

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 September 2006 (21.09.2006)

PCT

(10) International Publication Number
WO 2006/099357 A2

(51) International Patent Classification:
G02B 1/04 (2006.01)

(21) International Application Number:
PCT/US2006/009007

(22) International Filing Date: 10 March 2006 (10.03.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/077,598 11 March 2005 (11.03.2005) US

(71) Applicant (for all designated States except US): 3M INNOVATIVE PROPERTIES COMPANY [US/US]; 3m Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): JONES, Clinton L., [US/US]; 3m Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). GOENNER, Emily S., [US/US]; 3m Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). OLSON, David B., [US/US]; 3m Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). KOLB, Brant U., [US/US]; 3m Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(74) Agents: FISCHER, Carolyn A., et al.; 3m Center, Office Of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

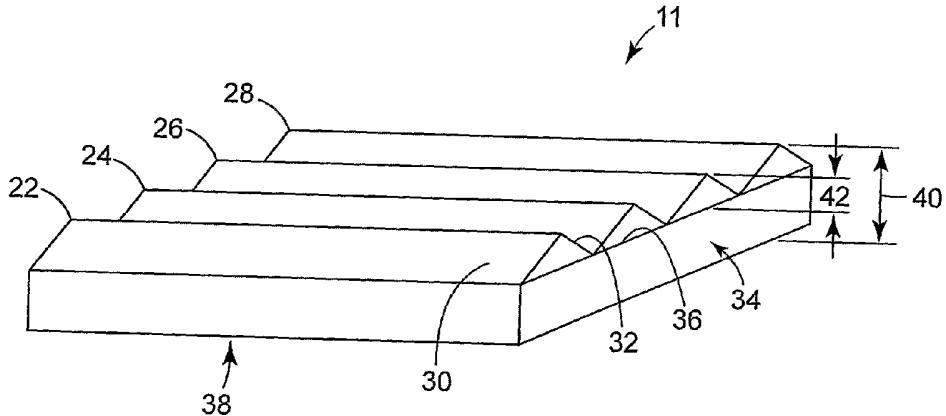
Published:

- without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: POLYMERIZABLE COMPOSITION COMPRISING LOW MOLECULAR WEIGHT ORGANIC COMPONENT

WO 2006/099357 A2



(57) Abstract: Polymerizable compositions comprising particularly useful for brightness enhancing films.

POLYMERIZABLE COMPOSITION COMPRISING LOW MOLECULAR WEIGHT ORGANIC COMPONENT

BACKGROUND

Certain microreplicated optical products, such as described in U.S. Patent Nos. 5,175,030 and 5,183,597, are commonly referred to as a "brightness enhancing films". Brightness enhancing films are utilized in many electronic products to increase the brightness of a backlit flat panel display such as a liquid crystal display (LCD) including those used in electroluminescent panels, laptop computer displays, word processors, desktop monitors, televisions, video cameras, as well as automotive and aviation displays.

Brightness enhancing films desirably exhibit specific optical and physical properties including the index of refraction of a brightness enhancing film that is related to the brightness gain (i.e. "gain") produced. Improved brightness can allow the electronic product to operate more efficiently by using less power to light the display, thereby reducing the power consumption, placing a lower heat load on its components, and extending the lifetime of the product.

Brightness enhancing films have been prepared from high index of refraction monomers that are cured or polymerized, as described for example in U.S. Pat. Nos. 5,908,874; 5,932,626; 6,107,364; 6,280,063; 6,355,754; as well as EP 1 014113 and WO 03/076528.

Although various polymerizable compositions that are suitable for the manufacture of brightness enhancing films are known, industry would find advantage in alternative compositions.

Summary of the Invention

Presently described are brightness enhancing films that comprise a brightness enhancing polymerized structure comprising the reaction product of a substantially solvent free polymerizable composition comprising an organic component and optionally an inorganic component.

In one embodiment, the organic component comprises one or more monomers and is free of any oligomeric ethylenically unsaturated monomer having a molecular weight

(M_n) of greater than 450 g/mole. The organic component preferably has a viscosity of less than 1000 cps at 180°F.

In another embodiment, the brightness enhancing film comprises a brightness enhancing polymerized structure comprising the reaction product of a substantially solvent free polymerizable composition comprising an organic component having a viscosity of less than 1000 cps at 180°F at least 10 wt-% inorganic nanoparticles. The organic component comprises up to about 10 wt-% of ethylenically unsaturated monomers having a number average molecular weight of greater than 450 g/mole. The organic component further comprises up to about 90 wt-% of ethylenically unsaturated monomer(s) having a number average molecular weight up to 450 g/mole.

The polymerizable composition comprises at least one ingredient that comprises at least two ethylenically unsaturated groups. For embodiments wherein the organic component is the totality of the polymerizable composition, at least one of the monomers comprises at least two ethylenically unsaturated groups. However, for embodiments wherein the organic component is combined with surface modified nanoparticles, the nanoparticles may have sufficient functionality such that the monomer(s) of the organic component may be monofunctional.

In a preferred embodiment, the polymerizable composition comprises the organic component and at least 10 wt-% inorganic nanoparticles.

Brief Description of the Drawings

The invention may be more completely understood in consideration of the following detailed description of various embodiments of the invention in connection with the accompanying drawings, in which:

FIG. 1 is a schematic view of an illustrative micro-structured article of the present invention in a backlit liquid crystal display;

FIG. 2 is a perspective view of an illustrative polymerized structure bearing a micro-structured surface;

FIG. 3 is a cross-sectional view of an illustrative micro-structured article that has prism elements of varying height;

FIG. 4 is a cross-sectional view of an illustrative micro-structured article that has prism elements of varying height;

FIG. 5 is a cross-sectional view of an illustrative micro-structured article;

FIG. 6 is a cross-sectional view of an illustrative micro-structured article in which the prism elements are of different heights and have their bases in different planes;

FIG. 7 is a cross-sectional view of an illustrative micro-structured article;

FIG. 8 is a cross-sectional view of an illustrative micro-structured article;

FIG. 9 is a cross-sectional view of an illustrative micro-structured article;

FIG. 10 is a schematic view of an illumination device including a turning film;

FIG. 11 is a cross-sectional view of a turning film;

FIG. 12 is a cross-sectional view of another turning film.

While the invention is amenable to various modifications and alternative forms, specifics thereof have been shown by way of example in the drawings and will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention.

Detailed Description

Brightness enhancing films generally enhance on-axis luminance (referred herein as “brightness”) of a lighting device. Brightness enhancing films can be light transmissible, microstructured films. The microstructured topography can be a plurality of prisms on the film surface such that the films can be used to redirect light through reflection and refraction. The heights of the prisms typically range from about 1 to 75 microns. When used in an optical display such as that found in laptop computers, watches, etc., the microstructured optical film can increase brightness of an optical display by limiting light escaping from the display to within a pair of planes disposed at desired angles from a normal axis running through the optical display. As a result, light that would exit the display outside of the allowable range is reflected back into the display where a portion of it can be “recycled” and returned back to the microstructured film at an angle that allows it to escape from the display. The recycling is useful because it can reduce power consumption needed to provide a display with a desired level of brightness.

As described in Lu and Lu et al., a microstructure-bearing article (e.g. brightness enhancing film) can be prepared by a method including the steps of (a) preparing a polymerizable composition (i.e. the polymerizable composition of the invention); (b) depositing the polymerizable composition onto a master negative microstructured molding surface in an amount barely sufficient to fill the cavities of the master; (c) filling the cavities by moving a bead of the polymerizable composition between a preformed base and the master, at least one of which is flexible; and (d) curing the composition. The master can be metallic, such as nickel, nickel-plated copper or brass, or can be a thermoplastic material that is stable under the polymerization conditions, and that preferably has a surface energy that allows clean removal of the polymerized material from the master. One or more the surfaces of the base film can optionally be primed or otherwise be treated to promote adhesion of the optical layer to the base.

The brightness enhancing or other microstructured articles comprise a polymerized structure comprising the reaction product of an organic component optionally comprising a plurality of (e.g. surface modified colloidal) nanoparticles. The polymerized structure can be an optical element or optical product constructed of a base layer and an optical layer. The base layer and optical layer can be formed from the same or different polymer material.

As used herein "polymerizable composition" refers to the total composition including the organic component that comprises at least one polymerizable monomer and the optional inorganic nanoparticles. The "organic component" refers to all of the components of the composition except for the inorganic nanoparticles. For embodiments wherein the polymerizable composition is free of inorganic nanoparticles, the organic component and polymerizable composition are one in the same. The composition is particularly amenable to the method of forming microstructured articles that is described in Lu and Lu et al., as previously described.

The organic component as well as the polymerizable composition is preferably substantially solvent free. "Substantially solvent free" refer to the polymerizable composition having less than 5 wt-%, 4 wt-%, 3 wt-%, 2 wt-%, 1 wt-% and 0.5 wt-% of (e.g. organic) solvent. The concentration of solvent can be determined by known methods, such as gas chromatography. Solvent concentrations of less than 0.5 wt-% are preferred.

The components of the organic component are preferably chosen such that the organic component has a low viscosity. Typically the viscosity of the organic component is substantially lower than the organic component of compositions previously employed. The viscosity of the organic component is less than 1000 cps and typically less than 900 cps. The viscosity of the organic component may be less than 800 cps, less than 450 cps, less than 600 cps, or less than 500 cps at the coating temperature. As used herein, viscosity is measured (at a shear rate up to 1000 sec-1) with 25 mm parallel plates using a Dynamic Stress Rheometer. Further, the viscosity of the organic component is typically at least 10 cps, more typically at least 50 cps, even more typically at least 100 cps, and most typically at least 200 cps at the coating temperature.

The coating temperature typically ranges from ambient temperature, (i.e. 25°C) to 180°F (82°C). The coating temperature may be less than 170°F (77°C), less than 160°F (71°C), less than 150°F (66°C), less than 140°F (60°C), less than 130°F (54°C), or less than 120°F (49°C). The organic component can be a solid or comprise a solid component provided that the melting point in the polymerizable composition is less than the coating temperature. The organic component can be a liquid at ambient temperature.

The organic component as well as the polymerizable composition has refractive index of at least 1.47, for most product applications; whereas the polymerizable resin composition of a turning film may have a refractive index as low as 1.44. The refractive index of the organic component or the polymerizable composition may be at least 1.48, 1.49, 1.50, 1.51, 1.52, 1.53, 1.54, 1.55, 1.56, 1.57, 1.58, 1.59, or 1.60. The polymerizable composition including the nanoparticles can have a refractive index as high as 1.70. (e.g. at least 1.61, 1.62, 1.63, 1.64, 1.65, 1.66, 1.67, 1.68, or 1.69) High transmittance in the visible light spectrum is also typically preferred.

The polymerizable composition is energy curable in time scales preferably less than five minutes such as for a brightness enhancing film having a 75 micron thickness. The polymerizable composition is preferably sufficiently crosslinked to provide a glass transition temperature that is typically greater than 45°C. The glass transition temperature can be measured by methods known in the art, such as Differential Scanning Calorimetry (DSC), modulated DSC, or Dynamic Mechanical Analysis. The polymerizable composition can be polymerized by conventional free radical polymerization methods.

Various kinds and amounts of monomers alone or in combination with each other can be employed to provide compositions meeting the viscosity and/or refractive index criteria just described.

In one embodiment, the organic component comprises one or more monomers and is free of any oligomeric ethylenically unsaturated monomer having a molecular weight (M_n) of greater than 450 g/mole.

Suitable monomers having a high refractive index and a number average molecular weight no greater than 450 g/mole include for example phenoxy ethyl acrylate; phenoxy-2-methylethyl (meth)acrylate; phenoxyethoxyethyl (meth)acrylate; 3-hydroxy-2-hydroxypropyl (meth)acrylate; benzyl (meth)acrylate, 4-(1-methyl-1-phenethyl)phenoxyethyl (meth)acrylate; phenylthio ethyl acrylate; 2-naphthylthio ethyl acrylate; 1-naphthylthio ethyl acrylate; 2,4,6-tribromophenoxy ethyl acrylate; 2,4-dibromophenoxy ethyl acrylate; 2-bromophenoxy ethyl acrylate; 1-naphthoxy ethyl acrylate; 2-naphthoxy ethyl acrylate; phenoxy 2-methylethyl acrylate; 3-phenoxy-2-hydroxy propyl acrylate; 2-phenylphenoxy ethyl acrylate; 4-phenylphenoxy ethyl acrylate; 2,4-dibromo-6-sec-butylphenyl acrylate; 2,4-dibromo-6-isopropylphenyl acrylate; benzyl acrylate; phenyl acrylate; 2,4,6-tribromophenyl acrylate.

In another embodiment, the substantially solvent free polymerizable composition comprises an organic component having a viscosity of less than 1000 cps at 180°F and at least 10 wt-% inorganic nanoparticles. The organic component comprises less than 15 wt-%, less than 14 wt-%, less than 13 wt-%, less than 12 wt-% and typically up to about 10 wt-% (e.g. about 1 wt-%, 2 wt-%, 3 wt-%, 4 wt-%, 5 wt-%, 6 wt-%, 7 wt-%, 8 wt-% or 9 wt-%) of ethylenically unsaturated monomers and/or oligomers having a number average molecular weight of greater than 450 g/mole. The organic component further comprises up to about 90 wt-% of ethylenically unsaturated monomer(s) having a number average molecular weight up to 450 g/mole.

A variety of ethylenically unsaturated monomers and/or oligomers having a number average molecular weight of greater than 450 g/mole are known and include for example certain (meth)acrylated aromatic epoxy oligomers, urethane (meth)acrylate oligomers, polyester (meth)acrylates, phenolic (meth)acrylates, and (meth)acrylated acrylic oligomers.

At least one of the ingredients of the polymerizable composition comprises at least two ethylenically unsaturated groups. It is preferred that the polymerizable ingredient comprises at least one ingredient that comprises two or more (meth)acrylate groups. If surface modified nanoparticles are employed that comprise sufficient polymerizable (meth)acrylate groups, all the monomers of the organic component may be monofunctional.

Monomers that comprise at least two (meth)acrylate groups are also described as crosslinkers. Suitable crosslinkers include for example hexanediol diacrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolpropane ethoxylate tri(meth)acrylate, glycetyl tri(meth)acrylate, and pentaerythritol propoxylate tri(meth)acrylate. Any one or combination of crosslinkers may be employed. Since methacrylate groups tend to be less reactive than acrylate groups, the crosslinker(s) are preferably free of methacrylate functionality.

When a crosslinker is present, it is preferably present in the organic component of the polymerizable composition in an amount of at least about 2 wt-%. Typically, the amount of crosslinker is not greater than about 25 wt-%.

Various crosslinkers are commercially available. For example, pentaerythritol triacrylate (PETA) is commercially available from Sartomer Company, Exton, PA under the trade designation "SR444"; from Osaka Organic Chemical Industry, Ltd. Osaka, Japan under the trade designation "Viscoat #300"; from Toagosei Co. Ltd., Tokyo, Japan under the trade designation "Aronix M-305"; and from Eternal Chemical Co., Ltd., Kaohsiung, Taiwan under the trade designation "Etermec 235". Trimethylol propane triacrylate (TMPTA) is commercially available from Sartomer Company under the trade designations "SR351". TMPTA is also available from Toagosei Co. Ltd. under the trade designation "Aronix M-309". Further, ethoxylated trimethylolpropane triacrylate and ethoxylated pentaerythritol triacrylate are commercially available from Sartomer under the trade designations "SR454" and "SR494" respectively.

Provided that the organic component and polymerizable composition as a whole has the desired refractive index, the organic component can comprise other (e.g. lower refractive index) monomers. Suitable monomers may provide other beneficial characteristics such as improved adhesion or reduced viscosity. Suitable monomers

include mono- or di-functional ethylenically unsaturated monomers such as (meth)acrylates or monomeric N-substituted or N,N-disubstituted (meth)acrylamides, especially acrylamide. These include N-alkylacrylamides and N,N-dialkylacrylamides, especially those containing C₁₋₄ alkyl groups. Examples are N-isopropylacrylamide, N-t-butylacrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, N-vinyl pyrrolidone, N-vinyl caprolactam.

The polymerizable compositions described herein preferably comprise inorganic particles. In general, the viscosity of the organic component is generally within the lower target ranges as previously described when relatively high concentrations (e.g. 40 wt-% to 70 wt-%) of inorganic nanoparticles as employed. When lower concentrations of nanoparticles are employed (e.g. 10 wt-% to 40 wt-%), the organic component may fall within the higher viscosity target ranges.

The viscosity of the (i.e. nanoparticle-containing) polymerizable composition is generally within the ranges previously described for the organic component alone. In general, as the concentration of inorganic nanoparticles of the polymerizable composition increases, the viscosity can increase. There is generally a substantial increase in viscosity as a function of concentration for inorganic nanoparticles lacking a suitable surface treatment as will subsequently be described.

The size of the particles is generally chosen to avoid significant visible light scattering. The inorganic oxide particle selected can impart refractive index or scratch resistance increase or both. It may be desirable to use a mix of inorganic oxide particle types to optimize an optical or material property and to lower total composition cost.

The inclusion of the inorganic nanoparticles can improve the durability. Preferably, the polymerized microstructured surface has a scratch contrast ratio value in a range of 1.0 to 1.15, or 1.0 to 1.12, or 1.0 to 1.10, or 1.0 to 1.05 as determined according to the test method described in U.S. Patent Application Serial No. 10/938006 filed Sept. 10, 2004. In the case of rounded prism apexes, e.g. having a radius ranging from about 0.5 to 15 micrometers, the scratch contrast ratio value can range from 1.0 to 1.65, or 1.0 to 1.4, or 1.0 to 1.10.

Although inorganic nanoparticles lacking polymerizable surface modification can usefully be employed, the inorganic nanoparticles are preferably surface modified such that the nanoparticles are polymerizable with the organic component. Surface modified

(e.g. colloidal) nanoparticles can be present in the polymerized structure in an amount effective to enhance the durability and/or refractive index of the article or optical element. The surface modified colloidal nanoparticles described herein can 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 can provide reactivity of the nanoparticle with the resin system making the composite more durable, properly surface modified nanoparticles added to resin systems provide a low impact on uncured composition viscosity. A combination of surface modifiers can be used to manipulate the uncured and cured properties of the composition. Appropriately surface modified nanoparticles can improve the optical and physical properties of the optical element such as, for example, improve resin mechanical strength, minimize viscosity changes while increasing solid volume loading in the resin system and maintain optical clarity while increasing solid volume loading in the resin system.

The surface modified colloidal nanoparticles can be oxide particles having a primary particle size or associated particle size of greater than 1 nm and less than 100 nm. It is preferred that the nanoparticles are unassociated. Their measurements can be based on transmission electron microscopy (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.

Fully condensed nanoparticles, such as the collidal silica used herein, typically have substantially no hydroxyls in their interiors.

Non-silica containing fully condensed nanoparticles typically have a degree of crystallinity (measured as isolated metal oxide particles) greater than 55%, preferably greater than 60%, and more preferably greater than 70%. For example, the degree of crystallinity can range up to about 86% or greater. The degree of crystallinity can be determined by X-ray defraction techniques. Condensed crystalline (e.g. zirconia) nanoparticles have a high refractive index whereas amorphous nanoparticles typically have a lower refractive index.

Silica nanoparticles can have a particle size from 5 to 75 nm or 10 to 30 nm or 20 nm. Silica nanoparticles are typically in an amount from 10 to 60 wt-%. Typically the amount of silica is less than 40 wt-%.

Suitable silicas are commercially available from Nalco Chemical Co. (Naperville, Ill.) under the trade designation NALCO COLLOIDAL SILICAS. For example, silicas include NALCO trade designations 1040, 1042, 1050, 1060, 2327 and 2329. Suitable fumed silicas include for example, products sold under the tradename, AEROSIL series OX-50, -130, -150, and -200 available from DeGussa AG, (Hanau, Germany), and CAB-O-SPERSE 2095, CAB-O-SPERSE A105, CAB-O-SIL M5 available from Cabot Corp. (Tuscola, Ill.).

Zirconia nanoparticles can have a particle size from approximately 5 to 50 nm, or 5 to 15 nm, or 10 nm. Zirconia nanoparticles can be present in the durable article or optical element 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 OOSOO8 and from Buhler AG Uzwil, Switzerland under the trade designation "Buhler zirconia Z-WO sol". Zirconia nanoparticle can also be prepared such as described in U.S. Patent Application serial No. 11/027426 filed Dec. 30, 2004 and U.S. Patent No. 6,376,590.

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 can be present 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.

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 result 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 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 for 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. It is preferred in the case of silanes to react the silanes with the particle or nanoparticle surface before incorporation into the resin. The required amount of surface modifier is dependant upon several factors such particle size, particle type, modifier molecular wt, and modifier type. In general it is preferred that approximately a monolayer of modifier is attached to the surface of the particle. The attachment procedure or reaction conditions required also depend on the surface modifier used. For silanes it is preferred to surface treat at elevated temperatures under acidic or basic conditions for from 1-24 hr approximately. Surface treatment agents such as carboxylic acids may not require elevated temperatures or extended time.

Representative embodiments of surface treatment agents suitable for the compositions include compounds such as, for example, isoctyl trimethoxy-silane, N-(3-triethoxysilylpropyl) methoxyethoxyethoxyethyl carbamate (PEG3TES), N-(3-triethoxysilylpropyl) methoxyethoxyethoxyethyl carbamate (PEG2TES), 3-(methacryloyloxy)propyltrimethoxysilane, 3-acryloxypropyltrimethoxysilane, 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, vinyltriisopropenoxyxilane, vinyltris(2-methoxyethoxy)silane, styrylethyltrimethoxysilane, mercaptopropyltrimethoxysilane, 3-glycidoxypolypropyltrimethoxysilane, 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. Further, a proprietary silane surface modifier, commercially available from OSI Specialties, Crompton South Charleston, WV under the trade designation "Silquest A1230", has been found particularly suitable.

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 one method, the mixture can be reacted at about 85 degree C for about 24 hours, resulting in the surface modified sol. In another 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 heavy metal oxide preferably takes place at room temperature.

The surface modification of ZrO_2 with silanes can be accomplished under acidic conditions or basic conditions. In one case the silanes are 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 one method the particles are precipitated from the dispersion and separated from the liquid component.

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. A cyclic functional group subject to ring opening polymerization generally contains a heteroatom such as oxygen, sulfur or nitrogen, and preferably a 3-membered ring containing oxygen such as an epoxide.

A preferred combination of surface modifying agents includes at least one surface modifying agent having a functional group that is co-polymerizable with the (organic component of the) hardenable resin and a second modifying agent different than the first

modifying agent. The second modifying agent is optionally co-polymerizable with the organic component of the polymerizable composition. The second modifying agent may have a low refractive index (i.e. less than 1.52 or less than 1.50). The second modifying agent is preferably a polyalkyleneoxide containing modifying agent that is optionally co-polymerizable with the organic component of the polymerizable composition.

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.

The polymerizable compositions described herein can also contain one or more other useful additives as known in art including but not limited to surfactants, pigments, fillers, polymerization inhibitors, antioxidants, anti-static agents, and other possible ingredients.

The radiation curable articles of this invention may be prepared by simply blending the components thereof, with efficient mixing to produce a homogeneous mixture, and then removing any solvent employed in preparation of said components. Air bubbles can be removed by application of vacuum or the like, with gentle heating if the mixture is viscous, and casting or otherwise creating a film of the resulting blend on a desired surface. The film can then be charged to a mold bearing the microstructure to be replicated and polymerized by exposure to ultraviolet radiation, producing cured optical resinous articles of the invention having the aforementioned properties. If polymerized on a surface other than the one on which it is to be used, the optical resinous article can be transferred to another surface.

Such a polymerization process lends itself to rapid, mass production of articles with no adverse environmental impact because no or only a minor amount of solvent or other volatiles are evolved. The process also lends itself to replication of articles with microstructure comprising utilitarian discontinuities, such as projections and depressions, which are readily released from the mold without loss of the detail of the mold and with retention of the replication of such detail under a wide variety of conditions during use. The articles can be formed with a wide variety of desired properties, such as toughness, flexibility, optical clarity and homogeneity, and resistance to common solvents, the microstructure of such articles having high thermal dimensional stability, resistance to abrasion and impact, and integrity even when the articles are bent.

Suitable methods of polymerization include solution polymerization, suspension polymerization, emulsion polymerization, and bulk polymerization, as are known in the art. Suitable methods include heating in the presence of a free-radical initiator as well as irradiation with electromagnetic radiation such as ultraviolet or visible light in the presence of a photoinitiator. Inhibitors are frequently used in the synthesis of the polymerizable composition to prevent premature polymerization of the resin during synthesis, transportation and storage. Suitable inhibitors include hydroquinone, 4-methoxy phenol, and hindered amine nitroxide inhibitors at levels of 50-1000 ppm. Other kinds and/or amounts of inhibitors may be employed as known to those skilled in the art.

The radiation (e.g. UV) curable compositions comprise a least one photoinitiator. A single photoinitiator or blends thereof may be employed in the brightness enhancement film of the invention. In general the photoinitiator(s) are at least partially soluble (e.g. at the processing temperature of the resin) and substantially colorless after being polymerized. The photoinitiator may be (e.g. yellow) colored, provided that the photoinitiator is rendered substantially colorless after exposure to the UV light source.

Suitable photoinitiators include monoacylphosphine oxide and bisacylphosphine oxide. Commercially available mono or bisacylphosphine oxide photoinitiators include 2,4,6-trimethylbenzoyldiphenylphosphine oxide, commercially available from BASF (Charlotte, NC) under the trade designation "Lucirin TPO"; ethyl-2,4,6-trimethylbenzoylphenyl phosphinate, also commercially available from BASF under the trade designation "Lucirin TPO-L"; and bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide commercially available from Ciba Specialty Chemicals under the trade designation

"Irgacure 819". Other suitable photoinitiators include 2-hydroxy-2-methyl-1-phenyl-propan-1-one, commercially available from Ciba Specialty Chemicals under the trade designation "Darocur 1173" as well as other photoinitiators commercially available from Ciba Specialty Chemicals under the trade designations "Darocur 4265", "Irgacure 651", "Irgacure 1800", "Irgacure 369", "Irgacure 1700", and "Irgacure 907".

The photoinitiator can be used at a concentration of about 0.1 to about 10 weight percent. More preferably, the photoinitiator is used at a concentration of about 0.5 to about 5 wt-%. Greater than 5 wt-% is generally disadvantageous in view of the tendency to cause yellow discoloration of the brightness enhancing film. Other photoinitiators and photoinitiator may also suitably be employed as may be determined by one of ordinary skill in the art.

Surfactants such as fluorosurfactants and silicone based surfactants can optionally be included in the polymerizable composition to reduce surface tension, improve wetting, allow smoother coating and fewer defects of the coating, etc.

Composition that are too high in viscosity to be used in the process just described can optionally be prepared into brightness enhancing film with extrusion processes as are known in the art.

The optical layer can directly contact the base layer or be optically aligned to the base layer, and can be of a size, shape and thickness allowing the optical layer to direct or concentrate the flow of light. The optical layer can have a structured or micro-structured surface that can have any of a number of useful patterns such as described and shown in the FIGURES. The micro-structured surface can be a plurality of parallel longitudinal ridges extending along a length or width of the film. These ridges can be formed from a plurality of prism apexes. These apexes can be sharp, rounded or flattened or truncated. For example, the ridges can be rounded to a radius in a range of 4 to 7 to 15 micrometers.

These include regular or irregular prismatic patterns can be an annular prismatic pattern, a cube-corner pattern or any other lenticular microstructure. A useful microstructure is a regular prismatic pattern that can act as a totally internal reflecting film for use as a brightness enhancement film. Another useful microstructure is a corner-cube prismatic pattern that can act as a retro-reflecting film or element for use as reflecting film. Another useful microstructure is a prismatic pattern that can act as an optical element for

use in an optical display. Another useful microstructure is a prismatic pattern that can act as an optical turning film or element for use in an optical display.

The base layer can be of a nature and composition suitable for use in an optical product, i.e. a product designed to control the flow of light. Almost any material can be used as a base material as long as the material is sufficiently optically clear and is structurally strong enough to be assembled into or used within a particular optical product. A base material can be chosen that has sufficient resistance to temperature and aging that performance of the optical product is not compromised over time.

The particular chemical composition and thickness of the base material for any optical product can depend on the requirements of the particular optical product that is being constructed. That is, balancing the needs for strength, clarity, temperature resistance, surface energy, adherence to the optical layer, among others.

Useful base materials include, for example, styrene-acrylonitrile, cellulose acetate butyrate, cellulose acetate propionate, cellulose triacetate, polyether sulfone, polymethyl methacrylate, polyurethane, polyester, polycarbonate, polyvinyl chloride, polystyrene, polyethylene naphthalate, copolymers or blends based on naphthalene dicarboxylic acids, polycyclo-olefins, polyimides, and glass. Optionally, the base material can contain mixtures or combinations of these materials. In an embodiment, the base may be multi-layered or may contain a dispersed component suspended or dispersed in a continuous phase.

For some optical products such as microstructure-bearing products such as, for example, brightness enhancement films, examples of preferred base materials include polyethylene terephthalate (PET) and polycarbonate. Examples of useful PET films include photograde polyethylene terephthalate and MELINEX™ PET available from DuPont Films of Wilmington, Del.

Some base materials can be optically active, and can act as polarizing materials. A number of bases, also referred to herein as films or substrates, are known in the optical product art to be useful as polarizing materials. Polarization of light through a film can be accomplished, for example, by the inclusion of dichroic polarizers in a film material that selectively absorbs passing light. Light polarization can also be achieved by including inorganic materials such as aligned mica chips or by a discontinuous phase dispersed within a continuous film, such as droplets of light modulating liquid crystals dispersed

within a continuous film. As an alternative, a film can be prepared from microfine layers of different materials. The polarizing materials within the film can be aligned into a polarizing orientation, for example, by employing methods such as stretching the film, applying electric or magnetic fields, and coating techniques.

Examples of polarizing films include those described in U.S. Pat. Nos. 5,825,543 and 5,783,120. The use of these polarizer films in combination with a brightness enhancement film has been described in U.S. Pat. No. 6,111,696.

A second example of a polarizing film that can be used as a base are those films described in U.S. Pat. No. 5,882,774. Films available commercially are the multilayer films sold under the trade designation DBEF (Dual Brightness Enhancement Film) from 3M. The use of such multilayer polarizing optical film in a brightness enhancement film has been described in U.S. Pat. No. 5,828,488.

This list of base materials is not exclusive, and as will be appreciated by those of skill in the art, other polarizing and non-polarizing films can also be useful as the base for the optical products of the invention. These base materials can be combined with any number of other films including, for example, polarizing films to form multilayer structures. A short list of additional base materials can include those films described in U.S. Pat. Nos. 5,612,820 and 5,486,949, among others. The thickness of a particular base can also depend on the above-described requirements of the optical product.

Durable microstructure-bearing articles can be constructed in a variety of forms, including those having a series of alternating tips and grooves sufficient to produce a totally internal reflecting film. An example of such a film is a brightness enhancing film having a regular repeating pattern of symmetrical tips and grooves, while other examples have patterns in which the tips and grooves are not symmetrical. Examples of microstructure bearing articles useful as brightness enhancing films are described by U.S. Pat. Nos. 5,175,030 and 5,183,597.

According to these patents, a microstructure-bearing article can be prepared by a method including the steps of (a) preparing a polymerizable composition; (b) depositing the polymerizable composition onto a master negative microstructured molding surface in an amount barely sufficient to fill the cavities of the master; (c) filling the cavities by moving a bead of the polymerizable composition between a preformed base and the master, at least one of which is flexible; and (d) curing the composition. The master can be

metallic, such as nickel, nickel-plated copper or brass, or can be a thermoplastic material that is stable under polymerization conditions and that preferably has a surface energy that permits clean removal of the polymerized material from the master. The particular method used to create the microstructure topography described herein can be similar to the molding process described in U.S. Patent No. 5,691,846. The microstructure article according to the invention can be formed from a continuous process at any desired length such as, for example, 5, 10, 100, 1000 meters or more.

The durable article can be used in applications needing durable micro-structured film including, for example, brightness enhancing films. The structure of these durable brightness enhancing films can include a wide variety of micro-structured films such as, for example, U.S. Patent No. 5,771,328, U.S. Patent No. 5,917,664, U.S. Patent No. 5,919,551, U.S. Patent No. 6,280,063, and U.S. Patent No. 6,356,391.

A backlit liquid crystal display generally indicated at 10 in FIG. 1 includes a brightness enhancement film 11 of the present invention that can be positioned between a diffuser 12 and a liquid crystal display panel 14. The backlit liquid crystal display can also include a light source 16 such as a fluorescent lamp, a light guide 18 for transporting light for reflection toward the liquid crystal display panel 14, and a white reflector 20 for reflecting light also toward the liquid crystal display panel. The brightness enhancement film 11 collimates light emitted from the light guide 18 thereby increasing the brightness of the liquid crystal display panel 14. The increased brightness enables a sharper image to be produced by the liquid crystal display panel and allows the power of the light source 16 to be reduced to produce a selected brightness. The brightness enhancement film 11 in the backlit liquid crystal display is useful in equipment such as computer displays (laptop displays and computer monitors), televisions, video recorders, mobile communication devices, handheld devices (i.e. cellphone, PDA), automobile and avionic instrument displays, and the like, represented by reference character 21.

The brightness enhancement film 11 includes an array of prisms typified by prisms 22, 24, 26, and 28, as illustrated in FIG. 2. Each prism, for example, such as prism 22, has a first facet 30 and a second facet 32. The prisms 22, 24, 26, and 28 can be formed on a body portion 34 that has a first surface 36 on which the prisms are formed and a second surface 38 that is substantially flat or planar and opposite the first surface.

A linear array of regular right prisms can provide both optical performance and ease of manufacture. By right prisms, it is meant that the apex angle θ is approximately 90°, but can also range from approximately 70° to 120° or from approximately 80° to 100°. The prism facets need not be identical, and the prisms may be tilted with respect to each other. Furthermore, the relationship between the thickness 40 of the film and the height 42 of the prisms is not critical, but it is desirable to use thinner films with well defined prism facets. The angle that the facets can form with the surface 38 if the facets were to be projected can be 45°. However, this angle would vary depending on the pitch of the facet or the angle θ of the apex.

FIGS. 3-9 illustrate representative embodiments of a construction for an optical element. It should be noted that these drawings are not to scale and that, in particular, the size of the structured surface is greatly exaggerated for illustrative purposes. The construction of the optical element can include combinations or two or more of the described embodiments below.

Referring to FIG. 3, there is illustrated a representative cross-section of a portion of one embodiment of an optical element or light directing film. The film 130 includes a first surface 132 and an opposing structured surface 134 which includes a plurality of substantially linearly extending prism elements 136. Each prism element 136 has a first side surface 138 and a second side surface 138', the top edges of which intersect to define the peak, or apex 142 of the prism element 136. The bottom edges of side surfaces 138, 138' of adjacent prism elements 136 intersect to form a linearly extending groove 144 between prism elements. In the embodiment illustrated in FIG. 3, the dihedral angle defined by the prism apex 142 measures approximately 90 degrees, however it will be appreciated that the exact measure of the dihedral angle in this and other embodiments may be varied in accordance with desired optical parameters.

The structured surface 134 of film 130 may be described as having a plurality of alternating zones of prism elements having peaks which are spaced at different distances from a common reference plane. The common reference plane may be arbitrarily selected. One convenient example of a common reference plane is the plane which contains first surface 132; another is the plane defined by the bottom of the lower most grooves of the structured surface, indicated by dashed line 139. In the embodiment illustrated in FIG. 3, the shorter prism elements measure approximately 50 microns in width and approximately

25 microns in height, measured from dashed line 139, while the taller prism elements measure approximately 50 microns in width and approximately 26 microns in height. The width of the zone which includes the taller prism elements can measure between about 1 micron and 300 microns. The width of the zone that includes the shorter prism elements is not critical and can measure between 200 microns and 4000 microns. In any given embodiment the zone of shorter prism elements can be at least as wide as the zone of taller prism elements. It will be appreciated by one of ordinary skill in the art that the article depicted in FIG. 3 is merely exemplary and is not intended to limit the scope of the present invention. For example, the height or width of the prism elements may be changed within practicable limits--it is practicable to machine precise prisms in ranges extending from about 1 micron to about 200 microns. Additionally, the dihedral angles may be changed or the prism axis may be tilted to achieve a desired optical effect.

The width of the first zone can be less than about 200 to 300 microns. Under normal viewing conditions, the human eye has difficulty resolving small variations in the intensity of light that occur in regions less than about 200 to 300 microns in width. Thus, when the width of the first zone is reduced to less than about 200 to 300 microns, any optical coupling that may occur in this zone is not detectable to the human eye under normal viewing conditions.

A variable height structured surface may also be implemented by varying the height of one or more prism elements along its linear extent to create alternating zones which include portions of prism elements having peaks disposed at varying heights above a common reference plane.

FIG. 4 illustrates another embodiment of the optical element similar to FIG. 3 except that the film 150 includes a structured surface 152 which has a zone of relatively shorter prism elements 154 separated by a zone including a single taller prism element 156. Much like the embodiment depicted in FIG. 3, the taller prism element limits the physical proximity of a second sheet of film to structured surface 152, thereby reducing the likelihood of a visible wet-out condition. It has been determined that the human eye is sensitive to changes in facet heights in light directing films and that relatively wide zones of taller prism elements will appear as visible lines on the surface of a film. While this does not materially affect the optical performance of the film, the lines may be undesirable in certain commercial circumstances. Reducing the width of a zone of taller prism

elements correspondingly reduces the ability of a human eye to detect the lines in the film caused by the taller prism elements.

FIG. 5 is a representative example of another embodiment of an optical element in which the prism elements are approximately the same size but are arranged in a repeating stair step or ramp pattern. The film 160 depicted in FIG. 5 includes a first surface 162 and an opposing structured surface 164 including a plurality of substantially linear prism elements 166. Each prism element has opposing lateral faces 168, 168' which intersect at their upper edge to define the prism peaks 170. The dihedral angle defined by opposing lateral faces 168, 168' measures approximately 90 degrees. In this embodiment the highest prisms may be considered a first zone and adjacent prisms may be considered a second zone. Again, the first zone can measure less than about 200 to 300 microns.

FIG. 6 illustrates a further embodiment of an optical element. The film 180 disclosed in FIG. 6 includes a first surface 182 and an opposing structured surface 184. This film may be characterized in that the second zone which includes relatively shorter prism elements contains prism elements of varying height. The structured surface depicted in FIG. 6 has the additional advantage of substantially reducing the visibility to the human eye of lines on the surface of the film caused by the variations in the height of the prism elements.

FIG. 7 shows another embodiment of an optical element for providing a soft cutoff. FIG. 7 shows a brightness enhancement film, designated generally as 240, according to the invention. Brightness enhancement film 240 includes a substrate 242 and a structured surface material 244. Substrate 242 can generally be a polyester material and structured surface material 244 can be an ultraviolet-cured acrylic or other polymeric material discussed herein. The exterior surface of substrate 242 is preferably flat, but could have structures as well. Furthermore, other alternative substrates could be used.

Structured surface material 244 has a plurality of prisms such as prisms 246, 248, and 250, formed thereon. Prisms 246, 248, and 250 have peaks 252, 254, and 256, respectively. All of peaks 252, 254, and 256 have peak or prism angles of preferably 90 degrees, although included angles in the range 60 degrees to 120 degrees. Between prisms 246 and 248 is a valley 258. Between prisms 248 and 250 is a valley 260. Valley 258 may be considered to have the valley associated with prism 246 and has a valley angle of 70 degrees and valley 260 may be considered the valley associated with prism 248 and has a

valley angle of 110 degrees, although other values could be used. Effectively, brightness enhancement film 240 increases the apparent on axis brightness of a backlight by reflecting and recycling some of the light and refracting the remainder like prior art brightness enhancement film, but with the prisms canted in alternating directions. The effect of canting the prisms is to increase the size of the output light cone.

FIG. 8 shows another embodiment of an optical element having rounded prism apexes. The brightness enhancement article 330 features a flexible, base layer 332 having a pair of opposed surfaces 334, 336, both of which are integrally formed with base layer 332. Surface 334 features a series of protruding light-diffusing elements 338. These elements may be in the form of "bumps" in the surface made of the same material as layer 332. Surface 336 features an array of linear prisms having blunted or rounded peaks 340 integrally formed with base layer 332. These peaks are characterized by a chord width 342, cross-sectional pitch width 344, radius of curvature 346, and root angle 348 in which the chord width is equal to about 20-40% of the cross-sectional pitch width and the radius of curvature is equal to about 20-50% of the cross-sectional pitch width. The root angle ranges from about 70-110 degrees, or from about 85-95 degrees, with root angles of about 90 degrees being preferred. The placement of the prisms within the array is selected to maximize the desired optical performance.

Rounded prism apex brightness enhancement articles usually suffer from decreased gain. However, the addition of high refractive index surface modified nanoparticles can offset the lost gain from the rounded prism apex brightness enhancement articles.

FIG. 9 shows another embodiment of an optical element having flat or planar prism apexes. The brightness enhancement article 430 features a flexible, base layer 432 having a pair of opposed surfaces 434, 436, both of which are integrally formed with base layer 432. Surface 434 features a series of protruding light-diffusing elements 438. These elements may be in the form of "flat bumps" in the surface made of the same material as layer 432. Surface 436 features an array of linear prisms having flattened or planar peaks 440 integrally formed with base layer 432. These peaks are characterized by a flattened width 442 and cross-sectional pitch width 444, in which the flattened width can be equal to about 0-30% of the cross-sectional pitch width.

Another method of extracting light from a lightguide is by use of frustrated total internal reflection (TIR). In one type of frustrated TIR the lightguide has a wedge shape,

and light rays incident on a thick edge of the lightguide are totally internally reflected until achieving critical angle relative to the top and bottom surfaces of the lightguide. These sub-critical angle light rays are then extracted, or more succinctly refract from the lightguide, at a glancing angle to the output surface. To be useful for illuminating a display device, these light rays must then be turned substantially parallel to a viewing, or output, axis of the display device. This turning is usually accomplished using a turning lens or turning film.

FIGs. 10-12 illustrate an illumination device including a turning film. The turning film can include the inventive material disclosed herein for form a durable turning film. A turning lens or turning film typically includes prism structures formed on an input surface, and the input surface is disposed adjacent the lightguide. The light rays exiting the lightguide at the glancing angle, usually less than 30 degrees to the output surface, encounter the prism structures. The light rays are refracted by a first surface of the prism structures and are reflected by a second surface of the prism structures such that they are directed by the turning lens or film in the desired direction, e.g., substantially parallel to a viewing axis of the display. Turning films may have rounded apexes, having a radius for example of at least 0.5 micrometers and typically no greater than 10 micrometers.

Referring to FIG. 10, an illumination system 510 includes optically coupled a light source 512; a light source reflector 514; a lightguide 516 with an output surface 518, a back surface 520, an input surface 521 and an end surface 522; a reflector 524 adjacent the back surface 520; a first light redirecting element 526 with an input surface 528 and an output surface 530; a second light redirecting element 532; and a reflective polarizer 534. The lightguide 516 may be a wedge or a modification thereof. As is well known, the purpose of the lightguide is to provide for the uniform distribution of light from the light source 512 over an area much larger than the light source 512, and more particularly, substantially over an entire area formed by output surface 518. The lightguide 516 further preferably accomplishes these tasks in a compact, thin package.

The light source 512 may be a CCFL that is edge coupled to the input surface 521 of the lightguide 516, and the lamp reflector 514 may be a reflective film that wraps around the light source 512 forming a lamp cavity. The reflector 524 backs the lightguide 516 and may be an efficient back reflector, e.g., a lambertian or a specular film or a combination.

The edge-coupled light propagates from the input surface 521 toward the end surface 522, confined by TIR. The light is extracted from the lightguide 516 by frustration of the TIR. A ray confined within the lightguide 516 increases its angle of incidence relative to the plane of the top and bottom walls, due to the wedge angle, with each TIR bounce. Thus, the light eventually refracts out of each of the output surface 518 and the back surface 520 because it is no longer contained by TIR. The light refracting out of the back surface 520 is either specularly or diffusely reflected by the reflector 524 back toward and largely through the lightguide 516. The first light redirecting element 526 is arranged to redirect the light rays exiting the output surface 518 along a direction substantially parallel to a preferred viewing direction. The preferred viewing direction may be normal to the output surface 518, but will more typically be at some angle to the output surface 518.

As shown in FIG. 11, the first light redirecting element 526 is a light transmissive optical film where the output surface 530 is substantially planar and the input surface 528 is formed with an array 536 of prisms 538, 540 and 542. The second light redirecting element 532 may also be a light transmissive film, for example a brightness enhancing film such as the 3M Brightness Enhancement Film product (sold as BEFIII) available from 3M Company, St. Paul, Minn. The reflective polarizer 534 may be an inorganic, polymeric, cholesteric liquid crystal reflective polarizer or film. A suitable film is the 3M Diffuse Reflective Polarizer film product (sold as DRPF) or the Specular Reflective Polarizer film product (sold as DBEF), both of which are available from 3M Company.

Within array 536, each prism 538, 540 and 542 may be formed with differing side angles as compared to its respective neighbor prisms. That is, prism 540 may be formed with different side angles (angles C and D) than prism 538 (angles A and B), and prism 542 (angles E and F). As shown, prisms 538 have a prism angle, i.e., the included angle, equal to the sum of the angles A and B. Similarly, prisms 540 have a prism angle equal to the sum of the angles C and D, while prisms 542 have a prism angle equal to the sum of the angles E and F. While array 536 is shown to include three different prism structures based upon different prism angle, it should be appreciated that virtually any number of different prisms may be used.

Prisms 538, 540 and 542 may also be formed with a common prism angle but with a varied prism orientation. A prism axis "1" is illustrated in FIG. 11 for prism 538. The

prism axis 1 may be arranged normal to the output surface 530, as shown for prism 538, or at an angle to the output surface either toward or away from the light source as illustrated by phantom axes "1⁺" and "1⁻", respectively, for prisms 540 and 542.

Prisms 538, 540 and 542 may be arranged within array 536 as shown in FIG. 11 in a regular repeating pattern or clusters 543 of prisms, and while the array 536 is not shown to have like prisms adjacent like prisms, such a configuration may also be used.

Moreover, within the array 536, the prisms 538, 540 and 542 may change continuously from a first prism configuration, such as prism configuration 538, to a second prism configuration, such as prism configuration 540, and so on. For example, the prism configuration may change in a gradient manner from the first prism configuration to the second prism configuration. Alternatively, the prisms may change in a step-wise manner, similar to the configuration shown in FIG. 11. Within each cluster 543, the prisms have a prism pitch, which is selected to be smaller than the spatial ripple frequency. Likewise, the clusters may have a regular cluster pitch. The prism array can be symmetrical as shown in FIG. 11 or the prism array can be non-symmetrical.

While the array 536 shown in FIG. 11 has prisms having a symmetric configuration, an array of prisms, such as array 536' shown in FIG. 12 formed in light redirecting element 526', may be used. Referring then to FIG. 12, in the array 536', prisms 538', for example, has angle A' unequal to angle B'. Similarly for prisms 540' and 542', angle C' is unequal to angle A' and angle D', and angle E' is unequal to either of angle A', angle C' or angle F'. The array 536' may be advantageously formed using a single diamond cutting tool of a predetermined angle, and tilting the tool for each cut producing prisms of differing prism angle and symmetry. However, it will be appreciated that with the use of a single cutting tool, the prism angles will be the same, i.e., A+B=C+D=E+F.

It is contemplated that as few as two different prism configurations may be used and arranged in clusters within the array 536, although as many prism sizes as necessary to accomplish a modification of the output profile from the lightguide 516 may be used. One purpose of the prism side angle variation is to spread and add variable amounts of optical power into the first light redirecting element 526. The varying configuration of prisms 538, 540 and 542 serves to provide substantially uniform sampling of the input aperture of the lightguide, which minimizes non-uniformities in the light extracted from the lightguide

516. The net result is an effective minimization of the ripple effect particularly near the entrance end 521 of the lightguide 516.

For the following defined terms, these definitions shall be applied, unless a different definition is given in the claims or elsewhere in this specification.

The term "microstructure" is used herein as defined and explained in U.S. Pat. No. 4,576,850. Thus, it means the configuration of a surface that depicts or characterizes the predetermined desired utilitarian purpose or function of the article having the microstructure. Discontinuities such as projections and indentations in the surface of said article will deviate in profile from the average center line drawn through the microstructure such that the sum of the areas embraced by the surface profile above the center line is equal to the sum of the areas below the line, said line being essentially parallel to the nominal surface (bearing the microstructure) of the article. The heights of said deviations will typically be about +/- 0.005 to +/- 750 microns, as measured by an optical or electron microscope, through a representative characteristic length of the surface, e.g., 1-30 cm. Said average center line can be piano, concave, convex, aspheric or combinations thereof. Articles where said deviations are of low order, e.g., from +/- 0.005 +/- 0.1 or, preferably, +/- 0.05 microns, and said deviations are of infrequent or minimal occurrence, i.e., the surface is free of any significant discontinuities, are those where the microstructure-bearing surface is an essentially "flat" or "smooth" surface, such articles being useful, for example, as precision optical elements or elements with a precision optical interface, such as ophthalmic lenses. Articles where said deviations are of low order and of frequent occurrence include those having anti-reflective microstructure. Articles where said deviations are of high-order, e.g., from +/- 0.1 to +/- 750 microns, and attributable to microstructure comprising a plurality of utilitarian discontinuities which are the same or different and spaced apart or contiguous in a random or ordered manner, are articles such as retroreflective cube-corner sheeting, linear Fresnel lenses, video discs and brightness enhancing films. The microstructure-bearing surface can contain utilitarian discontinuities of both said low and high orders. The microstructure-bearing surface may contain extraneous or non-utilitarian discontinuities so long as the amounts or types thereof do not significantly interfere with or adversely affect the predetermined desired utilities of said articles.

Retro-reflective films generally are capable of returning a significant percentage of incident light at relatively high entrance angles regardless of the rotational orientation of the sheeting about an axis perpendicular to its major surface. Cube corner retro-reflective film can include a body portion typically having a substantially planar base surface and a structured surface comprising a plurality of cube corner elements opposite the base surface. Each cube corner element can include three mutually substantially perpendicular optical faces that typically intersect at a single reference point, or apex. The base of the cube corner element acts as an aperture through which light is transmitted into the cube corner element. In use, light incident on the base surface of the sheeting is refracted at the base surface of the sheeting, transmitted through the respective bases of the cube corner elements disposed on the sheeting, reflected from each of the three perpendicular cube corner optical faces, and redirected toward the light source, as described in U.S. Patent No., 5,898,523.

The term "polymer" will be understood to include polymers, copolymers (e.g., polymers formed using two or more different monomers), oligomers and combinations thereof, as well as polymers, oligomers, or copolymers that can be formed in a miscible blend by, for example, coextrusion or reaction, including transesterification. Both block and random copolymers are included, unless indicated otherwise.

The term "(meth)acrylate" refers to both acrylate and methacrylate compounds.

The term "refractive index" is defined herein as the absolute refractive index of a material that is understood to be the ratio of the speed of electromagnetic radiation in free space to the speed of the radiation in that material. The refractive index can be measured using known methods and is generally measured using an Abbe Refractometer in the visible light region.

The term "nanoparticles" is defined herein to mean particles (primary particles or associated primary particles) with a diameter less than about 100 nm.

The term "associated particles" as used herein refers to a grouping of two or more primary particles that are aggregated and/or agglomerated.

The term "aggregation" as used herein is descriptive of a strong association between primary particles that may be chemically bound to one another. The breakdown of aggregates into smaller particles is difficult to achieve.

The term “agglomeration” as used herein is descriptive of a weak association of primary particles that may be held together by charge or polarity and can be broken down into smaller entities.

The term “primary particle size” is defined herein as the size of a non-associated single particle.

The term “sol” is defined herein as a dispersion or suspension of colloidal particles in a liquid phase.

The term “stable dispersion” is defined herein as a dispersion in which the colloidal nanoparticles do not agglomerate after standing for a period of time, such as about 24 hours, under ambient conditions - e.g. room temperature (about 20-22° C.), atmospheric pressure, and no extreme electromagnetic forces.

The term “gain” is defined herein as a measure of the improvement in brightness of a display due to a brightness enhancing film, and is a property of the optical material, and also of the geometry of the brightness enhancing film. Typically, the viewing angle decreases as the gain increases. A high gain is desired for a brightness enhancing film because improved gain provides an effective increase in the brightness of the backlight display.

The recitation of numerical ranges by endpoints includes all numbers subsumed within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5).

As used in this specification and the appended claims, the singular forms “a”, “an”, and “the” include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to a composition containing “a compound” includes a mixture of two or more compounds. As used in this specification and the appended claims, the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

Unless otherwise indicated, all numbers expressing quantities of ingredients, measurement of properties and so forth used in the specification and claims are to be understood as being modified in all instances by the term “about.”

The present invention should not be considered limited to the particular examples described herein, but rather should be understood to cover all aspects of the invention as fairly set out in the attached claims. Various modifications, equivalent processes, as well as numerous structures to which the present invention can be applicable will be readily

apparent to those of skill in the art to which the present invention is directed upon review of the instant specification.

The following ingredients of Table I were used in the preparation of the organic component of the examples.

Table I

Generic Chemical Description		Supplier (Location)
Trimethylolpropane triacrylate	SR-351	Sartomer Co. (Exton, PA) DAI-ICHI KOGYO
Tribromophenoxyethyl acrylate	BR-31	SEIYAKU CO., LTD (Kyoto, Japan)
Phenoxyethyl acrylate	SR-339	Sartomer Co.
(Methoxyethoxy) ethoxy acetic acid		Sigma-Aldrich (Milwaukee, WI)
(trimethyoxyisilyl)propyl methacrylate	Silquest A174	OSI Specialties (South Charleston, WV)
proprietary silane	Silquest A1230	OSI Specialties
Lucirin TPO-L	LR 8893	BASF (Charlotte, NC)
Hexanedioldiacrylate	SR 238	Sartomer Co. Surface Specialties
Beta-carboxyethyl acrylate	BCEA	(Smyrna, Ga)
napthyloxyethylacrylate	NOEA	As described in US 6,541,591 As described in Ex. 4-10 of U.S. Patent Application Serial No. 11/026573 filed Dec. 30, 2004.
napthylthiolethylacrylate	NSEA	

Three ZrO₂ sols were prepared as described in U.S. Patent Application Serial No. 11/027426 filed Dec. 30, 2004.

ZrO₂ Sol 1

38.58 g Yttrium Acetate Hydrate (Aldrich) was dissolved in 1500 g Zirconium Acetate Solution (MEI Corp) and the solution was dried at room temperature overnight then in a forced air oven at 90°C for 4hrs. The solid was dissolved in sufficient deionized water to give a 12.5% solution. This was pumped at a rate of 80 mL/min through 100 feet of ¼" outside-diameter stainless steel tubing that was immersed in a bath of oil heated to 206°C. The flow then passed to an additional 40-foot length of tubing immersed in an ice/water bath to cool the stream. A backpressure regulator was placed at the end of the tubing to maintain an exit pressure of 260-290 psig. The product of this step was a liquid suspension of fine particles of a white solid.

The liquid suspension was concentrated to 14.5% solids using a rotovap. This concentrate was pumped at a rate of 10 mL/min through 100 feet of ¼" outside diameter stainless steel tubing that was immersed in a bath of oil heated to 206°C. The flow then passed to an additional 40-foot length of tubing immersed in an ice/water bath to cool the stream. A backpressure regulator was placed at the end of the tubing to maintain an exit pressure of 260-270 psig. The product of this step was a liquid sol (10.5 % solids).

ZrO₂ Sol 2

79.5 g Yttrium Acetate Hydrate (Aldrich) was dissolved in 3000 g Zirconium Acetate Solution (MEI Corp) and the solution was dried at room temperature overnight then in a forced air oven at 90°C for 4hrs. The solid was dissolved in sufficient deionized water to give a 12.5% solution. This was pumped at a rate of 80 mL/min through 100 feet of ¼" outside-diameter stainless steel tubing that was immersed in a bath of oil heated to 206°C. The flow then passed to an additional 40-foot length of tubing immersed in an ice/water bath to cool the stream. A backpressure regulator was placed at the end of the tubing to maintain an exit pressure of 250 - 310 psig. The product of this step was a liquid suspension of fine particles of a white solid.

The liquid suspension was concentrated to about 18.5% solids using a rotovap. This concentrate was pumped at a rate of 15 mL/min through 100 feet of ¼" outside diameter stainless steel tubing that was immersed in a bath of oil heated to 206°C. The flow then passed to an additional 40-foot length of tubing immersed in an ice/water bath to cool the stream. A backpressure regulator was placed at the end of the tubing to maintain an exit pressure of 230 - 340 psig. The product of this step was a liquid sol. The sol was further concentrated via rotary evaporation to yield a final of 40.47 % solids.

ZrO₂ Sol 3 can be produced in the same manner yielding a sol with 45.78% solids.

The three ZrO₂ sols were tested according to the following ZrO₂ Test Methods:

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.

Crystalline Structure and Size (XRD Analysis)

The particle size of a dried zirconia sample was reduced by hand grinding using an agate mortar and pestle. A liberal amount of the sample was applied by spatula to a glass microscope slide on which a section of double coated tape had been adhered. The sample was pressed into the adhesive on the tape by forcing the sample against the tape with the spatula blade. Excess sample was removed by scraping the sample area with the edge of the spatula blade, leaving a thin layer of particles adhered to the adhesive. Loosely adhered materials remaining after the scraping were removed by forcefully tapping the microscope slide against a hard surface. In a similar manner, corundum (Linde 1.0 μ m alumina polishing powder, Lot Number C062, Union Carbide, Indianapolis, IN) was prepared and used to calibrate the diffractometer for instrumental broadening.

X-ray diffraction scans were obtained using a Philips vertical diffractometer having a reflection geometry, copper K_{α} radiation, and proportional detector registry of the scattered radiation. The diffractometer was fitted with variable incident beam slits, fixed diffracted beam slits, and graphite diffracted beam monochromator. The survey scan was conducted from 25 to 55 degrees two theta (2θ) using a 0.04 degree step size and 8 second dwell time. X-ray generator settings of 45 kV and 35 mA were employed. Data collections for the corundum standard were conducted on three separate areas of several individual corundum mounts. Data was collected on three separate areas of the thin layer sample mount.

The observed diffraction peaks were identified by comparison to the reference diffraction patterns contained within the International Center for Diffraction Data (ICDD) powder diffraction database (sets 1-47, ICDD, Newton Square, PA) and attributed to either cubic/tetragonal (C/T) or monoclinic (M) forms of zirconia. The (111) peak for the cubic phase and (101) peak for the tetragonal phase could not be separated so these phases were reported together. The amounts of each zirconia form were evaluated on a relative basis

and the form of zirconia having the most intense diffraction peak was assigned the relative intensity value of 100. The strongest line of the remaining crystalline zirconia form was scaled relative to the most intense line and given a value between 1 and 100.

Peak widths for the observed diffraction maxima due to corundum were measured by profile fitting. The relationship between mean corundum peak widths and corundum peak position (2θ) was determined by fitting a polynomial to these data to produce a continuous function used to evaluate the instrumental breadth at any peak position within the corundum testing range. Peak widths for the observed diffraction maxima due to zirconia were measured by profile fitting observed diffraction peaks. The following peak widths were evaluated depending on the zirconia phase found to be present:

Cubic/Tetragonal (C/T): (1 1 1)

Monoclinic (M): (-1 1 1), and (1 1 1)

A Pearson VII peak shape model with $K_{\alpha 1}$ and $K_{\alpha 2}$ wavelength components accounted for, and linear background model were employed in all cases. Widths were found as the peak full width at half maximum (FWHM) having units of degrees. The profile fitting was accomplished by use of the capabilities of the JADE diffraction software suite. Sample peak widths were evaluated for the three separate data collections obtained for the same thin layer sample mount.

Sample peaks were corrected for instrumental broadening by interpolation of instrumental breadth values from corundum instrument calibration and corrected peak widths converted to units of radians. The Scherrer equation was used to calculate the primary crystal size.

$$\text{Crystallite Size (D)} = K\lambda/\beta (\cos \theta)$$

In the Scherrer equation,

K = form factor (here 0.9);

λ = wavelength (1.540598 Å);

β = calculated peak width after correction for instrumental broadening (in radians) = [calculated peak FWHM – instrumental breadth] (converted to radians)
where FWHM is full width at half maximum; and

θ = $\frac{1}{2}$ the peak position (scattering angle).

The cubic/tetragonal crystallite size was measured as the average of three measurements using (1 1 1) peak.

Cubic/Tetragonal Mean Crystallite Size =

$$[D(1\ 1\ 1)_{\text{area}\ 1} + D(1\ 1\ 1)_{\text{area}\ 2} + D(1\ 1\ 1)_{\text{area}\ 3}] / 3$$

The monoclinic crystallite size was measured as the average of three measurement using the (-1 1 1) peak and three measurements using the (1 1 1) peak.

Monoclinic Mean Crystallite Size =

$$[D(-1\ 1\ 1)_{\text{area}\ 1} + D(-1\ 1\ 1)_{\text{area}\ 2} + D(-1\ 1\ 1)_{\text{area}\ 3} + D(1\ 1\ 1)_{\text{area}\ 1} + D(1\ 1\ 1)_{\text{area}\ 2} + D(1\ 1\ 1)_{\text{area}\ 3}] / 6$$

The weighted average of the cubic/tetragonal (C/T) and monoclinic phases (M) were calculated.

$$\text{Weighted average} = [(\% \text{ C/T})(\text{C/T size}) + (\% \text{ M})(\text{M size})]/100$$

In this equation,

%C/T = the percent crystallinity contributed by the cubic and tetragonal crystallite content of the ZrO₂ particles;

C/T size = the size of the cubic and tetragonal crystallites;

% M = the percent crystallinity contributed by the monoclinic crystallite content of the ZrO₂ particles; and

M size = the size of the monoclinic crystallites.

Dispersion Index

The Dispersion Index is equal to the volume-average size measured by PCS divided by the weighted average crystallite size measured by XRD.

Weight Percent Solids

The weight percent solids were determined by drying a sample weighing 3 to 6 grams at 120 °C for 30 minutes. The percent solids can be calculated from the weight of the wet sample (i.e., weight before drying, weight_{wet}) and the weight of the dry sample (i.e., weight after drying, weight_{dry}) using the following equation.

$$\text{wt-\% solids} = 100 (\text{weight}_{\text{dry}}) / \text{weight}_{\text{wet}}$$

The results were as shown in Table 2 and 3 as follows:

Table 2

	Intensity-average Size (nm)	Volume-average Size (nm)	Intensity-average: Volume-average Ratio
ZrO ₂ Sol 1	21.0	12.9	1.62
ZrO ₂ Sol 2	33.8	16.4	2.06
ZrO ₂ Sol 3	42.1	17.5	2.41

Table 3

	M Intensity	M Size (nm)	C/T Intensity	C/T Size (nm)	% C/T	XRD Average Size (nm)	Dispersion Index
ZrO ₂ Sol 1	18	4.0	100	8.0	85	7.4	1.74
ZrO ₂ Sol 1	NA	NA	NA	NA	NA	NA	NA
ZrO ₂ Sol 3	9	6.5	100	8.0	92	7.9	2.21

Example 1

ZrO₂ Sol 1 was dialyzed for approximately 12 hr (Sigma 250-7U MWCO > 12,000 available from Aldrich) to yield a stable sol at 10.93% solids. The dialyzed ZrO₂ Sol 1 (435.01 g) and MEEAA (9.85 g) were charged to a 1 liter round bottom flask and were concentrated via rotary evaporation. Isopropanol (30 g) and NSEA (35.00 g) were then added to the concentrated sol. The dispersion was then concentrated via rotary evaporation. The ZrO₂ filled NSEA had a refractive index of 1.674 and was 48.83% ZrO₂.

0.39 g of TPO-L was added to 40.09g of the concentrated dispersion. To 10.03 g of this mixture, 0.98 g of SR 351 was added.

Example 2

ZrO_2 Sol 1 was dialyzed for approximately 12 hr (Sigma 250-7U MWCO > 12,000 available from Aldrich) to yield a stable sol at 10.93% solids. The dialyzed ZrO_2 Sol 1 (437.02 g) and MEEAA (10 g) were charged to a 1L round bottom flask. The water and acetic acid were removed via rotary evaporation. The powder thus obtained was redispersed in D.I. water. The dispersion was 21.45 wt% ZrO_2 . The aqueous ZrO_2 sol (206.5 g) was charged to a jar to which was added, with stirring, 300 g 1-methoxy-2-propanol, 9.89 g A174, 6.64g Silquest A-1230. This mixture was then poured into a 1L jar, sealed and heated to 90°C for 3 hours. The contents of the jar were removed and concentrated to approximately 25.4 wt % ZrO_2 via rotary evaporation. Deionized water (450 g) and concentrated aqueous ammonia (29 % NH₄OH) (13.9 g) were charged to a 1L beaker. The concentrated ZrO_2 dispersion was added slowly to the beaker with stirring. The white precipitate thus obtained was isolated via vacuum filtration and washed with additional D.I. water. The damp solids were dispersed in 1-methoxy-2-propanol. The resultant silane modified zirconia sol contained 20.53 wt % solids and 17.44 wt% ZrO_2 .

The silane modified ZrO_2 sol (117.03 g), PEA (15.12g), HDDA (1.68 g) and a 5% solution of Prostab 5198 in water (0.13 g) were added to a round bottom flask. The water and 1-methoxy-2-propanol were removed via rotary evaporation. The ZrO_2 filled resin had a refractive index of 1.584 and was 47% ZrO_2 .

Example 3

ZrO_2 Sol 2 was dialyzed for approximately 4.5 hr (Spectra/Por Membrane MWCO 12-14,000 available from VWR) to yield a stable sol at 33.85 % solids. The dialyzed ZrO_2 Sol 2 (53.13 g), MEEAA (1.59 g), BCEA (1.14 g), 1-methoxy-2-propanol (133 g), NSEA (7.09 g) and TMPTA (0.97 g) were charged to a round bottom flask and concentrated via rotary evaporation. The ZrO_2 containing resin was 58.57 % ZrO_2 and had a refractive index of 1.682. The ZrO_2 containing resin (21.94 g) and TPO-L (0.09 g) were mixed together.

Example 4

ZrO₂ Sol 2 was dialyzed for approximately 4.5 hr (Spectra/Por Membrane MWCO 12-14,000 available from VWR) to yield a stable sol at 33.85 % solids. The dialyzed ZrO₂ Sol 2 (109.90 g), MEEAA (3.28 g), BCEA (2.36 g), 1-methoxy-2-propanol (200 g), NOEA (14.68 g) and TMPTA (2.00 g) were charged to a round bottom flask and concentrated via rotary evaporation. The ZrO₂ containing resin was 57.22 % ZrO₂ and had a refractive index of 1.661. The ZrO₂ containing resin (29.47 g) and TPO-L (0.13 g) were mixed together.

Example 5

ZrO₂ Sol 2 was dialyzed for approximately 4.5 hr (Spectra/Por Membrane MWCO 12-14,000 available from VWR) to yield a stable sol at 33.85 % solids. The dialyzed ZrO₂ Sol 2 (144.02 g), MEEAA (4.30 g), BCEA (3.09 g), 1-methoxy-2-propanol (300 g), NOEA (10.22 g), TMPTA (4.38 g), BR31 (21.89 g) and a 5% solution of Prostab 5198 in water (0.3 g) were charged to a round bottom flask and the alcohol and water were removed via rotary evaporation. The ZrO₂ containing resin was 46.97 % ZrO₂ and had a refractive index of 1.636. The ZrO₂ containing resin (49.03 g) and TPO-L (0.26 g) were mixed together.

Example 6

ZrO₂ Sol 3 (100.00 g), MEEAA (4.44 g), BCEA (2.13 g), 1-methoxy-2-propanol (115 g), a 50/50 mix of PEA/BR31 (29.78 g) and a 5% solution of Prostab 5198 in water (0.12 g) were charged to a round bottom flask and the alcohol and water were removed via rotary evaporation. The ZrO₂ containing resin was approximately 53.3% ZrO₂ and had a refractive index of 1.642. 0.47 pph of TPO-L was added to the above mixture.

Example 7

ZrO₂ Sol 3 (200 g), MEEAA (8.81 g), BCEA (4.22 g), 1-methoxy-2-propanol (230 g), a 38/50/12 mix of BR31/PEA/TMPTA (59.1 g), and a 5% solution of Prostab 5198 in water (0.24 g) were charged to a round bottom flask and the alcohol and water were

removed via rotary evaporation. The ZrO₂ containing resin was 52.31 % ZrO₂ and had a refractive index of 1.638. The ZrO₂ filled resin (116 g) and TPO-L (0.55 g) were mixed together.

The organic component of all the examples as well as the polymerizable compositions of all the examples have a solvent content of less than 2 wt-%. All of the organic components employed in the examples have a viscosity of less than 100 cps at 50°C. All of the organic components employed in the examples have a viscosity of less than 1000 cps at 25°C provided that the organic component is a homogeneous mixture at 25°C. All the polymerizable compositions of the examples (i.e. including the nanoparticles) have a viscosity of less than 1000 cps at 50°C.

In three sets of experiments, polymerizable resin compositions were prepared into brightness enhancing films using a master tool that had a 90° apex angles as defined by the slope of the sides of the prisms.

In the first set of experiments, the mean distance between adjacent apices was about 50 micrometers, the apexes of the prism are sharp, and the prisms varied in height along their length similar to that of a brightness enhancing film sold by 3M Company under the trade designation "Vikuiti BEF III90/50 Film".

In the second and third set of experiments, the mean distance between adjacent apices was about 24 micrometers and the apex of the prism vertices was sharp.

For each experiment polymerizable resin compositions were heated to a temperature of about 50°C and poured onto the master tool in a sufficient volume to create a continuous film. The master tool and polymerizable resin were pulled through a coating bar device to create a thickness of polymerizable resin of approximately 25 microns in the first set of experiments and approximately 13 microns in the second and third set of experiments. After coating, a 5 mil PET film was laminated onto the polymerizable resin for Experiment 1; a 2 mil PET film was used for Experiment two; and a reflective polarizer substantially the same as commercially available from 3M Company under the trade designation "Vikuiti DBEF-P" was used for Experiment 3. The master tool, polymerizable resin, and PET or reflective polarizer film were then placed into UV curing machine and exposed at 3000 millijoules/cm². After curing, the polymerized resin and PET were peeled from the master tool.

The gain of the resulting brightness enhancing films was measured on a SpectraScan™ PR-650 SpectraColorimeter available from Photo Research, Inc, Chatsworth, CA. Results of this method for each example formed below are reported in the RESULTS section below. In order to measure the single sheet gain (i.e. "SS") film samples were cut and placed on a Teflon light cube that is illuminated via a light-pipe using a Foster DCR II light source such that the grooves of the prisms are parallel to the front face of the Teflon light cube. For crossed sheet gain (i.e. "XS") a second sheet of the same material is placed underneath the first sheet and orientated such that the grooves of the second sheet are normal to the front face of the Teflon light cube.

The results are reported in Table IV as follows:

Table IV

Example	Uncured Resin RI	SS Gain of BEF Film of Exp. 1	XS Gain of BEF Film of Exp. 1	SS Gain of BEF Film of Exp. 2	XS Gain of BEF Film of Exp. 2
1	1.674	1.799	2.361		
2	1.584	1.766	2.434		
3	1.682	1.955	2.606		
4		1.901	2.568	1.89	2.595
5		1.854	2.573		
6	1.642				
7	1.638	1.889	2.684		

Example 8

The brightness enhancing film commercially available from 3M Company under the trade designation "Vikuiti T-BEF" was placed underneath a brightness enhancing film having the same composition as Example 6 prepared according to Experiment 3 such that the grooves of the second sheet are normal to the front face of the Teflon light cube. The single sheet gain of Example 6 prepared according to Experiment 3 was 2.519. The gain of this sheet combined with "Vikuiti T-BEF" was 3.143.

What is claimed is:

1. A brightness enhancing film comprising:
a brightness enhancing polymerized structure comprising the reaction product of a substantially solvent free polymerizable composition comprising
an organic component comprising one or more ethylenically unsaturated monomers, wherein the organic phase is free of oligomeric monomer having a number average molecular weight of greater than 450 g/mole; and
at least 10 wt-% inorganic nanoparticles.
2. The brightness enhancing film of claim 1 wherein the polymerizable composition has a refractive index of at least 1.47.
3. The brightness enhancing film of claim 1 wherein the organic component has a viscosity of less than 1000 cps at 180°F.
4. The brightness enhancing film of 1 wherein the polymerizable composition comprises photoinitiator.
5. The brightness enhancing film of claim 4 where in the polymerizable composition is cured by means of ultraviolet radiation.
6. The brightness enhancing film of claim 1 wherein the organic component comprises at least one monomer having a refractive index of at least 1.47.
7. The brightness enhancing film of claim 6 wherein the organic component comprises a monomer selected from the group consisting of phenoxy ethyl acrylate; phenylthio ethyl acrylate; 2-naphthylthio ethyl acrylate; 1-naphthylthio ethyl acrylate; 2,4,6-tribromophenoxy ethyl acrylate; 2,4-dibromophenoxy ethyl acrylate; 2-bromophenoxy ethyl acrylate; 1-naphthoxy ethyl acrylate; 2-naphthoxy ethyl acrylate; phenoxy 2-methylethyl acrylate; phenoxyethoxy ethyl acrylate; 3-phenoxy-2-hydroxy propyl acrylate; 2-phenylphenoxy ethyl acrylate; 4-phenylphenoxy ethyl acrylate; 2,4-dibromo-6-sec-

butylphenyl acrylate; 2,4-dibromo-6-isopropylphenyl acrylate; benzyl acrylate; phenyl acrylate; 2,4,6-tribromophenyl acrylate; and mixtures thereof.

8. The brightness enhancing film of claim 1 wherein the organic component comprises at least one monomer having a refractive index of at least 1.50 in combination with a second monomer having a refractive index of less than 1.50.

9. The brightness enhancing film of claim 8 wherein the second monomer has a refractive index of less than 1.47.

10. The brightness enhancing film of claim 1 wherein at least one monomer of the organic component has at least two ethylenically unsaturated groups.

11. The brightness enhancing film of claim 10 where the monomer is selected from hexanediol diacrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, trimethylolpropane tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, trimethylolpropane ethoxylate tri(meth)acrylate, glyceryl tri(meth)acrylate, pentaerythritol propoxylate tri(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, and mixtures thereof.

12. The brightness enhancing film of claim 1, wherein the polymerized structure has a plurality of ridges extending along a first surface.

13. The brightness enhancing film of claim 12 wherein the ridges have rounded apexes having a radius ranging from 4 to 15 micrometers.

14. The brightness enhancing film of claim 1, wherein the inorganic nanoparticles have a primary particle size in a range selected from 1 nm to 100 nm.

15. The brightness enhancing film according to claim 1, wherein the inorganic nanoparticles comprise 10 wt-% to 60 wt-% of the polymerized structure.

16. The brightness enhancing film according to claim 1, wherein the nanoparticles are selected from silica, zirconia, titania, antimony oxides, alumina, tin oxides, mixed metal oxides thereof, or mixtures thereof.
17. The brightness enhancing film according to claim 1, wherein the nanoparticles are surface modified such that the nanoparticles are polymerizable with the organic component.
18. The brightness enhancing film according to claim 1 wherein the base layer is a polarizing layer.
19. The brightness enhancing film according to claim 18 wherein the base layer is a reflective polarizing layer.
20. A brightness enhancing film comprising:
a brightness enhancing polymerized structure comprising the reaction product of a substantially solvent free polymerizable composition comprising
an organic component having a viscosity of less than 1000 cps at 180°F at least 10 wt-% inorganic nanoparticles; wherein the organic component comprises up to about 10 wt-% of ethylenically unsaturated monomers having a number average molecular weight of greater than 450 g/mole.
21. A device comprising:
 - (a) a lighting device having a light-emitting surface; and
 - (b) the brightness enhancing film of claim 1 placed substantially parallel to said light-emitting surface.
22. The device according to claim 21, wherein the lighting device is a back-lit display device or a liquid crystal display device.
23. The device according to claim 21, wherein the device is selected from a handheld device, a computer display and a television.

24. The brightness enhancing film of claim 1 wherein the film is a turning film and the refractive index of the polymerizable composition is at least 1.44.

25. The brightness enhancing film of claim 24 wherein the film has rounded apexes having a radius ranging from 0.5 to 10 micrometers.

26. An illumination device comprising:

- (a) a lighting source having a lightguide having a light-emitting surface; and
- (b) the turning film of claim 25 placed substantially parallel to said lightguide, said turning film having a first surface and a second surface and an array of prisms formed on the first surface, the turning film disposed with the first surface disposed in relation to the light-emitting surface such that light rays exiting the light-emitting surface of the lightguide encounter the array of prisms and are reflected and refracted by the array of prisms such that the light rays exit the turning film via the second surface and substantially along a desired angular direction,
wherein the array of prisms includes a first plurality of prisms, each of the first plurality of prisms having a first prism configuration, and a second plurality of prisms each having a second prism configuration, different than the first prism configuration, the first prism configuration and the second prism configuration being such the light rays exiting the second surface correspond to a substantially uniform sampling of the light rays entering the lightguide.

27. A brightness enhancing film comprising:

a brightness enhancing polymerized structure comprising the reaction product of a substantially solvent free polymerizable composition comprising an organic component comprising one or more ethylenically unsaturated monomers, wherein the organic phase is free of oligomeric monomer having a number average molecular weight of greater than 450 g/mole and the polymerizable composition comprises at least one ingredient that comprises at least two ethylenically unsaturated groups.

28. A microstructured article comprising the reaction product of a substantially solvent free polymerizable composition comprising an organic component comprising one or more ethylenically unsaturated monomers and optionally inorganic nanoparticles, wherein the organic component is free of oligomeric monomer having a number average molecular weight of greater than 450 g/mole and the polymerizable composition comprises at least one ingredient that comprises at least two (meth)acrylate groups.
29. The microstructured article of claim 28 wherein the article is retroreflective.
30. The microstructured article of claim 28 wherein the article is a flexible mold suitable for making barrier ribs fro a plasma display panel.

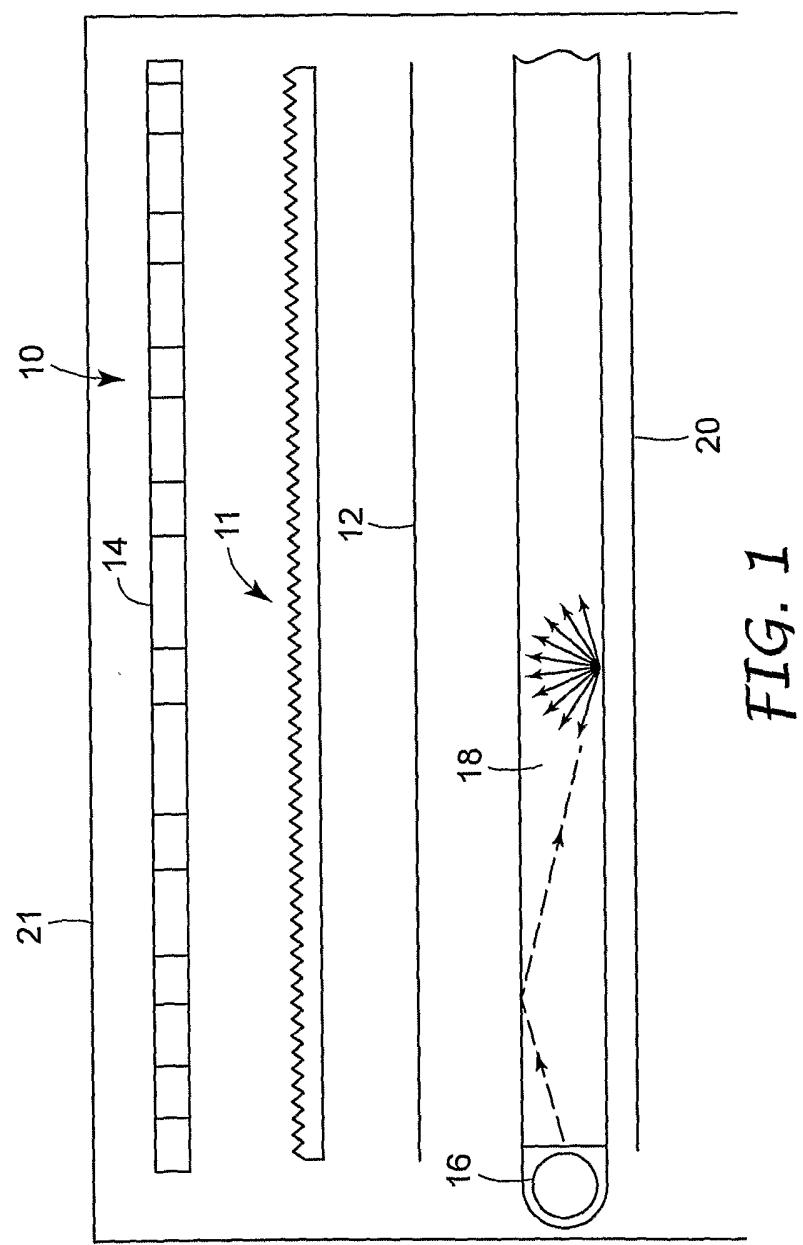


FIG. 1

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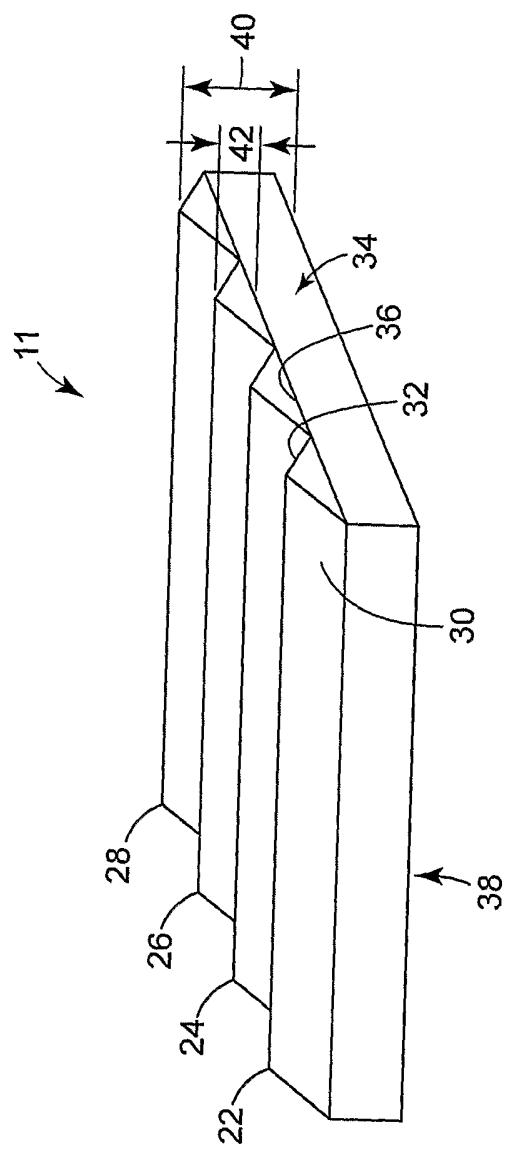


FIG. 2

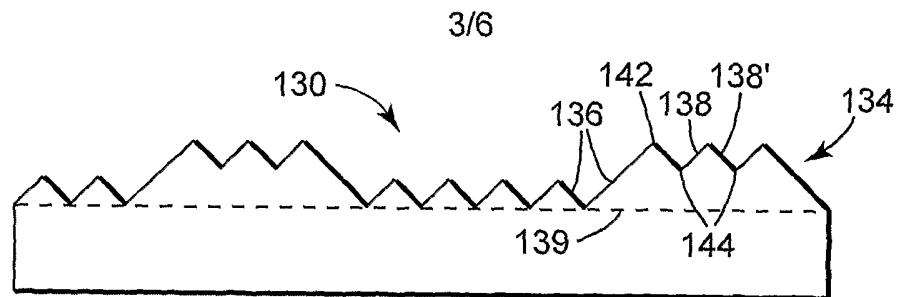


FIG. 3

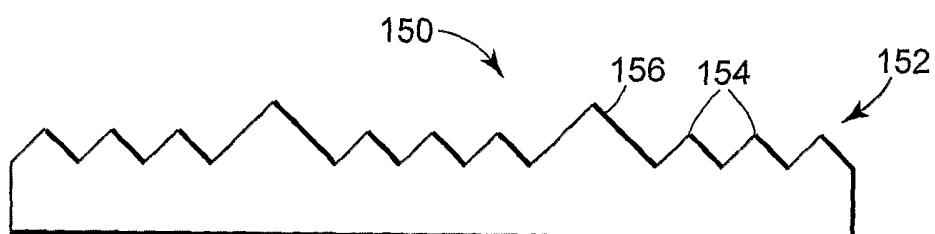


FIG. 4

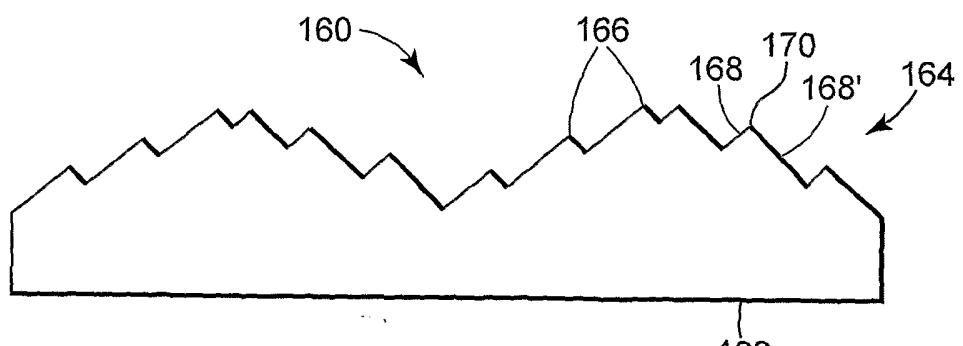


FIG. 5

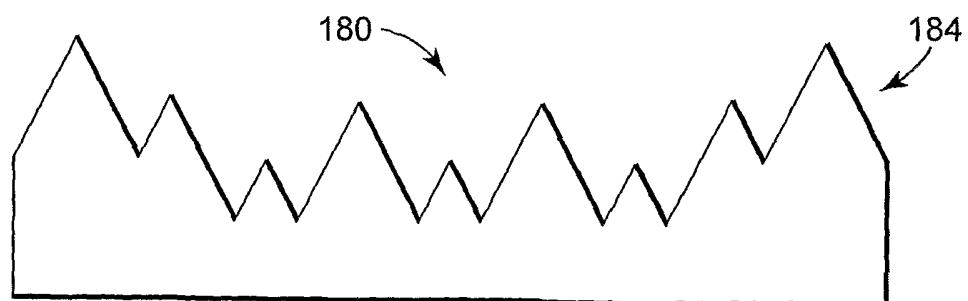


FIG. 6

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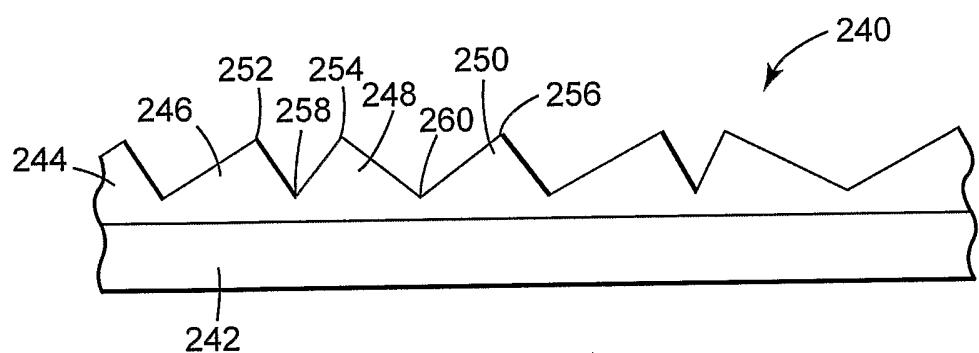


FIG. 7

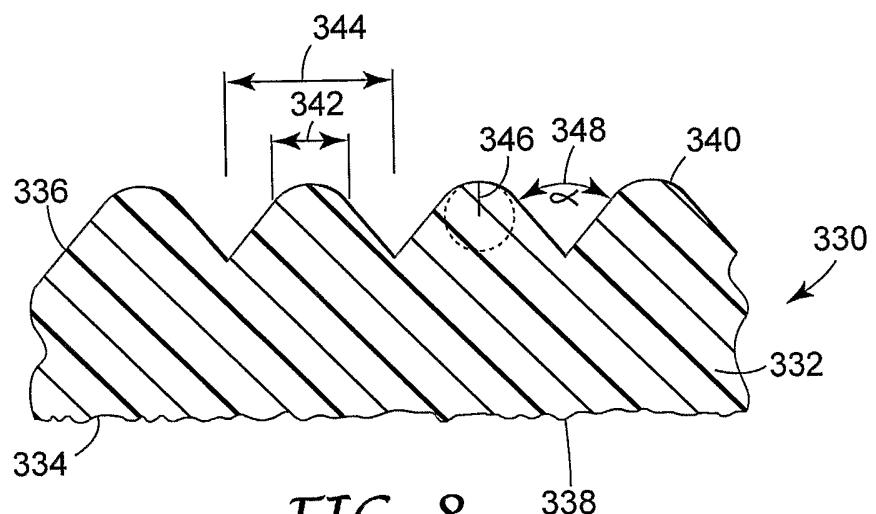


FIG. 8

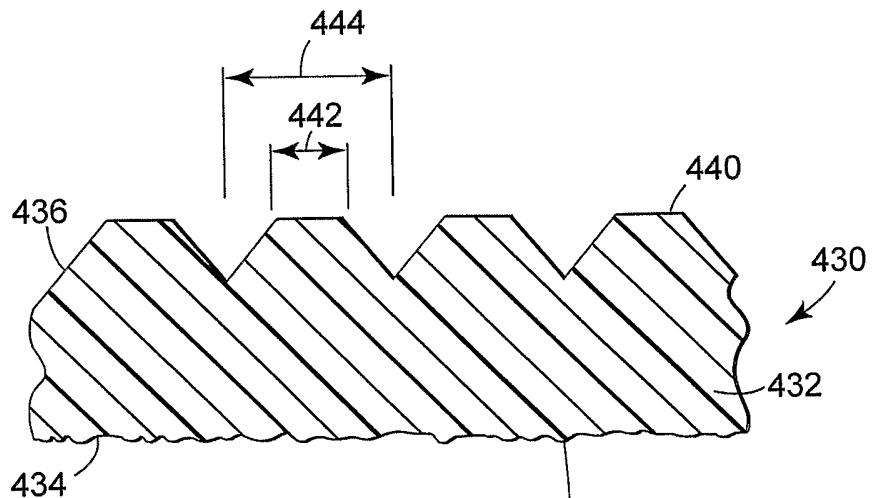


FIG. 9

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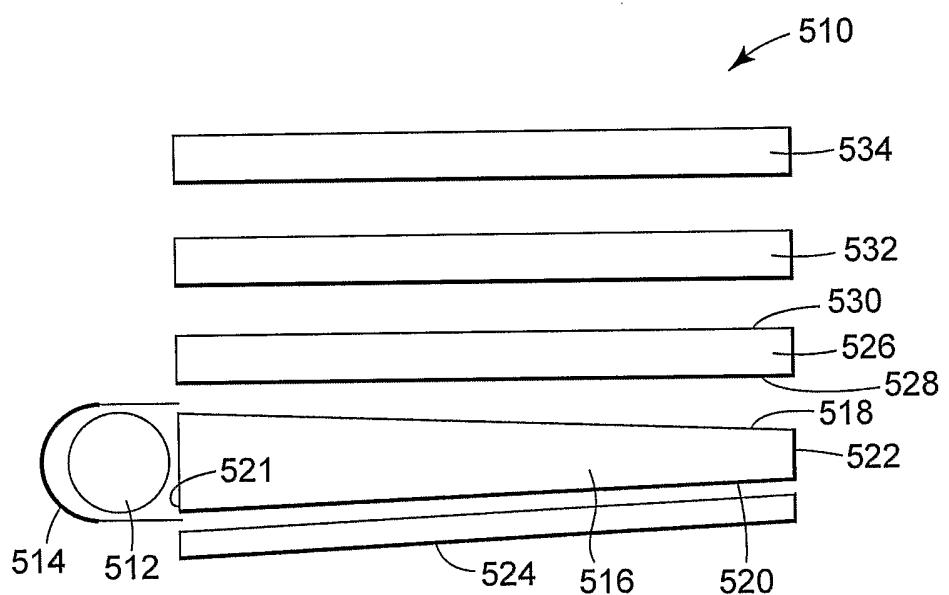


FIG. 10

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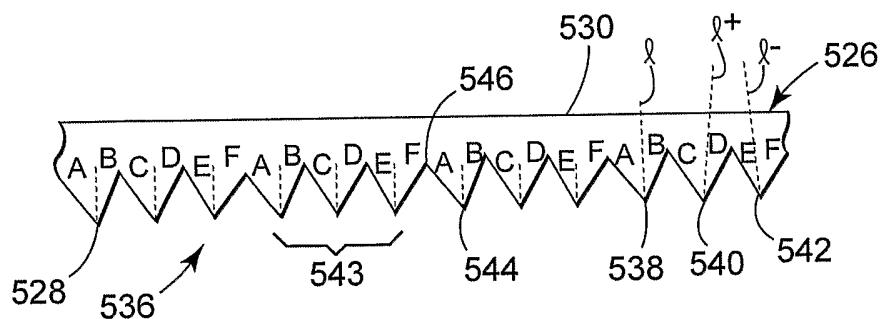


FIG. 11

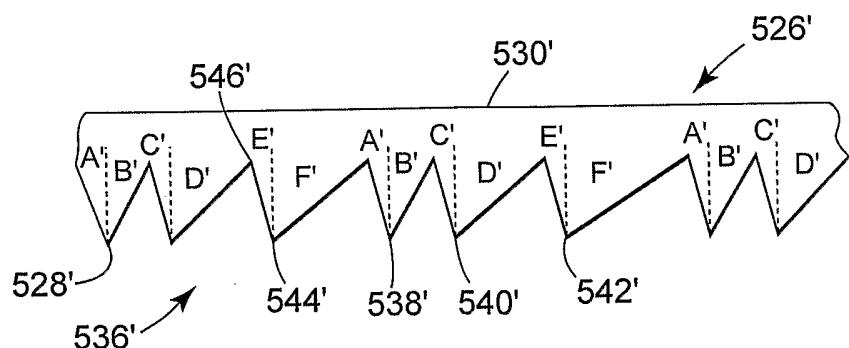


FIG. 12