting, ambient temperature) the coating should be reproducibly cured to give the durability results we report. It is understood that if greater UV power (more lamps or more powerful lamps) were employed, that faster line speeds could be employed.

	Energy - J/cm²				Power – W/cm²			
	A	B	C	V	A	B	C	V
	J/cm²	J/cm²	J/cm²	J/cm²	W/cm²	W/cm²	W/cm²	W/cm²
H Bulb	1.186	0.973	0.127	0.685	2.04	1.585	0.21	1.16
D Bulb	2.139	0.617	0.06	0.994	3.968	1.086	0.102	1.778

The tables given below illustrate sample formulations coated and cured, the photoinitiator employed, the refractive index of the liquid coating (or a calculated value), the cured refractive index value (in a few cases), the solvent and concentration employed, the UV source (Fusion H or D bulb), the UVVIS maximum of the sample on the hardcoat (the target is 550 nm as the reflection maximum for a ¼ wave, values lower than 550 imply thinner coating, values higher represent a thicker coating), and the abrasion resistance results to date.

The cured samples were evaluated for durability by mechanically rubbing the sample with a 6mm "stylus" wrapped with 24 layers of cheesecloth with a 2.2 kg weight on to of the stylus (plus the weight of the stylus) and noting how many passes or "rubs" were performed without damage being observed and at how many passes or "rubs" damage was observed. The results are given in an X/Y format, where the number X indicates the number of passes where the sample remained unchanged visually from the abrasion. The number Y represents the point at which damage was observed. Unacceptable abrasion resistance is defined as failure below 25 rubs. Passing abrasion resistance is indicated by failure between 50-100 rubs. Very good abrasion resistance is indicated by failure above 200 rubs.

The refractive index of neat liquid formulations was measured on a Zeiss refractometer.

Refractive index measurements of cured films were performed by spin coating on a silica wafer and measuring by ellipsometry. The coating solution was applied to a silica wafer using spin coating and then UV cured. The spin coating speed is 1000 RPM. The UV process conditions are 500w, D bulb, N_2, 25 ft/min. and 2 passes.

The refractive index is measured by using ellipsometer. Reflected ellipsometric data was collected at θ = 55°, 65°, 75°, λ = 350-1000nm. The refractive index n is the average of two measurements at 550 nm. $n_1 = 1.6227$, $n_2 = 1.615$. $n_{ave} = 1.6189$

Refractive indices were calculated on the basis of a volume average of the RI of the individual components. Refractive indices are calculated employing known densities, refractive indices of the particles or resins, and weight ratios using a volume average method. Weight percents are converted to volume percentages and the net refractive index is the sum of (volume fraction 1 times index 1) + (volume fraction 2 times index 2) and so on. Refractive indices of liquids are measured with a Zeiss refractometer while refractive indices of cured, crosslinked solids are measured with the Metricon (described elsewhere in the text). It is well known in the art that during curing coatings shrink thereby increasing the refractive index.

UVVIS measurements were made on the Shimadzu spectrophotometer. First surface reflection measurements were obtained using an MPC 3100 spectrophotometer in accordance with standardized testing method, *First Surface Total and CP Reflection Measurement Using the Shimadzu Spectrophotometer*. The thickness of the single high index optical layer on the hardcoated PET can be calculated from the following relationship:

$$t=\lambda/4\eta$$

where:

t=thickness (nm)

λ=wavelength (nm)

η=refractive index

Ideally, the samples will reflect maximally at 550nm. For the compositions of refractive index=1.62, a cured coating thickness of about 85 nm is appropriate to provide the wavelength of maximum reflection of 550 nm.

Table 1a

Ex	Wt-% ZrO_2 Prep	SM	Wt-% SM	Wt-% Resin	Resins	Wt-% Irgacure™819 on total solids
29	50 Prep 1 SOL 4	3:1 A174:A1230	18.5	30.5	Dipentaerythritol pentaacrylate	1%
30	50 Prep 1 SOL 4	3:1 A174:A1230	18.5	31	Dipentaerythritol pentaacrylate	0.5%
31	50 Prep 10 SOL 1	3:1 A174:A1230	9.03	39.97	Dipentaerythritol pentaacrylate	1%
32	50 Prep 6 sol 5	A174	8.82	40.18	Dipentaerythritol pentaacrylate	1%

Table 1b

Ex	Calc RI	Wt-% Solids in Solvent	UVVIS Max (nm)	UV lamp	Durability Testing 80nm samples 2kg/cheese cloth
29	1.60	5% in MEK	500	D	<50, <100, <100, 100/200, <50, <50, <50
30	1.60	5% in MEK	500	D	<50, <50, <50, <25, <25
31	1.61	10% In acetone	550	D	25/50, 25/50, 50/100, 50/100, 25/50, <25
32	1.61	7.5% in Methoxypropanol	0	D	<25, <25, <25

The examples of Table 1 provide very high index, of appropriate optical thickness with modest to fair durability.

Table 2a

Ex	wt% ZrO_2	Surface Modification	wt% SM	wt% Resin	Resins and Ratios
33	38.12 Prep 2 sol 4	3:1 acrylated silane:A1230	13.19	47.7	48% pentaerythritol tri and tetraacrylate mixture; 35% diacrylate of bisphenol A; 17% phenoxyethyl acrylate
34	30 Prep 4 sol 4	3:1 A174:A1230	11.1	57.9	50:50 diacrylate of bisphenol A:pentaerythritol tri and tetraacrylate mixture
35	38.5 Prep 10 sol 1	3:1 A174:A1230	6.94	53.57	Same resin as Example 33
36	38.5 Prep 9 sol 1	3:1 Acrylate: A1230	6.8	53.7	Same resin as Example 33
37	50 Prep 9 sol 1	3:1 Acrylate: A1230	8.83	40.17	Dipentaerythritol pentaacrylate
38	50 Prep 11 sol 5	3:1 Acrylate: A1230	8.82	40.17	Dipentaerythritol pentaacrylate
39	50 Prep 12 sol 2	3:1 Acrylate: A1230	8.83	40.17	Dipentaerythritol pentaacrylate
40	50 Prep 5 sol 5	3:1 Acrylate: A1230	8.83	40.17	Dipentaerythritol pentaacrylate
41	50 Prep 7 sol 5and 6 wt-% SiO_2 sol 1 Prep 8	3:1 Acrylate: A1230	9.02	33.98	Dipentaerythritol pentaacrylate
42	60 Prep 12 sol 2	3:1 Acrylate: A1230	10.81	28.19	Dipentaerythritol pentaacrylate
43	70 Prep 12 sol 2	3:1 Acrylate: A1230	12.61	16.39	Dipentaerythritol pentaacrylate

Each of Examples 33-43 included 1.0 wt-% Irgacure 819 photointiator.

Table 2b

Ex	Calc RI	Wt-% Solids in solvent	UVVIS Max (nm)	UV lamp	Durability Testing 80nm samples 2kg/cheese cloth
33	1.58	4% in acetone	430		250/300 <50 200
34	1.58	5% MEK	580	D	50/100 150/200 50 100 150 50
35	1.59	5% in acetone	525	D	25/50, 150/200, 25/50
36	1.59	5% in acetone	500	D	150/200, 150/200, 150/200
37	1.61 uncured and 1.62 cured	5% in acetone	500	D	300/350, 450/500, 450/500
38	1.61	10% in acetone		D	50/100, 100/150, 50/100, 25/50, 25/50, 50/100, 100/150, 100/150, 100/150, 50/100
39	1.61	10% in acetone	560	D	200/250, 150/200, 100/150, 150/200, 250/300, 200/250
40	1.61	10% in Methoxypropanol	501		100/150 100/150
41	1.61	10% in	567		100/150, 50/100

		Methoxypropanol			
42	1.65	6.76% solids in 89.4: 10.6 Acetone: Dowanol	0	D	50/100, 25/50, 100/150, 150/200, 100/150, 50/100, 300/400, 400/500
43	1.71	6.76% solids in 89.4: 10.6 Acetone: Dowanol	527	D	<25, <25, <25

Table 2 shows many very durable, very high index formulations. The use of 3:1 acrylate silane: A1230 as a surface modifier for zirconia sol 5 in examples 38 and 40 to generate a very high index formulation with good durability should be noted. Even higher durability with equivalent high index (1.62) is exemplified in Examples 37 and 39, employing the zirconia sols (1 and 2) with acrylate silane: A1230 surface modification.

Example 42, with 60 wt% zirconia sol 2 and functionalized with acrylate silane/A1230 is the highest index durable formulation developed, possessing an index of 1.65 and durability averaging 100 passes. At 70 wt% loading (Example 43) durability becomes lower. Below is a table describing additional formulations employing either mixtures of the ZrO_2 sol 5 and Silica sol 1or additional examples with ZrO_2 sol 3.

Table 3a

Ex	Nanoparticles	Wt % ZrO_2/SiO_2	Surface Modifier	Wt-% SM	Resins and Ratios
44	Prep 4 sol 3	50.0	3:1 Acrylate Silane: A1230	9	Same resin as Example 33
45	Prep 4 sol 3	50	3:1 Acrylate Silane: A1230	9	Dipentaerythritol pentaacrylate
48	Prep 3 sol 5 and Silica sol 1 Prep 8	50 ZrO_2 5 SiO_2	3:1 Acrylate Silane: A1230	9	Same resin as Example 33
49	Same as Ex. 48	50 ZrO_2 10 SiO_2	3:1 Acrylate Silane: A1230	9.17	Same resin as Example 33
50	Same as Ex. 48	40 ZrO_2 10 SiO_2	3:1 Acrylate Silane: A1230	7.4	Same resin as Example 33
51	Same as Ex. 48	40 ZrO_2 20 SiO_2	3:1 Acrylate Silane: A1230	7.74	Same resin as Example 33
52	Same as Ex. 48	50 ZrO_2 10 SiO_2	3:1 Acrylate Silane: A1230	9.17	Dipentaerythritol pentaacrylate

53	Same as Ex. 48	50 ZrO_2 15 SiO_2	3:1 Acrylate Silane: A1230	9.32	Dipentaerythritol pentaacrylate

Each of Examples 44-53 included 1.0 wt-% Irgacure 819 photointiator.

Table 3b

Ex	Wt % Resin	Calc RI	Wt-% Solids in Solvent
44	40.00	1.62	7.5% in 10:1 Acetone: Methoxy Propanol
45	40.00	1.60	10% in 10:1 Acetone: Methoxy Propanol
48	35.00	1.62	7.5% in 90:10 MEK: Dowanol
49	29.83	1.63	7.5% in 90:10 MEK: Dowanol
50	41.60	1.59	7.5% in 90:10 MEK: Dowanol
51	31.26	1.59	7.5% in 90:10 MEK: Dowanol
52	29.83	1.61	7.5% in 90:10 MEK: Dowanol
53	24.68		7.5% in 90:10 MEK: Dowanol

Table 3c

Ex	UV-VIS max nm	UV lamp	Durability Testing 80nm samples 2kg/cheesecloth
44	580	D	25/50 25/50 100/150 50/100 50/100 50/100
45	520-540	D	100/200 300/400 100/150 150/200 200/250 300/400
46		D	50/100 50/100 100/150
47		D	100/150 100/150 100/150 50/100
48	598	D	50/100 50/100 50/100
49	517	D	150/200 150/200 50/100
50	584	D	400/500
51	573 565	D	200/250 200/250 200/250
52	581	D	150/200 300/350 400/500
53	512	D	400/500

USE OF ACRYLATE SILANE

Comparison of Examples 37 and 39 vs. Example 31, where the selection of surface modifier is the only difference, strongly supports the advantage of acrylate silane functionality over methacrylate silane, where the acrylate silane is 3-(Acryloxypropyl)trimethoxysilane from Gelest. A similar improvement is observed when comparing Example 36 vs. Example 35. Example 32 was surface functionalized with all A174, whereas Examples 38 and 40 were 3:1 acrylate silane:A1230. Examples 38 and 40 exhibit better durability. As shown in Table 3c, the bimodal approach to thin coatings has been exemplified therein especially with regard to the durability when employing 10-20 wt-% of the larger particles.

Although methacrylate silane treated particles are known to provide abrasion resistant hardcoat coatings, such coatings has a refractive index of less than 1.60.At the higher zirconia loadings high index (>1.60) coatings and combination with high durability was achieved with particle functionalization with acrylate silane in thin (<100 nm) coatings.

Broad particle size distribution

The samples of zirconia sols (lots 1 and 2) were employed in the examples 31, 35, 36, 37, 39, 42, and 43. ZrO2 sol lot 3 was employed in examples 44- 47. For reasons that are not understood, the protrusion of larger particles is greater when the resin is the SR399 resin in contrast to the 48:35:17 SR295:CN120Z:SR339 resins system. It is reasonable from the particle size measurement above that the zirconia sols lots 1 and 2 would give protrusion, given their diameter compared to the coated thickness target of 85 nm, but it is surprising that the zirconia sol lot 3 does (although to a lesser degree).

Measured topography

It is believed that the very high durability of a 50 wt% zirconia (sols 1 and 2) cured formulation as given in Examples 37 and 39 may be a consequence of surface topography. This is supported by atomic force microscopy (AFM). In contrast to the relatively flat surface found in the formulations employing the small nanoparticles (such as given in Example 38, the AFM reveals "peaks" that rise up out of the surface as much as 120 nm high, as exemplified in Examples 37 and 39. These peaks may serve to keep the source of abrasion away from the cured surface. It is believed that the source of these peaks is larger particles present in the zirconia sols 1 and 2.

The respective surface of each of the UV cured films of the invention has been studied by AFM (atomic force microscopy). The "10 pt mean" is the mean value of the highest 10 points observed in a 10 um by 10 um square on the surface of the film. The films with the higher 10 pt mean values are obviously rougher and performed better (with the preferred surface modification) in the cheesecloth abrasion test.

Table 4

patent example #	10 pt peak mean (nm)
44	23.8
45	40.2
46	12.8
39	64.9
31	61.5
38	25.2
35	92
36	123
37	121
40	9
41	56
41	87
42	94
42	104

Table 4 lists the "10 point mean roughness" in nanometers, as measured by atomic force microscopy (AFM), as well as the cheesecloth durability data. Coatings made in accordance with the present invention exhibit a 10 point mean roughness value of at least 30 nanometers, but preferably about 120 nanometers, as examined using Atomic Force Microscopy on a typical 10 x 10 micrometer area. The examples compare the effects of the two reins systems, the effect of reactive surface modifier (acrylate vs methacrylate), and the effect of zirconia sols of different sizes on surface roughness and durability. The best performing high refractive index samples employed the broad dispersity ZrO_2 sols, the acrylate functionality, and preferably the highly multifunctional acrylate resin. In addition, Table 4 establishes the durability and roughness of two the bimodal examples, in which a high % of low dispersity small particles in conjunction with a low% of low dispersity large particles (110nm) performs well.

It is contemplated that the present invention will find primary application in optical coatings and films including antireflective film, for example. However, it is not limited thereto. It will also be understood that the foregoing description of an embodiment of the present invention is for illustrative purposes only. As such, the various structural and operational features herein disclosed are susceptible to a number of modifications commensurate with the abilities of one of ordinary skill in the art, none of which departs from the scope of the present invention as defined in the appended claims.

What Is Claimed Is:

1. A UV curable optical coating comprising:
a polymerizable monomer/oligomer mixture; and
surface modified inorganic nanoparticles comprising surface modified zirconia nanoparticles, wherein said optical coating has a refractive index of at least 1.6, wherein said coating has a 10 point mean roughness value of at least 30 nanometers.

2. The coating of claim 1 wherein said zirconia nanoparticlesare surface modified with acrylate silane.

3. The coating of claim 2 wherein said monomer/oligomer resin is crosslinked with one or more monomers having substantial acrylate functionality.

4. The coating of claim 1 wherein said surface modified nanoparticles comprise a majority of nanoparticles having an average cross-sectional diameter of about 10-30 nanometers and a minority of nanoparticles having an average cross-sectional diameter of about 80-150 nanometers.

5. The coating of claim 4 wherein said majority of nanoparticles comprises about 67 to 90 wt% of the total weight of the nanoparticles.

6. The coating of claim 1 wherein said inorganic nanoparticles comprise relatively smaller zirconia nanoparticles and relatively larger silica nanoparticles, and, said larger particles represent about 10 to 33 wt% of the total nanoparticle weight.

7. A display system comprising the coating of claim 1.

8. An antireflective coating comprising the coating of claim 1.

9. The coating of claim 1 wherein said inorganic nanoparticles are selected from the group consisting of zirconia, silica, titanium, antimony, mixed metal oxides, and mixtures thereof.

10. An antireflective film comprising:
a polymeric substrate;

a hard coat layer coupled to the polymeric substrate;
a high refractive index optical layer coupled to the hard coat layer; and
an optional low refractive index optical layer coupled to the high refractive index optical layer,
wherein said high refractive index optical layer comprises a bimodal system of functionalized zirconia nanoparticles comprising a majority of nanoparticles sized to about 10-30 nanometers and a minority of nanoparticles sized to about 80-150 nanoparticles.

11. The antireflective film of claim 10 wherein said bimodal system further comprises silica nanoparticles.

12. The antireflective film coating of claim 10 wherein said majority of nanoparticles are zirconia and said minority of nanoparticles are zirconia.

13. A display system comprising the antireflective film of claim 10.

14. The coating of claim 10 wherein said zirconia nanoparticles exhibit a 10 point mean average of at least 30 nanometers.

15. The coating of claim 10 wherein said zirconia nanoparticles generally exist as discrete particles within the polymeric substrate.

16. The coating of claim 10 having a refractive index of at least 1.6.

17. A protective film comprising:
a polymeric substrate; and
a hard coat layer fixed to the polymeric substrate, said hard coat layer having a refractive index of at least 1.6;
wherein said hard coat layer comprises a bimodal system of functionalized inorganic nanoparticles comprising surface modified zirconia nanoparticles, wherein a majority of nanoparticles are sized to about 10-30 nanometers and a minority of nanoparticles are sized to about 80-150 nanoparticles.

18. The protective film of claim 17 further comprising a low refractive index optical layer coupled to the hard coat layer.

19. A display system comprising the protective film of claim 17.

20. The coating of claim 17 wherein said inorganic nanoparticles comprise ground zirconia nanoparticles.

21. The coating of claim 17 comprising less than 70 weight percent of inorganic nanoparticles.

22. The coating of claim 17 comprising zirconia nanoparticles defined by a polydispersity ranging from about 0.4 to about 0.8 and a z-average mean of about 20 to 80.

23. The coating of claim 17 comprising zirconia nanoparticles defined by a volume mean average of about 10 to 30 nm and an intensity average: volume average ratio of about 1.5:18.

24. A composition containing:
a polymerizable monomer/oligomer resin mixture; and
surface modified inorganic nanoparticles comprising surface modified zirconia nanoparticles dispersed within said mixture,
wherein said nanoparticles are defined by a polydispersity ranging from about 0.4 to about 0.8 and a z-average mean of about 20 to 80.

25. The composition of claim 24 wherein said nanoparticles are defined by a volume mean average of about 10 to 30 nm and an intensity average: volume average ratio of about 1.5:18.

26. The composition of claim 24 wherein said nanoparticles define a bimodal system comprised of functionalized zirconia nanoparticles comprising a majority of nanoparticles sized to about 10-30 nanometers and a minority of nanoparticles sized to about 80-150 nanoparticles.

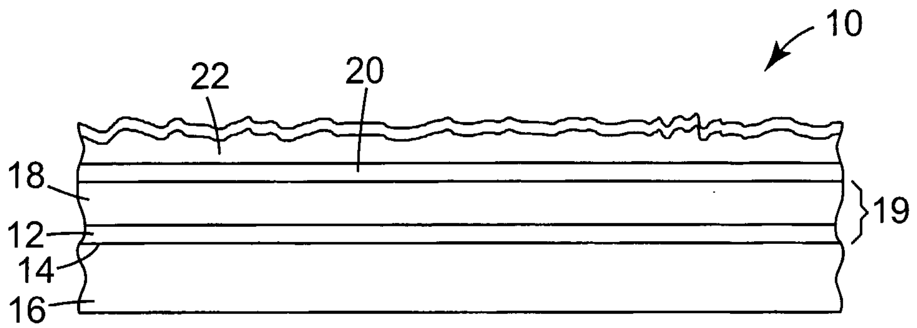

Fig. 1

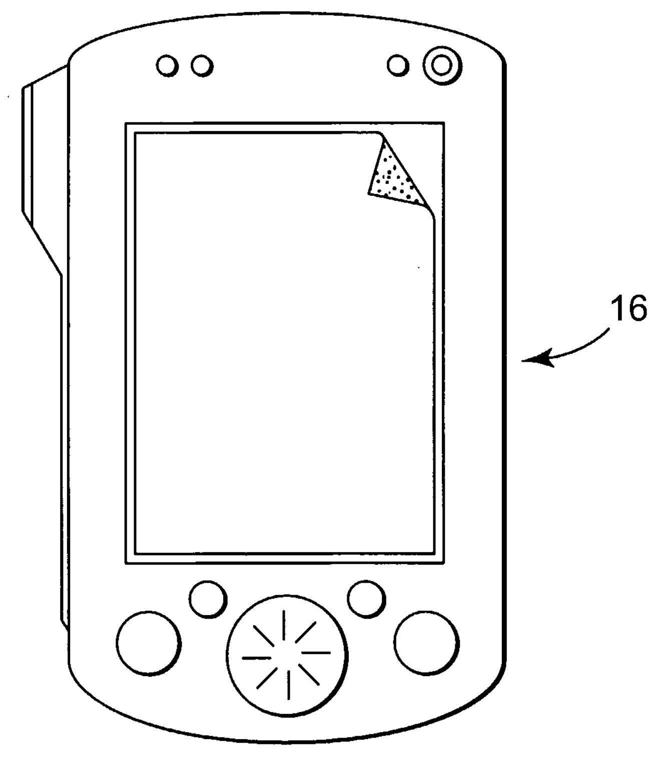

Fig. 2