

**ANTI GLARE FILMS COMPRISING**  
**MICROSTRUCTURED SURFACE**

5     **BACKGROUND**

Various matte films (also described as antiglare films) have been described. A matte film can be produced having an alternating high and low index layer. Such matte film can exhibit low gloss in combination with antireflection. However, in the absence of an alternating high and low index layer, such film would be exhibit antiglare, yet not antireflection.

As described at paragraph 0039 of US 2007/0286994, matte antireflective films typically have lower transmission and higher haze values than equivalent gloss films. For examples the haze is generally at least 5%, 6%, 7%, 8%, 9%, or 10% as measured according to ASTM D1003. Further gloss surfaces typically have a gloss of at least 130 as measured according to ASTM D 2457-03 at 60°; whereas matte surfaces have a gloss of less than 120.

There are several approaches for obtaining matte films.

For example, matte coating can be prepared by adding matte particles, such as described in US 6,778,240.

20     Further, matte antireflective films can also be prepared by providing the high and low refractive index layers on a matte film substrate.

In yet another approach, the surface of an antiglare or an antireflective film can be roughened or textured to provide a matte surface. According to U.S. Patent No. 5,820,957; “the textured surface of the anti-reflective film may be imparted by any of numerous texturing materials, surfaces, or methods. Non-limiting examples of texturing materials or surfaces include: films or liners having a matte finish, microembossed films, a microreplicated tool containing a desirable texturing pattern or template, a sleeve or belt, rolls such as metal or rubber rolls, or rubber-coated rolls.”

## SUMMARY

The present invention concerns antiglare films having a microstructured surface.

In some embodiments, the microstructured surface comprises a plurality of microstructures having a complement cumulative slope magnitude distribution such that at least 30% have a slope magnitude of at least 0.7 degrees and at least 25% have a slope magnitude less than 1.3 degrees.

In another embodiment, the antiglare film is characterized by a clarity of less than 90% and an average surface roughness (Ra) of at least 0.05 microns and no greater than 0.14 microns.

In another embodiment, the antiglare film is characterized by a clarity of less than 90% and an average maximum surface height (Rz) of at least 0.50 microns and no greater than 1.20 microns.

In another embodiment, the antiglare film is characterized by a clarity of no greater than 90% and the microstructured layer comprises peaks having a mean equivalent diameter of at least 5 microns and no greater than 30 microns.

In some embodiments, no greater than 50% of the microstructures of the antiglare film comprise embedded matte particles. In favored embodiments, the antiglare film is free of embedded matte particles.

The antiglare films generally have a clarity of at least 70% and a haze of no greater than 10%.

In some embodiments, at least 30%, at least 35%, or at least 40% of the microstructures have a slope magnitude of less than 1.3 degrees.

In some embodiments, less than 15%, or less than 10%, or less than 5% of the microstructures have a slope magnitude of 4.1 degrees or greater. Further, at least 70% of the microstructures typically have a slope magnitude of at least 0.3 degrees.

In some embodiments having low “sparkle”, the microstructures comprise peaks having a mean equivalent circular diameter (ECD) of at least 5 microns or at least 10 microns. Further, the mean ECD of the peaks is typically less than 30 microns or less than 25 microns. In some embodiments, the microstructures comprise peaks having a mean length of at least 5 microns or at least 10 microns. Further, the mean width of the microstructure peaks is typically at least 5 microns. In some embodiments, the mean width of the peaks is less than 15 microns.

**BRIEF DESCRIPTION OF DRAWINGS**

FIG. 1 is a schematic side-view of a matte film;

FIG. 2A is a schematic side-view of microstructure depressions;

5 FIG. 2B is a schematic side-view of microstructure protrusions;

FIG. 3A is a schematic top-view of regularly arranged microstructures;

FIG. 3B is a schematic top-view of irregularly arranged microstructures;

FIG. 4 is a schematic side-view of a microstructure;

10 FIG. 5 is a schematic side-view of an optical film comprising a portion of microstructures comprising embedded matte particles;

FIG. 6 is a schematic side-view of a cutting tool system;

FIGS. 7A-7D are schematic side-views of various cutters;

FIG. 8A is a two-dimensional surface profile of an exemplary microstructured surface (i.e. microstructured high refractive index layer H1);

15 FIG. 8B is a three-dimension surface profile of the exemplary microstructured surface of FIG. 8A;

FIG. 8C-8D are cross-sectional profiles of the microstructured surface of FIG. 8A along the x- and y- directions respectively;

20 FIG. 9A is a two-dimensional surface profile of another exemplary microstructured surface (i.e. microstructured high refractive index layer H4);

FIG. 9B is a three-dimension surface profile of the exemplary microstructured surface of FIG. 9A;

FIG. 9C-9D are cross-sectional profiles of the microstructured surface of FIG. 9A along the x- and y- directions respectively;

25 FIG. 10A-10B is a graph depicting percent complement cumulative slope magnitude distribution for various microstructured surfaces;

FIG. 11 is a graph depicting the complement cumulative slope magnitude distribution for various exemplified microstructured surfaces;

FIG. 12 depicts the manner in which curvature is calculated.

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**DETAILED DESCRIPTION**

Presently described are matte (i.e. antiglare) films. With reference to FIG. 1, the matte film 100 comprises a microstructured (e.g. viewing) surface layer 60 typically disposed on a light transmissive (e.g. film) substrate 50. The substrate 50, as well as the matte film, generally have a transmission of at least 85%, or 90%, and in some embodiments at least 91%, 92%, 93%, or greater.

The transparent substrate may be a film. The film substrate thickness typically depends on the intended use. For most applications, the substrate thicknesses is preferably less than about 0.5 mm, and more preferably about 0.02 to about 0.2 mm. Alternatively, the transparent film substrate may be an optical (e.g. illuminated) display through which text, graphics, or other information may be displayed. The transparent substrate may comprise or consist of any of a wide variety of non-polymeric materials, such as glass, or various thermoplastic and crosslinked polymeric materials, such as polyethylene terephthalate (PET), (e.g. bisphenol A) polycarbonate, cellulose acetate, poly(methyl methacrylate), and polyolefins such as biaxially oriented polypropylene which are commonly used in various optical devices.

The durable matte film typically comprises a relatively thick microstructured matte (e.g. viewing) surface layer. The microstructured matte layer typically has an average thickness ("t") of at least 0.5 microns, preferably at least 1 micron, and more preferably at least 2 or 3 microns. The microstructured matte layer typically has a thickness of no greater than 15 microns and more typically no greater than 4 or 5 microns. However, when durability of the matte film is not required, the thickness of the microstructured matte layer can be thinner.

In some embodiments, the microstructures can be depressions. For example, FIG. 2A is a schematic side-view of microstructured (e.g. matte) layer 310 that includes depressed microstructures 320 or microstructure cavities. The tool surface from which the microstructured surface is formed generally comprises a plurality of depressions. The microstructures of the matte film are typically protrusions. For example, FIG. 2B is a schematic side-view of a microstructured layer 330 including protruding microstructures 340. FIGS. 8A-9D depicts various microstructured surfaces comprising a plurality of microstructure protrusions.

In some embodiment, the microstructures can form a regular pattern. For example, FIG. 3A is a schematic top-view of microstructures 410 that form a regular pattern in a major surface 415. Typically however, the microstructures form an irregular pattern. For example, FIG. 3B is a schematic top-view of microstructures 420 that form an irregular pattern. In some cases, microstructures can form a pseudo-random pattern that appears to be random.

A (e.g. discrete) microstructure can be characterized by slope. FIG. 4 is a schematic side-view of a portion of a microstructured (e.g. matte) layer 140. In particular, FIG. 4 shows a microstructure 160 in major surface 120 and facing major surface 142. Microstructure 160 has a slope distribution across the surface of the microstructure. For example, the microstructure has a slope  $\theta$  at a location 510 where  $\theta$  is the angle between normal line 520 which is perpendicular to the microstructure surface at location 510 ( $\alpha = 90$  degrees) and a tangent line 530 which is tangent to the microstructure surface at the same location. Slope  $\theta$  is also the angle between tangent line 530 and major surface 142 of the matte layer.

In general, the microstructures of the matte film can typically have a height distribution. In some embodiments, the mean height (as measured according to the test method described in the examples ) of microstructures is not greater than about 5 microns, or not greater than about 4 microns, or not greater than about 3 microns, or not greater than about 2 microns, or not greater than about 1 micron. The mean height is typically at least 0.1 or 0.2 microns.

In some embodiments, the microstructures are substantially free of (e.g. inorganic oxide or polystyrene) matte particles. However, even in the absence of matte particles, the microstructures 70 typically comprise (e.g. zirconia or silica) nanoparticles 30, as depicted in FIG. 1.

The size of the nanoparticles is chosen to avoid significant visible light scattering. It may be desirable to employ a mixture of inorganic oxide particle types to optimize an optical or material property and to lower total composition cost. The surface modified colloidal nanoparticles can be inorganic oxide particles having a (e.g. unassociated) primary particle size or associated particle size of at least 1 nm or 5 nm. The primary or associated particle size is generally less than 100 nm, 75 nm, or 50 nm. Typically the primary or associated particle size is less than 40 nm, 30 nm, or 20 nm. It is preferred that

the nanoparticles are unassociated. Their measurements can be based on transmission electron microscopy (TEM). Surface modified colloidal nanoparticles can be substantially fully condensed.

Fully condensed nanoparticles (with the exception of silica) 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 diffraction techniques. Condensed crystalline (e.g. zirconia) nanoparticles have a high refractive index whereas amorphous nanoparticles typically have a lower refractive index.

Due to the substantially smaller size of nanoparticles, such nanoparticles do not form a microstructure. Rather, the microstructures comprise a plurality of nanoparticles.

In other embodiments, a portion of the microstructures may comprise embedded matte particles.

Matte particles typically have an average size that is greater than about 0.25 microns (250 nanometers), or greater than about 0.5 microns, or greater than about 0.75 microns, or greater than about 1 micron, or greater than about 1.25 microns, or greater than about 1.5 microns, or greater than about 1.75 microns, or greater than about 2 microns. Smaller matte particles are typical for matte films that comprise a relatively thin microstructured layer. However, for embodiments wherein the microstructured layer is thicker, the matte particles may have an average size up to 5 microns or 10 microns. The concentration of matte particles may range from at least 1 or 2 wt-% to about 5, 6, 7, 8, 9, or 10 wt-% or greater.

FIG. 5 is a schematic side-view of an optical film 800 that includes a matte layer 860 disposed on a substrate 850. Matte layer 860 includes a first major surface 810 attached to substrate 850 and a plurality of matte particles 830 and/or matte particle agglomerates dispersed in a polymerized binder 840. A substantial portion, such as at least about 50%, or at least about 60%, or at least about 70%, or at least about 80%, or at least about 90%, of microstructures 870 lack the presence of a matte particle 830 or matte particle agglomerate 880. Thus such microstructures are free of (e.g. embedded) matte particles. It is surmised that the presence of (e.g. silica or  $\text{CaCO}_3$ ) matte particles may provide improved durability even when the presence of such matte particles is insufficient

to provide the desired antireflection, clarity, and haze properties as will subsequently be described. However, due to the relatively large size of matte particles, it can be difficult to maintain matte particles uniformly dispersed in a coating composition. This can cause variations in the concentration of matte particles applied (particularly in the case of web coating), which in turn causes variations in the matte properties.

For embodiments wherein at least a portion of the microstructures comprise an embedded matte particle or agglomerated matte particle, the average size of the matte particles is typically sufficiently less than the average size of microstructures (e.g. by at least a factor of about 2 or more) such that the matte particle is surrounded by the polymerizable resin composition of the microstructured layer as depicted in FIG. 5.

When the matte layer includes embedded matte particles, the matte layer typically has an average thickness “t” that is greater than the average size of the particles by at least about 0.5 microns, or at least about 1 micron, or at least about 1.5 microns, or at least about 2 microns, or at least about 2.5 microns, or at least about 3 microns.

The microstructured surface can be made using any suitable fabrication method. The microstructures are generally fabricated using microreplication from a tool by casting and curing a polymerizable resin composition in contact with a tool surface such as described in U.S. Pat. Nos. 5,175,030 (Lu et al.) and 5,183,597 (Lu). The tool may be fabricated using any available fabrication method, such as by using engraving or diamond turning. Exemplary diamond turning systems and methods can include and utilize a fast tool servo (FTS) as described in, for example, PCT Published Application No. WO 00/48037, and U.S. Patent Nos. 7,350,442 and 7,328,638, the disclosures of which are incorporated by reference thereto.

FIG. 6 is a schematic side-view of a cutting tool system 1000 that can be used to cut a tool which can be microreplicated to produce microstructures 160 and matte layer 140. Cutting tool system 1000 employs a thread cut lathe turning process and includes a roll 1010 that can rotate around and/or move along a central axis 1020 by a driver 1030, and a cutter 1040 for cutting the roll material. The cutter is mounted on a servo 1050 and can be moved into and/or along the roll along the x-direction by a driver 1060. In general, cutter 1040 can be mounted normal to the roll and central axis 1020 and is driven into the engraveable material of roll 1010 while the roll is rotating around the central axis. The cutter is then driven parallel to the central axis to produce a thread cut. Cutter 1040 can be

simultaneously actuated at high frequencies and low displacements to produce features in the roll that when microreplicated result in microstructures 160.

Servo 1050 is a fast tool servo (FTS) and includes a solid state piezoelectric (PZT) device, often referred to as a PZT stack, which rapidly adjusts the position of cutter 1040. FTS 1050 allows for highly precise and high speed movement of cutter 1040 in the x-, y- and/or z-directions, or in an off-axis direction. Servo 1050 can be any high quality displacement servo capable of producing controlled movement with respect to a rest position. In some cases, servo 1050 can reliably and repeatably provide displacements in a range from 0 to about 20 microns with about 0.1 micron or better resolution.

Driver 1060 can move cutter 1040 along the x-direction parallel to central axis 1020. In some cases, the displacement resolution of driver 1060 is better than about 0.1 microns, or better than about 0.01 microns. Rotary movements produced by driver 1030 are synchronized with translational movements produced by driver 1060 to accurately control the resulting shapes of microstructures 160.

The engraveable material of roll 1010 can be any material that is capable of being engraved by cutter 1040. Exemplary roll materials include metals such as copper, various polymers, and various glass materials.

Cutter 1040 can be any type of cutter and can have any shape that may be desirable in an application. For example, FIG. 7A is a schematic side-view of a cutter 1110 that has an arc-shape cutting tip 1115 with a radius "R". In some cases, the radius R of cutting tip 1115 is at least about 100 microns, or at least about 150 microns, or at least about 200 microns. In some embodiments, the radius R of the cutting tip is or at least about 300 microns, or at least about 400 microns, or at least about 500 microns, or at least about 1000 microns, or at least about 1500 microns, or at least about 2000 microns, or at least about 2500 microns, or at least about 3000 microns.

Alternatively, the microstructured surface of the tool can be formed using a cutter 1120 that has a V-shape cutting tip 1125, as depicted in FIG. 7B, a cutter 1130 that has a piece-wise linear cutting tip 1135, as depicted in FIG. 7C, or a cutter 1140 that has a curved cutting tip 1145, as depicted in 7D. In one embodiment, a V-shape cutting tip having an apex angle  $\beta$  of at least about 178 degrees or greater was employed.

Referring back to FIG. 6, the rotation of roll 1010 along central axis 1020 and the movement of cutter 1040 along the x-direction while cutting the roll material define a

thread path around the roll that has a pitch  $P_1$  along the central axis. As the cutter moves along a direction normal to the roll surface to cut the roll material, the width of the material cut by the cutter changes as the cutter moves or plunges in and out. Referring to, for example FIG. 7A, the maximum penetration depth by the cutter corresponds to a maximum width  $P_2$  cut by the cutter. In general, the ratio  $P_2/P_1$  is in a range from about 2 to about 4.

Several microstructured high index layers were made by microreplicating nine different patterned tools to make high refractive index matte layers. Since the microstructured surface of the high refractive index matte layer was a precise replication of the tool surface, the forthcoming description of the microstructured high refractive index layer is also a description of the inverse tool surface. Microstructured surfaces H5 and H5A utilized the same tool and thus exhibit substantially the same complement cumulative slope magnitude distribution  $F_{cc}(\theta)$  and peak dimensional characteristics, as will subsequently be described. Microstructured surfaces H10A and H10B also utilized the same tool and thus also exhibit substantially the same complement cumulative slope magnitude distribution  $F_{cc}(\theta)$  and peak dimensional characteristics. Microstructured surfaces H2A, H2B and H2C also utilized the same tool. Hence, H2B and H2C have substantially the same complement cumulative slope magnitude distribution and peak dimensional characteristics as H2A.

Some examples of surface profiles of illustrative microstructured high index layers are depicted in FIGS. 8A-9D.

Representative portions of the surface of the fabricated samples, having an area ranging from about 200 microns by 250 microns to an area of about 500 microns by 600 microns, were characterized using atomic force microscopy (AFM), confocal microscopy, or phase shift interferometry according to the test method described in the examples.

The  $F_{cc}(\theta)$  complement cumulative slope magnitude distribution of the slope distribution is defined by the following equation

$$F_{cc}(\theta) = \frac{\sum_{q=\theta}^{\infty} N_G(q)}{\sum_{q=0}^{\infty} N_G(q)} .$$

$F_{cc}$  at a particular angle ( $\theta$ ) is the fraction of the slopes that are greater than or equal to  $\theta$ . The  $F_{cc}(\theta)$  of the microstructures of the microstructured (e.g. high refractive index layer) is depicted in the following Table 1.

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**Table 1 – Microstructured Layer Clarity, Haze & Complement Cumulative Slope Magnitude Characterization**

|                                                          | <b>Clarity</b> | <b>Haze</b> | <b>Fcc<br/>(0.1)</b> | <b>Fcc<br/>(0.3)</b> | <b>Fcc<br/>(0.7)</b> | <b>Fcc<br/>(1.3)</b> | <b>Fcc<br/>(4.1)</b> |
|----------------------------------------------------------|----------------|-------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| <b>Comparative<br/>Example A<br/>H11</b>                 | 87             | 5.5         | 97.5                 | 90.8                 | 70.9                 | 43.6                 | 7.5                  |
| <b>Comparative<br/>Example B<br/>H1<br/>(FIG. 8A-8D)</b> | 35             | 24          | 99.8                 | 99.3                 | 97.3                 | 91.1                 | 28.7                 |
| <b>H6</b>                                                | 79.7           | 1.65        | 97.3                 | 89.8                 | 62.6                 | 22.4                 | 0.0                  |
| <b>H8</b>                                                | 85.3           | 1.3         | 95.5                 | 83.7                 | 47.6                 | 8.4                  | 0.0                  |
| <b>H9</b>                                                | 67.4           | 3           | 98.8                 | 94.9                 | 78.7                 | 42.9                 | 0.0                  |
| <b>H2A</b>                                               | 72.9           | 8.42        | 97.7                 | 91.6                 | 74.9                 | 53.6                 | 5.7                  |
| <b>H3</b>                                                | 84.6           | 1.75        | 94.9                 | 81.0                 | 39.5                 | 4.7                  | 0.0                  |
| <b>H4<br/>(FIG. 9A-9D)</b>                               | 81             | 2.87        | 95.4                 | 82.7                 | 55.5                 | 27.3                 | 0.2                  |
| <b>H5</b>                                                | 86             | 2.47        | 95.4                 | 84.6                 | 56.0                 | 19.0                 | 0.0                  |
| <b>H5A</b>                                               |                |             | 95.3                 | 84.6                 | 55.9                 | 19.0                 | 0.0                  |
| <b>H7</b>                                                | 83.1           | 1.21        | 95.9                 | 83.5                 | 49.1                 | 9.3                  | 0.0                  |
| <b>H10A</b>                                              | 76.2           | 8.45        | 97.9                 | 92.1                 | 72.6                 | 37.7                 | 0.1                  |
| <b>H10B</b>                                              | 74.9           | 7.17        | 97.9                 | 92.1                 | 73.1                 | 38.6                 | 0.0                  |
| <b>H2B</b>                                               | 72             | 8.52        | Same as H2           |                      |                      |                      |                      |
| <b>H2C</b>                                               | 71.3           | 8.66        | Same as H2.          |                      |                      |                      |                      |

\*H11 is a commercially available matte AR film comprising SiO<sub>2</sub> particles.

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FIG. 10A shows the percent cumulative slope distribution for another sample, Sample A. As is evident from FIG. 10A, about 100% of the surface of sample A had a

slope magnitude less than about 3.5 degrees. Furthermore, about 52% of the analyzed surface had slope magnitudes less than about 1 degree, and about 72% of the analyzed surface had slope magnitudes less than about 1.5 degrees.

Three additional samples similar to sample A, and labeled B, C, and D were characterized. All four samples A-D had microstructures similar to microstructures 160 and were made using a cutting tool system similar to cutting tool system 1000 to make a patterned roll using a cutter similar to cutter 1120 and subsequently microreplicating the patterned tool to make matte layers similar to matter layer 140. Sample B had an optical transmittance of about 95.2%, an optical haze of about 3.28% and an optical clarity of about 78%; Sample C had an optical transmittance of about 94.9%, an optical haze of about 2.12%, and an optical clarity of about 86.1%; and sample D had an optical transmittance of about 94.6%, an optical haze of about 1.71%, and an optical clarity of about 84.8%. In addition, six comparative samples, labeled R1-R6, were characterized.

The  $F_{cc}(\theta)$  of the microstructures of Sample A-D was as follows:

|   | Fcc 0.1 | Fcc 0.3 | Fcc 0.7 | Fcc 1.3 | Fcc 4.1 |
|---|---------|---------|---------|---------|---------|
| A | 97.7    | 89.3    | 65.6    | 34.5    | 0.1     |
| B | 99.4    | 96.6    | 86.3    | 63.3    | 3.2     |
| C | 97.6    | 88.9    | 64.4    | 36.7    | 0.2     |
| D | 97.9    | 90.2    | 68.1    | 39.0    | 0.1     |

The optical clarity values disclosed herein were measured using a Haze-Gard Plus haze meter from BYK-Gardiner. As depicted in Table 1, the optical clarity of the polymerized (e.g. high refractive index) hardcoat microstructured surface is generally at least about 60% or 65%. In some embodiments, the optical clarity is at least 75% or 80%. In some embodiments, the clarity is no greater than 90%, or 89%, or 88%, or 87%, or 86%, or 85%.

Optical haze is typically defined as the ratio of the transmitted light that deviates from the normal direction by more than 2.5 degrees to the total transmitted light. The optical haze values disclosed herein were also measured using a Haze-Gard Plus haze meter (available from BYK-Gardiner, Silver Springs, Md.) according to the procedure described in ASTM D1003. As depicted in Table 1 above, the optical haze of the polymerized (e.g. high refractive index) hardcoat microstructured surface was less than 20% and preferably less than 15%. In favored embodiments, the optical haze ranges from

about 1%, or 2% or 3% to about 10%. In some embodiments the optical haze ranges from about 1%, or 2%, or 3% to about 5%.

Each value reported in the slope magnitude columns is the total percentage of microstructures (i.e. the total percentage of the microstructured surface) having such slope magnitude or greater. For example, in the case of microstructured surface H6, 97.3% of the microstructures had a slope magnitude of 0.1 degree or greater; 89.8% of the microstructures had a slope magnitude of 0.3 degrees or greater; 62.6% of the microstructures had a slope magnitude of 0.7 degrees or greater; 22.4% of the microstructures had a slope magnitude of 1.3 degrees greater; and 0 (none) of the microstructures (of the area measured) had a slope magnitude of 4.1 degrees or greater. Conversely, since 62.6% of the microstructures had a slope magnitude of 0.7 degrees or greater,  $100\% - 62.6\% = 37.4\%$  had slope magnitude less than 0.7 degrees. Further, since 22.4% of the microstructures had a slope magnitude of 1.3 degrees greater,  $100\% - 22.4\% = 77.6\%$  of the microstructures had a slope magnitude less than 1.3 degrees.

As indicated in Table 1 as well as FIGS. 10A, 10B, and FIG. 11 at least 90% or greater of the microstructures of each of the microstructured surfaces had a slope magnitude of at least 0.1 degrees or greater. Further, at least 75% of the microstructures had a slope magnitude of at least 0.3 degrees.

The preferred microstructured surface, having high clarity and low haze, suitable for use as a front (e.g. viewing) surface matte layer had different complement cumulative slope distribution characteristics than H1. In the case of H1 at least 97.3% of the microstructures had a slope magnitude of at least 0.7 degrees. Thus only 2.7% had a slope magnitude less than 0.7 degrees. For the other microstructured surfaces, at least 25% or 30% or 35% or 40% and in some embodiments at least 45% or 50% or 55% or 60% or 65% or 70% or 75% of the microstructures had a slope magnitude of at least 0.7 degrees. Thus, at least 25% or 30% or 35% or 40% or 45% or 50% or 55% or 60% or 65% or 70% had a slope magnitude less than 0.7 degrees.

Alternatively or in addition thereto, the preferred microstructured surfaces can be distinguished from H1, in that for H1 at least 91.1% of the microstructures had a slope magnitude of at least 1.3 degrees. Thus only 8.9% had a slope magnitude less than 1.3 degrees. For the other microstructured surfaces, at least 25% of the microstructures had a slope magnitude of less than 1.3 degrees. In some embodiments, at least 30%, or 35%, or

40%, or 45% of the microstructures had a slope magnitude of at least 1.3 degrees. Hence, 55% or 60% or 65% of the microstructures had a slope magnitude less than 1.3 degrees. In other embodiments, at least 5% or 10% or 15% or 20% of the microstructures had a slope magnitude of at least 1.3 degrees. Hence, 80% or 85% or 90% or 95% of the  
5 microstructures had a slope magnitude less than 1.3 degrees.

Alternatively or in addition thereto, the matte microstructured surface can be distinguished from H1, in that for H1 at least about 28.7% of the microstructures had a slope magnitude of at least 4.1 degrees; whereas in the case of the favored microstructured surface, less than 20% or 15% or 10% of the microstructures had a slope magnitude of 4.1  
10 degrees or greater. Thus, 80% or 85% or 90% had a slope magnitude less than 4.1 degrees. In one embodiment, 5 to 10% of the microstructures had a slope magnitude of 4.1 degrees or greater. In most embodiments, less than 5% or 4% or 3% or 2% or 1% of the microstructures had a slope magnitude of 4.1 degrees or greater.

The microstructured surface comprises a plurality of peaks, as characterized  
15 according to the test method described in the forthcoming examples. Dimensional characteristics of the peaks are reported in the following Table 2:

**Table 2 – Microstructured Layer Peak Dimensional Characterization**

|                            | <b>ECD<br/>mean<br/>microns</b> | <b>Length<br/>mean<br/>microns</b> | <b>Width<br/>mean<br/>microns</b> | <b>W/L<br/>mean</b> | <b>NN<br/>microns</b> | <b>Sparkle</b> |
|----------------------------|---------------------------------|------------------------------------|-----------------------------------|---------------------|-----------------------|----------------|
| <b>Comparative<br/>H11</b> | 3.37                            | 4.10                               | 3.05                              | 0.82                | 13.24                 | 2              |
| <b>Comparative<br/>H1</b>  | 12.35                           | 18.94                              | 9.23                              | 0.55                | 18.90                 | 1              |
| <b>H5</b>                  | 11.29                           | 14.52                              | 9.53                              | 0.67                | 17.25                 | 1              |
| <b>H4</b>                  | 23.46                           | 50.70                              | 12.15                             | 0.28                | 33.44                 | 2              |
| <b>H10A</b>                | 15.31                           | 20.72                              | 12.42                             | 0.61                | 22.60                 | 2              |
| <b>H10B</b>                | 14.7                            | 19.776                             | 11.986                            | 0.619               | 21.34                 | 2              |
| <b>H6</b>                  | 21.82                           | 28.66                              | 18.18                             | 0.64                | 29.36                 | 3              |
| <b>H8</b>                  | 24.38                           | 31.63                              | 20.74                             | 0.67                | 34.37                 | 3              |
| <b>H9</b>                  | 21.55                           | 29.47                              | 17.43                             | 0.60                | 29.11                 | 3              |
| <b>H3</b>                  | 58.23                           | 74.94                              | 48.69                             | 0.66                | 76.34                 | 4              |
| <b>H7</b>                  | 30.55                           | 41.44                              | 24.82                             | 0.61                | 40.37                 | 4              |
| <b>H2A</b>                 | Not determined.                 |                                    |                                   |                     |                       |                |

Such dimensional characteristics have been found to relate to “sparkle”, which is a visual degradation of an image displayed through a matte surface due to interaction of the matte surface with the pixels of an LCD. The appearance of sparkle can be described as a plurality of bright spots of a specific color that superimposes “graininess” on an LCD image detracting from the clarity of the transmitted image. The level, or amount, of sparkle depends on the relative size difference between the microreplicated structures and the pixels of the LCD (i.e. the amount of sparkle is display dependent). In general, the microreplicated structures need to be much smaller than LCD pixel size to eliminate sparkle. The amount of sparkle is evaluated by visual comparison with a set of physical acceptance standards (samples with different levels of sparkle) on a LCD display available under the trade designation “Apple iPod Touch” (having a pixel pitch of about 159  $\mu\text{m}$  as

measured with a microscope) in the white state. The scale ranges from 1 to 4, with 1 being the lowest amount of sparkle and 4 being the highest.

Although Comparative H1 had low sparkle, such microstructured (e.g. high refractive index) layer had low clarity and high haze as reported in Table 1.

Comparative H11 is a commercially available matte film wherein substantially all the peaks are formed by matte particles. Hence, the mean equivalent circular diameter (ECD), mean length, and mean width are approximately the same. The other examples (i.e. except for H1) demonstrate that low sparkle can be obtained with a matte film having substantially different peak dimensional characteristics than Comparative H11. For example, the peaks of all the other exemplified microstructured surfaces had a mean ECD of at least 5 microns and typically of at least 10 microns, substantially higher than Comparative H11. Further, the other examples having lower sparkle than H3 and H7 had a mean ECD (i.e. peak) of less than 30 microns or less than 25 microns. The peaks of the other exemplified microstructured surfaces had a mean length of greater than 5 microns (i.e. greater than H11) and typically greater than 10 microns. The mean width of the peaks of the exemplified microstructured surfaces is also at least 5 microns. The peaks of the low sparkle examples had a mean length of no greater than about 20 microns, and in some embodiments no greater than 10 or 15 microns. The ratio of width to length (i.e. W/L) is typically at least 1.0, or 0.9, or 0.8. In some embodiments, the W/L is at least 0.6. In another embodiment, the W/L is less than 0.5 or 0.4 and is typically at least 0.1 or 0.15. The nearest neighbor (i.e. NN) is typically at least 10 or 15 microns and no greater than 100 microns. In some embodiments, the NN ranges from 15 microns to about 20 microns, or 25 microns. Except for the embodiment wherein W/L is less than 0.5 the higher sparkle embodiments typically have a NN of at least about 30 or 40 microns.

With regard to the exemplified microstructured layers and matte films, the microstructures cover substantially the entire surface. However, without intending to be bound by theory it is believed that the microstructures having slope magnitudes of at least 0.7 degrees provide the desired matte properties. Hence, it is surmised that the microstructures having a slope magnitudes of at least 0.7 degrees may cover at least about 25%, or at least about 30%, or at least about 35%, or at least about 40%, or at least about 45%, or at least about 50%, or at least about 55%, or at least about 60%, or at least about

65%, or at least about 70%, of the major surface, yet still provide the desired high clarity and low haze.

The plurality of peaks of the microstructured surface can also be characterized with respect to mean height, average roughness (Ra), and average maximum surface height (Rz).

**Table 3 – Mean Height and Roughness**

|                        | <b>Mean Height<br/>(microns)</b> | <b>Ra<br/>(microns)</b> | <b>Rz<br/>(microns)</b> |
|------------------------|----------------------------------|-------------------------|-------------------------|
| <b>Comparative H11</b> | 0.604                            | 0.178                   | 2.875                   |
| <b>Comparative H1</b>  | 0.687                            | 0.189                   | 1.476                   |
| <b>H5</b>              | 0.380                            | 0.070                   | 0.590                   |
| <b>H5A</b>             | 0.380                            | 0.070                   | 0.630                   |
| <b>H4</b>              | 0.398                            | 0.093                   | 0.767                   |
| <b>H10A</b>            | 0.834                            | 0.100                   | 1.069                   |
| <b>H10B</b>            | 0.438                            | 0.102                   | 0.835                   |
| <b>H6</b>              | 0.507                            | 0.122                   | 0.945                   |
| <b>H8</b>              | 0.430                            | 0.101                   | 0.847                   |
| <b>H9</b>              | 0.592                            | 0.150                   | 1.201                   |
| <b>H3</b>              | 0.606                            | 0.176                   | 1.312                   |
| <b>H7</b>              | 0.502                            | 0.118                   | 0.899                   |
| <b>H2A</b>             | 0.482                            | 0.124                   | 1.074                   |

The average surface roughness (i.e. Ra) is typically less than 0.20 microns. The favored embodiments having high clarity in combination with sufficient haze exhibit a Ra of less no greater than 0.18 or 0.17 or 0.16 or 0.15 microns. In some embodiments, the Ra is less than 0.14, or 0.13, or 0.12, or 0.11, or 0.10 microns. The Ra is typically at least 0.04 or 0.05 microns.

The average maximum surface height (i.e. Rz) is typically less than 3 microns or less than 2.5 microns. The favored embodiments having high clarity in combination with sufficient haze exhibit an Rz of less no greater than 1.20 microns. In some embodiments, the Rz is less than 1.10 or 1.00 or 0.90, or 0.80 microns. The Rz is typically at least 0.40 or 0.50 microns.

The microstructured layer of the matte film typically comprises a polymeric material such as the reaction product of a polymerizable resin. The polymerizable resin preferably comprises surface modified nanoparticles. A variety of free-radically polymerizable monomers, oligomers, polymers, and mixtures thereof can be employed in the organic material of the high refractive index layer.

In some embodiments, the microstructured layer of the matte film has a high refractive index, i.e. of at least 1.60 or greater. In some embodiments, the refractive index is at least 1.62 or at least 1.63 or at least 1.64 or at least 1.65.

Various high refractive index particles are known including for example zirconia ("ZrO<sub>2</sub>"), titania ("TiO<sub>2</sub>"), antimony oxides, alumina, tin oxides, alone or in combination. Mixed metal oxide may also be employed. Zirconias for use in the high refractive index layer are available from Nalco Chemical Co. under the trade 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. Pat. No. 7,241,437 and U.S. Pat. No. 6,376,590. The maximum refractive index of the matte layer is typically no greater than about 1.75 for coatings having high refractive index inorganic (e.g. zirconia) nanoparticles dispersed in a crosslinked organic material.

In other embodiments, the microstructured layer of the matte film has a refractive index of less than 1.60. For example, the microstructured layer may have refractive index ranging from about 1.40 to about 1.60. In some embodiments, the refractive index of the microstructured layer is at least about 1.47, 1.48, or 1.49.

The microstructured layer having a refractive index of less than 1.60 typically comprises the reaction product of a polymerizable composition comprising one or more free-radically polymerizable materials and surface modified inorganic nanoparticles, typically having a low refractive index (e.g. less than 1.50).

Various free-radically polymerizable monomers and oligomers have been described for use in conventional hardcoat compositions including for example (a)

di(meth)acryl containing compounds such as 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol monoacrylate monomethacrylate, ethylene glycol diacrylate, alkoxylated aliphatic diacrylate, alkoxylated cyclohexane dimethanol diacrylate, alkoxylated hexanediol diacrylate, alkoxylated neopentyl glycol diacrylate, caprolactone modified neopentylglycol hydroxypivalate diacrylate, caprolactone modified neopentylglycol hydroxypivalate diacrylate, cyclohexanedimethanol diacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, ethoxylated (10) bisphenol A diacrylate, ethoxylated (3) bisphenol A diacrylate, ethoxylated (30) bisphenol A diacrylate, ethoxylated (4) bisphenol A diacrylate, hydroxypivalaldehyde modified trimethylolpropane diacrylate, neopentyl glycol diacrylate, polyethylene glycol (200) diacrylate, polyethylene glycol (400) diacrylate, polyethylene glycol (600) diacrylate, propoxylated neopentyl glycol diacrylate, tetraethylene glycol diacrylate, tricyclodecanedimethanol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate; (b) tri(meth)acryl containing compounds such as glycerol triacrylate, trimethylolpropane triacrylate, ethoxylated triacrylates (e.g., ethoxylated (3) trimethylolpropane triacrylate, ethoxylated (6) trimethylolpropane triacrylate, ethoxylated (9) trimethylolpropane triacrylate, ethoxylated (20) trimethylolpropane triacrylate), propoxylated triacrylates (e.g., propoxylated (3) glyceryl triacrylate, propoxylated (5.5) glyceryl triacrylate, propoxylated (3) trimethylolpropane triacrylate, propoxylated (6) trimethylolpropane triacrylate), trimethylolpropane triacrylate, tris(2-hydroxyethyl)isocyanurate triacrylate; (c) higher functionality (meth)acryl containing compounds such as ditrimethylolpropane tetraacrylate, dipentaerythritol pentaacrylate, ethoxylated (4) pentaerythritol tetraacrylate, caprolactone modified dipentaerythritol hexaacrylate; (d) oligomeric (meth)acryl compounds such as, for example, urethane acrylates, polyester acrylates, epoxy acrylates; polyacrylamide analogues of the foregoing; and combinations thereof. Such compounds are widely available from vendors such as, for example, Sartomer Company of Exton, Pennsylvania; UCB Chemicals Corporation of Smyrna, Georgia; and Aldrich Chemical Company of Milwaukee, Wisconsin. Additional useful (meth)acrylate materials include hydantoin moiety-containing poly(meth)acrylates, for example, as described in U.S. Patent No. 4,262,072 (Wendling et al.). Silicas for use in the moderate refractive index composition are commercially available from Nalco Chemical Co., Naperville, Ill. under the trade

designation "Nalco Collodial Silicas" such as products 1040, 1042, 1050, 1060, 2327 and 2329. Suitable fumed silicas include for example, products commercially available from DeGussa AG, (Hanau, Germany) under the trade designation, "Aerosil series OX-50", as well as product numbers -130, -150, and -200. Fumed silicas are also commercially available from Cabot Corp., Tuscola, Ill., under the trade designations CAB-O-SPERSE 2095, "CAB-O-SPERSE A105", and "CAB-O-SIL M5".

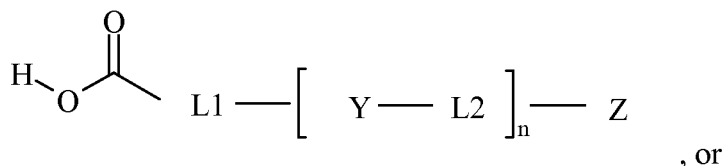
The concentration of (e.g. inorganic) nanoparticles in the microstructured matte layer is typically at least 25 wt-% or 30 wt-%. The moderate refractive index layer typically comprises no greater than 50 wt-% or 40 wt-% inorganic oxide nanoparticles. The concentration of inorganic nanoparticles in the high refractive index layer is typically at least 40 wt-% and no greater than about 60 wt-% or 70 wt-%.

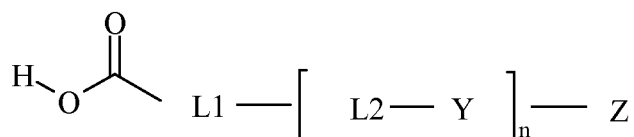
The inorganic nanoparticles are preferably treated with a surface treatment agent. Silanes are preferred for silica and other for siliceous fillers. Silanes and carboxylic acids are preferred for metal oxides such as zirconia. Various surface treatments are known, some of which are described in US2007/0286994.

In one embodiment, the microreplicated layer is prepared from a composition comprising about a 1 to 1 ratio of a crosslinking monomer (SR444) comprising at least three (meth)acrylate groups and surface modified silica. In another embodiment, the microreplicated layer is prepared from a composition that is free of silica nanoparticles. Such composition comprises an aliphatic urethane acrylate (CN9893) and hexanediol acrylate (SR238).

The high refractive index (e.g. zirconia) nanoparticles may be surface treated with a surface treatment comprising a compound comprising a carboxylic acid end group and a C<sub>3</sub>-C<sub>8</sub> ester repeat unit or at least one C<sub>6</sub>-C<sub>16</sub> ester unit, as described in PCT Application Number PCT/US2009/065352; incorporated herein by reference.

The compound typically has the general formula:



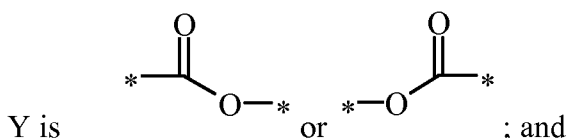


wherein

n averages from 1.1 to 6;

L1 is a C<sub>1</sub> - C<sub>8</sub> alkyl, arylalkyl, or aryl group, optionally substituted with one or more oxygen atoms or an ester group;

L2 is a C<sub>3</sub> - C<sub>8</sub> alkyl, arylalkyl, or aryl group, optionally substituted with one or more oxygen atoms;



Z is an end group comprising a C<sub>2</sub> - C<sub>8</sub> alkyl, ether, ester, alkoxy, (meth)acrylate, or a combination thereof.

In some embodiments, L2 comprises a C<sub>6</sub>-C<sub>8</sub> alkyl group and n averages 1.5 to 2.5. Z preferably comprises a C<sub>2</sub> - C<sub>8</sub> alkyl group. Z preferably comprises a (meth)acrylate end group.

Surface modifiers comprising a carboxylic acid end group and a C<sub>3</sub>-C<sub>8</sub> ester repeat unit can be derived from reacting a hydroxy polycaprolactone such as a hydroxy polycaprolactone (meth)acrylate with an aliphatic or aromatic anhydride. The hydroxy polycaprolactone compounds are typically available as a polymerized mixture having a distribution of molecules. At least a portion of the molecules have a C<sub>3</sub>-C<sub>8</sub> ester repeat unit, i.e. n is at least 2. However, since the mixture also comprises molecules wherein n is 1, the average n for the hydroxy polycaprolactone compound mixture may be 1.1, 1.2, 1.3, 1.4, or 1.5. In some embodiments, n averages 2.0, 2.1, 2.2, 2.3, 2.4 or 2.5.

Suitable hydroxy polycaprolactone (meth)acrylate compounds are commercially available from Cognis under the trade designation "Pemcure 12A" and from Sartomer under the trade designation "SR495" (reported to have a molecular weight of 344 g/mole).

Suitable aliphatic anhydrides include for example maleic anhydride, succinic anhydride, suberic anhydride, and glutaric anhydride. In some embodiments, the aliphatic anhydride is preferably succinic anhydride.

Aromatic anhydrides have a relatively higher refractive index (e.g. RI of at least 1.50). The inclusion of surface treatment compounds such as those derived from aromatic anhydrides can raise the refractive index of the overall polymerizable resin composition. Suitable aromatic anhydrides include for example phthalic anhydride.

Alternatively, or in addition thereto, the surface treatment may comprise a (meth)acrylate functionalized compound prepared by the reaction of an aliphatic or aromatic anhydride as previously described and a hydroxyl (e.g. C<sub>2</sub>-C<sub>8</sub>) alkyl (meth)acrylate.

Examples of surface modification agents of this type are succinic acid mono-(2-acryloyloxy-ethyl) ester, maleic acid mono-(2-acryloyloxy-ethyl) ester, and glutaric acid mono-(2-acryloyloxy-ethyl) ester, maleic acid mono-(4-acryloyloxy-butyl) ester, succinic acid mono-(4-acryloyloxy-butyl) ester, and glutaric acid mono-(4-acryloyloxy-butyl) ester. These species are shown in WO2008/121465; incorporated herein by reference.

The polymerizable compositions of the microstructured layer typically comprise at least 5 wt-% or 10 wt-% of crosslinker (i.e. a monomer having at least three (meth)acrylate groups). The concentration of crosslinker in the low refractive index composition is generally no greater than about 30 wt-%, or 25 wt-%, or 20 wt-%. The concentration of crosslinker in the high refractive index composition is generally no greater than about 15 wt-%.

Suitable crosslinker monomers include for example trimethylolpropane triacrylate (commercially available from Sartomer Company, Exton, Pa. under the trade designation "SR351"), ethoxylated trimethylolpropane triacrylate (commercially available from Sartomer Company, Exton, Pa. under the trade designation "SR454"), pentaerythritol tetraacrylate, pentaerythritol triacrylate (commercially available from Sartomer under the trade designation "SR444"), dipentaerythritol pentaacrylate (commercially available from Sartomer under the trade designation "SR399"), ethoxylated pentaerythritol tetraacrylate, ethoxylated pentaerythritol triacrylate (from Sartomer under the trade designation "SR494") dipentaerythritol hexaacrylate, and tris(2-hydroxy ethyl)isocyanurate triacrylate (from Sartomer under the trade designation "SR368"). In some aspects, a hydantoin

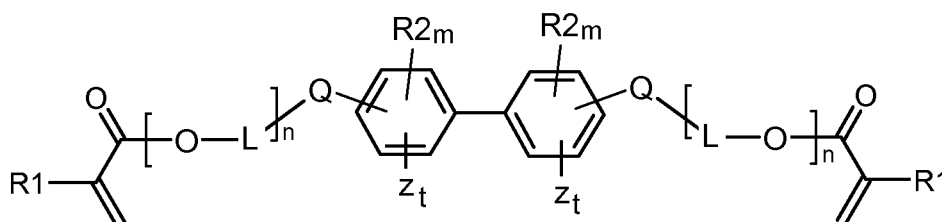
moiety-containing multi-(meth)acrylates compound, such as described in U.S. Pat. No. 4,262,072 (Wendling et al.) is employed.

The high refractive index polymerizable composition typically comprises at least one aromatic (meth)acrylate monomer having two (meth)acrylate groups (i.e. a di(meth)acrylate monomer).

In some embodiments, the di(meth)acrylate monomer is derived from bisphenol A. One exemplary bisphenol-A ethoxylated diacrylate monomer is commercially available from Sartomer under the trade designations "SR602" (reported to have a viscosity of 610 cps at 20°C and a Tg of 2°C). Another exemplary bisphenol-A ethoxylated diacrylate monomer is as commercially available from Sartomer under the trade designation "SR601" (reported to have a viscosity of 1080 cps at 20°C and a Tg of 60°C). Various other bisphenol A monomers have been described in the art, such as those described in U.S. Patent No. 7,282,272.

In other embodiments, the high refractive index layer and AR film is free of monomer derived from bisphenol A.

One suitable difunctional aromatic (meth)acrylate monomer is a biphenyl di(meth)acrylate monomer is described in US2008/0221291; incorporated herein by reference. The biphenyl di(meth)acrylate monomers may the general structure



wherein each R1 is independently H or methyl;

each R2 is independently Br;

m ranges from 0 to 4;

each Q is independently O or S;

n ranges from 0 to 10;

L is a C2 to C12 alkyl group optionally substituted with one or more hydroxyl groups;

z is an aromatic ring; and

t is independently 0 or 1.

At least one, and preferably both, of the  $-Q[L-O]_n C(O)C(R1)=CH_2$  groups are substituted at the ortho or meta position such that the monomer is a liquid at 25°C.

Such biphenyl di(meth)acrylate monomer may be used alone or in combination with a triphenyl tri(meth)acrylate monomer such as described in WO2008/112452; incorporated herein by reference. WO2008/112452 also describes triphenyl mono(meth)acrylates and di(meth)acrylates that are also surmised to be suitable components for the high refractive index layer.

In some embodiments, the difunctional aromatic (meth)acrylate monomer is combined with an aromatic mono(meth)acrylate monomer having a molecular weight less than 450 g/mole and having a refractive index of at least 1.50, 1.51, 1.52, 1.53, 1.54, 1.55, 1.56, 1.57 or 1.58. Such reactive diluents typically comprise a phenyl, biphenyl, or naphthyl group. Further such reactive diluents can be halogenated or non-halogenated (e.g. non-brominated). The inclusion of reactive diluents, such as biphenyl mono(meth)acrylate monomers, can concurrently raise the refractive index of the organic component and improve the processability of the polymerizable composition by reducing the viscosity.

The concentration of aromatic mono(meth)acrylate reactive diluents typically ranges from 1 wt-% or 2 wt-% to about 10 wt-%. In some embodiments, the high refractive index layer comprises no greater than 9, 8, 7, 6, or 5 wt-% of reactive diluent(s). When excess reactive diluent is employed, the high refractive index layer as well as antireflective film can exhibit reduced pencil hardness. For example, when the sum of the monofunctional reactive diluents is no greater than about 7 wt-%, the pencil hardness is typically about 3H to 4H. However, when the sum of the monofunctional diluents exceeds 7 wt-%, the pencil hardness can be reduced to 2H or lower.

Suitable reactive diluents include for example phenoxy ethyl (meth)acrylate; phenoxy-2-methylethyl (meth)acrylate; phenoxyethoxyethyl (meth)acrylate, 3-hydroxy-2-hydroxypropyl (meth)acrylate; benzyl (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-naphthyloxy ethyl acrylate; 2-naphthyloxy ethyl acrylate; phenoxy 2-methylethyl acrylate; phenoxyethoxyethyl acrylate; 3-phenoxy-2-hydroxy propyl acrylate; 2,4-dibromo-6-sec-butylphenyl acrylate; 2,4-dibromo-6-isopropylphenyl acrylate; benzyl acrylate; phenyl

acrylate; 2,4,6-tribromophenyl acrylate. Other high refractive index monomers such as pentabromobenzyl acrylate and pentabromophenyl acrylate can also be employed.

One suitable diluent is phenoxyethyl acrylate (PEA). Phenoxyethyl acrylate is commercially available from more than one source including from Sartomer under the trade designation "SR339"; from Eternal Chemical Co. Ltd. under the trade designation "Etermer 210"; and from Toagosei Co. Ltd under the trade designation "TO-1166".

Benzyl acrylate is commercially available from AlfaAeser Corp, Ward Hill, MA.

The method of forming a matte coating on an optical display or a film may include providing a light transmissible substrate layer; and providing a microstructured layer on the substrate layer.

The microstructured layer may be cured for example by exposure to ultraviolet radiation using an H-bulb or other lamp at a desired wavelength, preferably in an inert atmosphere (less than 50 parts per million oxygen). The reaction mechanism causes the free-radically polymerizable materials to crosslink. The cured microstructured layer may be dried in an oven to remove photoinitiator by-products or trace amount of solvent if present. Alternatively, a polymerizable composition comprising higher amounts of solvents can be pumped onto a web, dried, and then microreplicated and cured.

Although it is usually convenient for the substrate to be in the form of a roll of continuous web, the coatings may be applied to individual sheets.

The substrate can be treated to improve adhesion between the substrate and the adjacent layer, e.g., chemical treatment, corona treatment such as air or nitrogen corona, plasma, flame, or actinic radiation. If desired, an optional tie layer or primer can be applied to the substrate and/or hardcoat layer to increase the interlayer adhesion. Alternatively or in addition thereto the primer may be applied to reduce interference fringing, or to provide antistatic properties.

Various permanent and removable grade adhesive compositions may be provided on the opposite side of the film substrate. For embodiments that employ pressure sensitive adhesive, the antireflective film article typically include a removable release liner. During application to a display surface, the release liner is removed so the antireflective film article can be adhered to the display surface.

**Examples:****Microstructured Surface Characterization**

The following method was used to identify and characterize peak regions and of interest in height profiles that were obtained by atomic force microscopy (AFM), confocal scanning laser microscopy (CSLM), or phase shifting interferometry (PSI) by use of a Wyko Surface Profiler with a 10X objective, over an area ranging from about 200 microns by 250 microns to area of about 500 microns by 600 microns. The method uses thresholding on the curvature and an iterative algorithm to optimize the selection. Using curvature instead of a simple height threshold helps pick out relevant peaks that reside in valleys. In certain cases, it also helps avoid the selection of a single continuous network.

Prior to analyzing the height profiles, a median filter is used to reduce the noise. Then for each point in the height profile, the curvature parallel to the direction of the steepest slope (along the gradient vector) was calculated. The curvature perpendicular to this direction was also calculated. The curvature was calculated using three points and is described in the following section. Peak regions are identified by identifying areas that have positive curvature in at least one of these two directions. The curvature in the other direction cannot be too negative. To accomplish this, a binary image was created by using thresholding on these two curvatures. Some standard image processing functions were applied to the binary image to clean it up. In addition, peak regions that are too shallow are removed.

The size of the median filter and the distance between the points used for the curvature calculations are important. If they are too small, the main peaks may break up into smaller regions due to imperfections on the peak. If they are too large, relevant peaks may not be identified. These sizes were set to scale with the size of the peak regions or the width of the valley region between the peaks, whichever is smaller. However, the region sizes depend on the size of the median filter and the distance between the points for the curvature calculations. Therefore, an iterative process was used to identify a spacing that satisfies some preset conditions that result in good peak identification.

### **Slope and Curvature Analysis**

Surface profile data gives height of the surface as a function of x and y positions. We will represent this data as a function  $H(x,y)$ . The x direction of the image is the horizontal direction of the image. The y direction of the image is the vertical direction of the image. MATLAB was used to calculate the following:

1. gradient vector

$$\nabla H(x,y) = \left( \frac{\partial H(x,y)}{\partial x}, \frac{\partial H(x,y)}{\partial y} \right) = \left( \frac{H(x+\Delta x, y) - H(x-\Delta x, y)}{2\Delta x}, \frac{H(x, y+\Delta y) - H(x, y-\Delta y)}{2\Delta y} \right)$$

2. slope (in degrees) distribution –  $N_G(\theta)$

$$\theta = \arctan(\|\nabla H(x,y)\|) = \arctan\left(\sqrt{\left(\frac{H(x+\Delta x, y) - H(x-\Delta x, y)}{2\Delta x}\right)^2 + \left(\frac{H(x, y+\Delta y) - H(x, y-\Delta y)}{2\Delta y}\right)^2}\right)$$

3.  $F_{CC}(\theta)$  – complement cumulative distribution of the slope distribution

$$F_{CC}(\theta) = \frac{\sum_{q=\theta}^{\infty} N_G(q)}{\sum_{q=0}^{\infty} N_G(q)}$$

$F_{CC}(\theta)$  is the complement of the cumulative slope distribution and gives the fraction of slopes that are greater than or equal to  $\theta$ .

4. g-curvature, curvature in the direction of the gradient vector (inverse microns)

5. t-curvature, curvature in the direction transverse to the gradient vector (increase microns)

### **Curvature**

As depicted in Fig. 12, the curvature at a point is calculated using the two points used for the slope calculation and the center point. For this analysis, the curvature is defined as one divided by the radius of the circle that inscribes the triangle formed by these three points.

$$curvature = \pm 1/R = \pm 2 \sin(\theta)/d$$

where  $\theta$  is the angle opposite the hypotenuse, and  $d$  is the length of the hypotenuse of the triangle. The curvature is defined to be negative if the curve is concave up and positive if concave down.

- 5 The curvature is measured along the gradient vector direction (i.e. g-curvature) and along the direction transverse to the gradient vector (i.e. t-curvature). Interpolation is used to obtain the two end points.

### **Peak Sizing**

- 10 The curvature profile is used to obtain size statistics for peaks on the surface of samples. Thresholding of the curvature profile is used to generate a binary image that is used to identify peaks. Using MATLAB, the following thresholding was applied at each pixel to generate the binary images for peak identification:

- 15  $\max(\text{g-curvature}, \text{t-curvature}) > c0_{\max}$   
 $\min(\text{g-curvature}, \text{t-curvature}) > c0_{\min}$

where  $c0_{\max}$  and  $c0_{\min}$  are curvature cutoff values. Typically,  $c0_{\max}$  and  $c0_{\min}$  were assigned as follows:

- 20 
$$c0_{\max} = 2\sin(q_0)N_0 / fov \quad (q_0 \text{ and } N_0 \text{ are fixed parameters})$$

$$c0_{\min} = -c0_{\max}$$

- 25  $q_0$  should be an estimate of the smallest slope (in degrees) that is of significance.  $N_0$  should be an estimate of the least number of peak regions that is desirable to have across the longest dimension of the field of view.  $fov$  is the length of the longest dimension of the field of view.

- 30 MATLAB with the image processing tool box was used to analyze the height profiles and generate the peak statistics. The following sequence gives an outline of the steps in the MATLAB code used to characterize peak regions.

1. If number of pixels  $\geq 1001 \times 1001$  then reduce number of pixels
  - calculate  $n_{skip} = \text{fix}(na \times nb / 1001 / 1001) + 1$ 
    - original image has size  $na \times nb$  pixels
  - if  $n_{skip} > 1$  then carry out  $(2 \times \text{fix}(n_{skip}/2) + 1) \times (2 \times \text{fix}(n_{skip}/2) + 1)$  median averaging
    - $\text{fix}$  is a function that rounds down to the nearest integer.
  - create new image keeping every  $n_{skip}$  pixel in each direction (e.g. keep rows and columns 1, 4, 8, 11 ... if  $n_{skip} = 3$ )
2.  $r = \text{round}(\Delta x / pix)$ 
  - $\Delta x$  is the step size that will be used in the slope calculation
  - $pix$  is the pixel size.
  - $r$  is  $\Delta x$  rounded to the nearest whole numbers of pixels
  - an initial value for  $\Delta x$  is chosen to be equal to  $ffov \times fov$ .
    - $ffov$  is a parameter chosen by the user prior to running the program
3. Perform median averaging with window size of  $\text{round}(f_{MX} \times r) \times \text{round}(f_{MY} \times r)$  pixels.
  - If the regions are oriented then median averaging is done with a window with an aspect ratio (W/L) close to that of a typical region as defined below. The window aspect ratio is not allowed to go below the preset value  $rm\_aspect\_min$ .
    - Note that if the regions are oriented, the height profiling should be performed with the sample aligned such that this orientation is along the x or y axis.
  - For this analysis, the regions are considered oriented if
    - mean orientation angle of the regions (weighted by region area) is less than 15 degrees or greater than 75 degrees.
      1. orientation angle is defined as the angle that the major axis of the ellipse associated with the region makes with the y-axis.
    - standard deviation of this orientation angle is less than 25 degrees
    - coverage is greater than 10%

- If this is the first round or the regions are not oriented then
    - $f_{MX}$  and  $f_{MY}$  is set equal to  $f_M$
  - If the orientation is along the y - axis
    - $f_{MX} = \text{round}(f_M * r * \text{sqrt}(\text{aspect}));$
    - 5       ▪  $f_{MY} = \text{round}(f_M * r / \text{sqrt}(\text{aspect}));$
  - If the orientation is along the x – axis
    - $f_{MX} = \text{round}(f_M * r / \text{sqrt}(\text{aspect}));$
    - $f_{MY} = \text{round}(f_M * r * \text{sqrt}(\text{aspect}));$
  - $\text{aspect}$  = the mean aspect ratio weighted by region area
    - 10       ▪ if it is less than  $rm\_aspect\_min$ , it is set equal to  $rm\_aspect\_min$ .
  - $f_M$  is a fixed parameter chosen before running the program.
4. Remove tilt.
- effectively makes the average slope across the entire profile in all directions
  - 15       equal to zero
5. Calculate slope profiles as previously described.
6. Calculate curvature profiles in the direction parallel to the gradient vector (g-curvature) and in the direction transverse to the gradient vector (t-curvature).
7. Create a binary image using the curvature thresholding described above.
- 20
8. Erode the binary image.
- the number of times the image is eroded is set equal to  $\text{round}(r * f_E)$
  - $f_E$  is a fixed parameter (typically  $\leq 1$ ), chosen before initiating the program
  - this helps separate distinct regions that are connected by a narrow line and
  - 25       eliminate regions that are too small
9. Dilate the image.
- the number of times the image is dialed is typically chosen to be the same
  - number of times the image was eroded
10. Further dilate the image.
- 30       – in this round, the image is dilated before being eroded
  - helps remove cul-de-sacs, round edges, and combine regions that are very
  - close together

11. Erode the image.

- the number of times the image is eroded is typically chosen to be the same number of times the image was dilated in the last step

12. Eliminate regions that are too close to the edge of the image.

- 5 – typically, it is deemed too close if any part of the regions is within (*nerode* + 2) of the edge, where *nerode* is the number of times the image was eroded in step 9
- this eliminates regions that are only partially in the field of view

10 13. Fill in any holes in each region.

14. Eliminate regions with ECD (equivalent circular diameter)  $< 2\sin(q_0)N_0 / \text{fov}$ .

- $q_0$  and  $N_0$  are parameter used in the curvature cutoff calculations.
- this eliminates regions that are small compared to the hemisphere with radius R
- 15 – these regions is likely to have slope variations within the region that is less than  $q_0$
- another filter to consider in place of this one is to eliminate regions with standard deviations in the slope less than a cutoff value

20 15. Then calculate a new value for  $r$ .

- if number of peaks indentified equals zero then reduce  $r$  by two and round up
- go to step 4
- new  $r = \text{round}(f_W * L_0)$
- 25 –  $f_W$  is a fixed parameter (typically  $\leq 1$ ), chosen before initiating the program
- $L_0$  is a length defined in Table A1
- if new  $r$  is less than  $r_{MIN}$ , set equal to  $r_{MIN}$
- if new  $r$  is greater than  $r_{MAX}$ , set equal to  $r_{MAX}$
- 30 – if  $r$  is unchanged or is repeated, this is the value for  $r$  that is chosen. Go to step 17.

- if coverage drops by a factor of  $Kc$  or more or if the number of regions increases by a factor of  $Kn$  or more, then the previous value for  $r$  is chosen.

Go to step 17.

- if a value for  $r$  is not chosen, go to step 4.

5

16. For the  $r$  chosen, calculate the following dimensions for each region identified:

- ECD,  $L$ ,  $W$ , and aspect ratio.

17. Calculate the mean and standard deviation for each dimension.

18. Calculate *coverage* and *NN* (Table A2).

10

**Table A1.** Definitions for parameters

|                   |                                                                                                                                                                                   |
|-------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\Delta x$        | target step size that will be used in the slope calculations, actual step size is obtained by converting this to the nearest number of pixels                                     |
| $r$               | $\Delta x$ rounded to the nearest number of pixels                                                                                                                                |
| $f_W$             | new $r = \text{round}(f_W * L_0)$                                                                                                                                                 |
| $L_0$             | length representing the typical size scale of the regions, distance between regions or diameter of curvature of the regions, whichever is smallest. $L_0 = \min(W_0, W_1, D_0)$ . |
| $W_0$             | $W_0 = f_{W0} * W + (1 - f_{W0}) * L$                                                                                                                                             |
| $W_1$             | $W_1 = W_0 * (\text{coverage}^{-1/2} - 1)$                                                                                                                                        |
| $D_0$             | 10 percentile point for the diameter of curvature distribution (10% are less than this point)                                                                                     |
| $f_{W0}$          | parameter used to calculate $W_0$                                                                                                                                                 |
| $f_E$             | the number of times the binary image is eroded = $\text{round}(r * f_E)$                                                                                                          |
| $f_M$             | parameter that impacts the size of the window for median averaging                                                                                                                |
| $rm\_aspect\_min$ | lower limit for the width to length ratio of the median averaging window                                                                                                          |
| $fov$             | length of the longest dimension of the field of view                                                                                                                              |
| $ffov$            | Initially $\Delta x$ is either chosen by the user or set equal to $ffov * fov$<br>typical values for $ffov$ are 0.01 and 0.015                                                    |
| $c0max$           | $c0max = 2\sin(q_0)N_0 / fov$ curvature threshold for max(g-curvature, t-curvature)                                                                                               |
| $c0min$           | $c0min = -c0max$ curvature threshold for min(g-curvature, t-curvature)                                                                                                            |
| $N_0$             | estimate of the least number of peak regions that is desirable to have across the longest dimension of the field of view                                                          |
| $q_0$             | estimate of the smallest slope (in degrees) that is of significance                                                                                                               |
| $r_{MIN}$         | $r$ is not allowed to go below this value                                                                                                                                         |
| $r_{MAX}$         | $r$ is not allowed to go above this value                                                                                                                                         |
| $Kc$              | If (new coverage) < (old coverage) / $Kc$ then stop and keep old value for $r$                                                                                                    |
| $Kn$              | If (new number of regions) > (old number of regions) * $Kn$ then stop and keep old value for $r$                                                                                  |

**Table A2** Definitions for region dimensions

|                 |                                                                                                                                                                                                                                                                   |
|-----------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| ECD             | equivalent circular diameter (ECD) of a region                                                                                                                                                                                                                    |
| $L$             | length of major axis of the ellipse that has the same normalized second central moments as the region                                                                                                                                                             |
| $W$             | length of minor axis of the ellipse that has the same normalized second central moments as the region                                                                                                                                                             |
| aspect ratio    | $W / L$                                                                                                                                                                                                                                                           |
| $NN$            | Equals one divided by the squareroot of the number of regions per unit area. Partial regions are included in this calculation. This is equal to the nearest neighbor distance between the center of the regions if the regions were arranged in a square lattice. |
| <i>coverage</i> | Equals the total area occupied by the regions divided by the total area of the image. Partial regions are included in this calculation.                                                                                                                           |

The dimensions were averaged over two height profiles.

5

Typical parameter settings were as follow:

ffov 0.015  
 $f_w$  1/3  
 10  $f_M$  2/3  
 $f_E$  0.3  
 $f_{w0}$  3/4  
 $K_c$  1/2  
 $K_n$  2-4  
 15  $r_{min}$  2  
 $r_{max}$  50  
 $r_{m \text{ aspect min}}$  1/3  
 $N_0$  4  
 $q_0$  1/3-1/2

20

These parameter settings can be adjusted to insure that the major features (rather than minor features) are being identified.

## 25 **Height Frequency Distribution**

The minimum height value is subtracted from the height data so that the minimum height is zero. The height frequency distribution is generated by creating a histogram. The mean of this distribution is referred to as the mean height.

30

**Roughness Metrics**

**Ra** – Average roughness calculated over the entire measured array.

$$Ra = \frac{1}{MN} \sum_{i=1}^M \sum_{k=1}^N |Z_{jk}|$$

wherein  $Z_{jk}$  = the height of each pixel after the zero mean is removed.

**Rz** is the average maximum surface height of the ten largest peak-to-valley separations in the evaluation area,

$$Rz = \frac{1}{10} [(H_1 + H_2 + \dots + H_{10}) - (L_1 + L_2 + \dots + L_{10})].$$

where H is a peak height and L is a valley height, and H and L have a common reference plane.

Each value reported for the complement cumulative slope distribution, peak dimensions, and roughness were based on an average of two areas. For a large film, such as a typical 17" computer display, an average of 5-10 randomly selected areas would typically be utilized.

**High Refractive Index Hardcoat Compositions**

**Synthesis of biphenyl diacrylate - 2,2'-Diethoxybiphenyl diacrylate (DEBPDA)** - To a 12000ml 4 neck resin head round bottom equipped with a temperature probe, nitrogen purge tube, an overhead stirrer and heating mantel was added 2,2'-biphenol (1415g, 7.6 moles, 1.0 equivalents), potassium fluoride (11.8g, 0.2 moles, 0.027 equivalents), ethylene carbonate (1415g, 16.1 moles, 2.11 equivalents) and heated to 155°C. At 4.5 hours, GC analysis indicated 0% starting material, 0% monoethoxylated and 94% product. Cooled to 80°C, added toluene 5.4 liters, added 2.5 liters deionized water, mixed for 15min and phase separated. Removed the water and washed again with 2.5 liters deionized water, phase separated, removed the water and distilled solution to remove residual water and approximately 1.8 liters of toluene. The solution was cooled to 50°C and added cyclohexane 1.8 liters, 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy obtained from CIBA Specialty Chemicals under the trade designation Prostab 5198, commonly referred

to a 4-hydroxy TEMPO (0.52g, 0.003 moles, 0.00044 equivalents), phenothiazine (0.52g, 0.0026 moles, 0.00038 equivalents), acrylic acid (1089.4g, 15.12 moles, 2.2 equivalents), methane sulfonic acid (36.3g, 0.38 moles, 0.055 equivalents) and heated to reflux (pot temp was 92-95C). The flask was equipped with a dean stark trap to collect water. After 5 18 hours GC analysis indicated 8% monoacrylate intermediate. Added an additional 8g acrylic acid and continued refluxing for another 6 hours for a total of 24 hours. After 24 hours GC analysis indicated 3% monoacrylate intermediate. The reaction was cooled to 50°C and treated with 2356ml 7% sodium carbonate, stirred for 30min, phase separated, removed aqueous, washed again with 2356ml DI water, phase separated and removed 10 aqueous. To the (pink-red) toluene/cyclohexane solution was added 4-hydroxy TEMPO (0.52g, 0.003 moles, 0.00044 equivalents), phenothiazine (0.52g, 0.0026 moles, 0.00038 equivalents), aluminum n-nitrosophenylhydroxylamine (0.52g, 0.0012 moles, 0.00017 equivalents) and concentrated with vacuum to approximately 5000ml solution. Filtered through a pad of celite and the filtrate was concentrated with vacuum with an air purge, at 15 50°C and 12torr vacuum for 3 hours. The resulting yellow to brown oil is further purified by distilling on a roll film evaporator. The conditions for distillation were heating the barrel at 155°C, condenser at 50°C and 1-5 mtorr. The recovered yield was 2467g (85% of theoretical) and purity was approximately 90% DEBPDA.

#### 20 **Synthesis of triphenyl triacrylate 1,1,1-Tris(4-acryloyloxyethoxyphenyl)ethane (TAEPE)**

To a 1000ml 3 neck round bottom equipped with a temperature probe, an overhead stirrer and heating mantel was added 1,1,1-tris(4-hydroxyphenyl)ethane (200g, 0.65 moles, 1.0 equivalents), potassium fluoride (0.5g, 0.0086 moles, 0.013 equivalents), ethylene 25 carbonate (175g, 2.0 moles, 3.05 equivalents) and heated to 165°C. At 5 hours, GC analysis indicated 0% starting material, 0% monoethoxylated, 2% diethoxylated, and 95% product. Cooled to 100°C, added toluene 750ml, transferred to a 3000ml 3 neck round bottom and added another 750ml toluene. The solution was cooled to 50°C and added, 4-hydroxy TEMPO (0.2g, 0.00116 moles, 0.00178 equivalents), acrylic acid (155g, 2.15 30 moles, 3.3 equivalents), methane sulfonic acid (10.2g, 0.1 moles, 0.162 equivalents) and heated to reflux. The flask was equipped with a dean stark trap to collect water. After 6 hours GC analysis indicated 7% diacrylate intermediate and 85% product. The reaction

was cooled to 50°C and treated with 400ml 7% sodium carbonate, stirred for 30min, phase separated, removed aqueous, washed again with 400ml 20% sodium chloride water, phase separated and removed aqueous. The organic was diluted with 4000ml methanol, filtered through a 3 inch by 5 inch diameter pad of silica gel (250-400mesh) and the filtrate was concentrated with vacuum with an air purge, at 50°C and 12torr vacuum for 3 hours. Recovered a brown oil 332g (85% of theoretical) and purity was approximately 85% TAEPE.

### **Preparation of Zirconia Sol**

The ZrO<sub>2</sub> sols used in the examples had the following properties (as measured according to the methods described in U.S. Patent No. 7,241,437.

| Relative Intensities |            | Apparent Crystallite Size (nm) |               |              |               |              |                             |
|----------------------|------------|--------------------------------|---------------|--------------|---------------|--------------|-----------------------------|
| Cubic/<br>Tetragonal | Monoclinic | (C,T)<br>(1 1 1)               | M<br>(-1 1 1) | M<br>(1 1 1) | Avg M<br>Size | % C/T        | Weighted<br>Avg XRD<br>Size |
| 100                  | 6 - 12     | 7.0 - 8.5                      | 3.0 - 6.0     | 4.0 - 11.0   | 4.5 - 8.3     | 89% -<br>94% | 7.0 - 8.4                   |

% C/T = Primary particle size

### **Preparation of HEAS/DCLA Surface Modifier**

A three neck round bottom flask is equipped with a temperature probe, mechanical stirrer and a condenser. To the flask is charged the following reagents: 83.5 g succinic anhydride, 0.04 g Prostab 5198 inhibitor, 0.5 g triethylamine, 87.2 g 2-hydroxyethyl acrylate, and 28.7 g hydroxy-polycaprolactone acrylate from Sartomer under the trade designation "SR495" (n average about 2). The flask is mixed with medium agitation and heated to 80°C and held for ~6 hours. After cooling to 40°C, 200 g of 1-methoxy-2-propanol was added and the flask mixed for 1 hour. The reaction mixture was determined to be a mixture of the reaction product of succinic anhydride and 2-hydroxyethyl acrylate (i.e. HEAS) and the reaction product of succinic anhydride and hydroxy-polycaprolactone acrylate (i.e. DCLA) at a 81.5/18.5 by weight ratio according to infrared and gas chromatography analysis.

**HEAS Surface Modifier** – was produced by reacting succinic anhydride and 2-hydroxyethyl acrylate.

**Preparation of HIHC 1**

5 Zirconia sol (1000g @ 45.3% solids) and 476.4g 1-methoxy-2-propanol were charged to a 5L round bottomed flask. The flask was set up for vacuum distillation and equipped with an overhead stirrer, temperature probe, heating mantle attached to a therm-o-watch controller. The zirconia sol and methoxy propanol were heated to 50°C. HEAS/DCLA surface modifiers (233.5g @ 50% solids in 1-methoxy-2-propanol, HEAS/DCLA at an 10 81.5/18.5 by weight ratio), DEBPDA (120.5g), 2-phenyl-phenyl acrylate (HBPA) commercially available from Toagosei Co. Ltd. of Japan. (50.2g @ 46% solids in ethyl acetate), low viscosity trimethylolpropane triacrylate available from Sartomer under the trade designation “SR 351 LV” (85.3g) and “ProStab 5198” (0.17g) were charged individually to the flask with mixing. Therm-o-watch was set for 80°C and 80% power. 15 Water and solvents were removed via vacuum distillation until batch temperature reached 80°C. This process was repeated six times and then all six batches were combined into a 12L round bottomed flask set up for vacuum distillation and equipped with a heating mantle, temperature probe/thermocouple, temperature controller, overhead stirrer and a steel tube for incorporating water vapor into the liquid composition. The liquid 20 composition was heated to 80°C at which time a water vapor stream at a rate of 800 ml per hour was introduced into the liquid composition under vacuum. Vacuum distillation with the vapor stream was continuous for 6 hours after which the vapor stream was discontinued. The batch was vacuum distilled at 80°C for an additional 60 minutes. Vacuum was then broken using an air purge. Photoinitiator (17.7g “Darocure 4265”, a 25 50:50 mixture of diphenyl (2,4,6-trimethylbenzoyl)- phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-1-propanone) was charged and mixed for 30 minutes. The resultant product was approximately 68% surface modified zirconia oxide in acrylate monomers having a refractive index of 1.6288.

30 **Preparation of HIHC 2**

Zirconia sol (5000g @ 45.3% solids) and 2433g 1-methoxy-2-propanol were charged to a 12L round bottomed flask. The flask was set up for vacuum distillation and equipped with a heating mantle, temperature probe/thermocouple, temperature controller, overhead stirrer

and a steel tube for incorporating water vapor into the liquid composition. The zirconia Sol and methoxy propanol were heated to 50°C. HEAS surface modifier (1056g @ 50% solids in 1-methoxy-2-propanol, DEBPDA (454.5g), HBPA (197g @ 46% solids in ethyl acetate), SR 351 LV (317.1g) and ProStab 5198 (0.69g) were charged individually to the flask with mixing. Temperature controller was set for 80°C. Water and solvents were removed via vacuum distillation until batch temperature reached 80°C at which time a water vapor stream at a rate of 800 ml per hour was introduced into the liquid composition under vacuum. Vacuum distillation with the vapor stream was continuous for 6 hours after which the vapor stream was discontinued and batch was vacuum distilled at 80°C for an additional 60 minutes. Vacuum was then broken using an air purge. Photoinitiator (87.3g Darocure 4265) was charged and mixed for 30 minutes. Resultant product was approximately 73% surface modified zirconia oxide in acrylate monomers having the following properties.

**High Index Hardcoat Coating Compositions 3 – 9** were prepared in the same manner as HIHC 1 and HIHC 2. The (wt-% solids) of each of the components of the high index hardcoat were as follows.

|                                   | HIHC 1 | HIHC 2 | HIHC 3 | HIHC 4 | HIHC 5 |
|-----------------------------------|--------|--------|--------|--------|--------|
| ZrO <sub>2</sub> w/ HEAS and DCLA | 68     |        | 70.9   | 68     | 68     |
| ZrO <sub>2</sub> w HEAS only      |        | 73*    |        |        |        |
| DEBPDA                            | 15.6   | 12.9   | 16.3   | 15.6   | 15.6   |
| HBPA                              | 3      | 2.6    | 3.1    | 3      | 3      |
| SR351 LV                          | 11.1   | 9      | 7.3    | 11.1   | 11.1   |
| Darocure 1173                     |        |        | 2.4    | 2.3    |        |
| Darocure 4265                     | 2.3    | 2.5    |        |        | 2.3    |
| total                             | 100    | 100    | 100    | 100    | 100    |
| Viscosity** @60°C                 | 0.77   | 1.73   | 4.06   | 1.44   | 1.88   |
| Viscosity @70°C                   | 0.47   | 0.91   | 2.35   | 0.86   | 1.1    |
| Viscosity @80°C                   |        | 0.54   |        |        |        |
| Refractive index @ 25°C           | 1.6288 | 1.645  | 1.6378 | 1.6244 | 1.6288 |

\*73 wt-% surface modified ZrO<sub>2</sub> contains about 58 wt-% ZrO<sub>2</sub> and 15 wt-% surface modifier.

\*\* Measured on a TA Instruments AR2000 with 60mm 2deg cone, temperature ramp from 80°C to 45°C at 2°C/min, shear rate 1/s. Viscosity units are pascal-seconds.

|                                   | HIHC 6 | HIHC 7 | HIHC 8 | HIHC 9 |
|-----------------------------------|--------|--------|--------|--------|
| ZrO <sub>2</sub> w/ HEAS and DCLA | 68     | 73     |        |        |
| ZrO <sub>2</sub> w/ HEAS only     |        |        | 73     | 71.54  |
| DEBPDA                            |        |        | 12.9   | 12.6   |
| TAEPE                             |        |        | 6      | 0      |
| SR601                             | 15.6   | 12.9   |        | 0      |
| HBPA                              | 3      | 2.6    | 2.6    | 4.6    |
| SR351 LV                          | 11.1   | 9      |        | 8.8    |
| SR339                             |        |        | 3      | 0      |
| Darocure 1173                     |        |        | 2.5    | 0      |
| Darocure 4265                     | 2.3    | 2.5    |        | 2.5    |
| total                             | 100    | 100    | 100    | 100    |
| Viscosity @60°C                   | 3.07   | 3.39   | 3.59   | 1.18   |
| Viscosity @70°C                   | 1.61   | 1.96   | 1.69   | 0.64   |
| Viscosity @80°C                   | 0.95   |        | 0.95   | 0.39   |
| Refractive index@25°C             | 1.6198 | 1.6252 | 1.6676 | 1.6439 |

SR601 - trade designation of bisphenol-A ethoxylated diacrylate monomer is as commercially available from Sartomer (reported to have a viscosity of 1080 cps at 20°C and a Tg of 60°C).

Darocure 1173- 2-hydroxy-2-methyl-1-phenyl-propan-1-one photoinitiator, commercially available from Ciba Specialty Chemicals.

SR399 – trade designation of dipentaerythritolpentaacrylate commercially available from Sartomer.

#### Preparation of the Microstructured High Index Hard Coat:

**Examples H1, H2A, H3, H2B, H2C** – Handspread coatings were made using a rectangular microreplicated tool (4 inches wide and 24 inches long) preheated by placing them on a hot plate at 160°F. A “Catena 35” model laminator from General Binding Corporation (GBC) of Northbrook, IL, USA was preheated to 160°F (set at speed 5, laminating pressure at “heavy gauge”). The high index hardcoats were preheated in an oven at 60°C and a Fusion Systems UV processor was turned on and warmed up (60 fpm, 100% power, 600 watts/inch D bulb, dichroic reflectors). Samples of polyester film were

cut to the length of the tool (~2 feet). The high index hardcoat were applied to the end of the tool with a plastic disposable pipette, 4 mil (Mitsubishi O321E100W76) primed polyester was placed on top of the bead and tool, and the tool with polyester run through the laminator, thus spreading the coating approximately on the tool such that depressions of the tool were filled with the high refractive index hardcoat composition. The samples were placed on the UV processor belt and cured via UV polymerization. The resulting cured coatings were approximately 3-6 microns thick.

|     | HIHC formulation |
|-----|------------------|
| H1  | HIHC3            |
| H2A | HIHC4            |
| H3  | HIHC1            |
| H2B | HIHC9            |
| H2C | HIHC8            |

A web coater was used to apply the other high index hardcoat coatings (18 inches in width) on 4 mil PET substrates. The other high index hardcoat coatings, except for H10A and H10B, were applied to primed PET available from Mitsubishi under the trade designation "4 mil Polyester film 0321 E100W76" at a tool temperature of 170 °F, a die temperature of 160°F, and a high index hardcoat coating temperature of 160°F. High index hardcoat coatings H10A and H10B were applied to unprimed 4 mil polyester film available from 3M under the trade designation "ScotchPar" corona treated to 0.75 MJ/cm<sup>2</sup> at a tool temperature of 180°F, a die temperature of 170°F for H10A and 180°F for H10B; and a high index hardcoat coating temperature of 180°F. Before coating the substrate was also heated with an IR heater set at approximately 150-180°F. The high index hardcoat coatings were flood coated by creating a rolling bank of resin between the tool and nipped film. The coatings were UV cured at 50 to 100% power with a D bulb and dichoric reflectors. The resulting cured coatings were approximately 3-6 microns thick. Further process conditions are included in the following table.

|              | HIHC Coating | Nip Pressure (psi) | Tool Temp (°F) | Web Speed (fpm) | Resin Temp (°F) | UV setting ( % Power) | *Thickness (um) | IR Heater (°F) |
|--------------|--------------|--------------------|----------------|-----------------|-----------------|-----------------------|-----------------|----------------|
| <b>H6</b>    | HIHC 5       | 80                 | 170            | 40              | 160             | 100                   | 4 to 5          | 160            |
| <b>H8</b>    | HIHC 5       | 80                 | 170            | 40              | 160             | 100                   | 4 to 5          | 160            |
| <b>H9</b>    | HIHC 5       | 80                 | 170            | 40              | 160             | 100                   | 4 to 5          | 160            |
| <b>H4</b>    | HIHC 1       | 80                 | 170            | 40              | 160             | 50                    | 3 to 5          | 160            |
| <b>H5</b>    | HIHC 5       | 80                 | 170            | 40              | 160             | 100                   | 4 to 5          | 160            |
| <b>H5A</b>   | HIHC 7       | 80                 | 170            | 40              | 160             | 100                   | 4 to 5          | 160            |
| <b>H6</b>    | HIHC 5       | 80                 | 170            | 40              | 160             | 100                   | 4 to 5          | 160            |
| <b>H7</b>    | HIHC 5       | 80                 | 170            | 40              | 160             | 100                   | 4 to 5          | 160            |
| <b>H10 A</b> | HIHC 6       | 80                 | 180            | 25              | 146             | 100                   | 3 to 5          | 180            |
| <b>H10 B</b> | HIHC 2       | 80                 | 180            | 25              | 180             | 100                   | 4 to 5          | 180            |

\*Approximate Thickness

The clarity, haze, and complement cumulative slope distribution of the microstructured high index hardcoat samples were characterized as previously described in Table 1. The dimensions of the peaks of the microstructured surface were also characterized as previously described in Table 2.

#### **Fabrication of Matte Film from Moderate Refractive Index Hardcoat**

##### **Materials:**

SiO<sub>2</sub> surface modified with A174, as described in PCT/US2007/068197

SR444 multifunctional acrylate from Sartomer Co.

SR9893acrylate functional urethane oligomer available from Sartomer Co.

SR238 hexanediol acrylate from Sartomer Co.

Darocure 4265 photoinitiator blend available from Sartomer Co.

Formulation 1: A174 surface modified SiO<sub>2</sub> in 1-methoxy-2-propanol was mixed with SR444 and Darocur 4265 to provide the composition in the table below. When  
 5 homogeneous, the solvent was removed by rotary evaporation at 68°C (water aspirator), followed by drying with a vacuum pump for 20 minutes 68°C.

Formulation 2: The SR9893 was heated to 70°C and then blended with SR238 and Darocur 4265 and mechanically mixed overnight.

10 The concentration (wt-% solids) for each of the components utilized in the moderate refractive index hardcoat formulations is described as follows:

| Formulation | SiO <sub>2</sub> w/A174 | SR444 | Darocur 4265 | CN9893 | SR238 | RI    |
|-------------|-------------------------|-------|--------------|--------|-------|-------|
| 1           | 48.75                   | 48.75 | 2.5          | 0      | 0     | 1.478 |
| 2           | 0                       | 0     | 2.5          | 68.25  | 29.25 | 1.484 |

15 Handspread coating were prepared in the same manner as the microstructured high index hardcoat on two different substrates.

Substrate 1 - 4 mil PET from Mitsubishi O321E100W76

Substrate 2 - 4 mil PET from 3M trade designation "ScotchPar"

| Example | Composition | Microstructured surface example: | Substrate | % Transmission | % Haze | % Clarity |
|---------|-------------|----------------------------------|-----------|----------------|--------|-----------|
| H10C    | 1           | H10A & H10B                      | 1         | 92.6           | 1.76   | 85        |
| H2D     | 1           | H2A, H2B, H2C                    | 2         | 93.5           | 5.81   | 81.6      |
| H1 A    | 1           | H1                               | 2         | 92.4           | 14.6   | 52.7      |
| H2E     | 2           | H2A, H2B, H2C                    | 2         | 93.6           | 4.93   | 82        |
| H1 B    | 2           | H1                               | 2         | 93.9           | 13.9   | 51        |

**What is claimed is:**

1. A matte film comprising a microstructured surface layer comprising a plurality of microstructures having a complement cumulative slope magnitude distribution such that at  
5 least 30% have a slope magnitude of at least 0.7 degrees and at least 25% have a slope magnitude of less than 1.3 degrees; and wherein no greater than 50% of the microstructures comprise embedded matte particles.
2. The matte film of claim 1 wherein at least 30% of the microstructures have a slope  
10 magnitude of less than 1.3 degrees.
3. The matte film of claim 1 wherein at least 35% of the microstructures have a slope magnitude of less than 1.3 degrees.
- 15 4. The matte film of claim 1 wherein at least 40% of the microstructures have a slope magnitude of less than 1.3 degrees.
5. The matte film of claims 1-4 wherein less than 15% of the microstructure have a slope magnitude of 4.1 degrees or greater.  
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6. The matte film of claims 1-4 wherein less than 5% of the microstructures have a slope magnitude of 4.1 degrees or greater.
7. The matte film of claims 1-6 wherein at least 75% of the microstructures have a slope  
25 magnitude of at least 0.3 degrees.
8. The matte film of claims 1-7 wherein the surface layer comprises peaks having a mean equivalent circular diameter of at least 5 microns.
- 30 9. The matte film of claim 8 wherein the mean equivalent circular diameter is at least 10 microns.

10. The matte film of claims 8 or 9 wherein mean equivalent circular diameter is less than 30 microns.
11. The matte film of claims 8 or 9 wherein the mean equivalent circular diameter is less than 25 microns.
12. The matte film of claims 1-7 wherein the microstructured surface comprises peaks having a mean length of at least 5 microns.
13. The matte film of claim 12 wherein the peaks have a mean length of at least 10 microns.
14. The matte film of claims 1-7 wherein the microstructured surface comprises peaks having a mean width of at least 5 microns.
15. The matte film of claim 14 wherein the peaks have a mean width of less than 15 microns.
16. The matte film of any of the preceeding claims wherein the film has an average roughness (Ra) of less than 0.14 microns.
17. The matte film of any of the preceeding claims wherein the film has an average maximum surface height (Rz) of less than 1.20 microns.
18. A matte film comprising a microstructured layer wherein the matte film has a clarity of no greater than 90%, an average surface roughness of at least 0.05 microns and no greater than 0.14 microns, and wherein no greater than 50% of the microstructures comprise embedded matte particles.
19. A matte film comprising a microstructured layer comprising a plurality of microstructures wherein the matte film has a clarity of no greater than 90%, an average

maximum surface height of at least 0.50 microns and no greater than 1.20 microns, and wherein no greater than 50% of the microstructures comprise embedded matte particles.

20. A matte film comprising a microstructured layer comprising a plurality of microstructures wherein the matte film has a clarity of no greater than 90% and the microstructured layer comprises peaks having a mean equivalent diameter of at least 5 microns and no greater than 30 microns, and no greater than 50% of the microstructures comprise embedded matte particles.

21. The matte film of any of the preceding claims wherein the matte film has a clarity of at least 70%.

22. The matte film of any of the preceding claims wherein the matte film wherein the optical film has a haze of no greater than 10%.

23. The matte film of any of the preceding claims the microstructured layer comprises the reaction product of a polymerizable resin composition having a refractive index of greater than about 1.60.

24. The matte film of claim 23 wherein the polymerized resin composition comprises nanoparticles having a refractive index of at least about 1.60.

25. The matte film of claim 24 wherein the nanoparticles comprise zirconia.

26. The matte film of claims 23-24 wherein the nanoparticles are surface modified with a compound comprising a carboxylic acid end group.

27. The matte film of claim 26 wherein the compound comprises a C<sub>3</sub>-C<sub>8</sub> ester repeat unit or at least one C<sub>6</sub>-C<sub>16</sub> ester unit.

28. The matte film of claim 27 wherein the compound comprises the reaction product of  
i) at least one aliphatic anhydride, and  
ii) at least one hydroxy polycaprolactone (meth)acrylate.

29. The matte film of claims 24-28 wherein the nanoparticles are surface modified with a compound prepared by the reaction of an aliphatic anhydride and a hydroxyl C<sub>2</sub> - C<sub>8</sub> alkyl(meth)acrylate.

5 30. The matte film of claims 23-29 wherein the polymerizable resin composition comprises one or more aromatic di(meth)acrylate monomers in an amount ranging from about 10 to about 20 wt-%.

10 31. The matte film of claims 23-29 wherein the polymerizable resin composition comprises about 5 to about 15 wt-% of a crosslinker having at least three (meth)acrylate groups.

32. The matte film of claims 23-29 wherein the polymerizable resin composition comprises up to about 10 wt-% of an aromatic mono(meth)acrylate monomer.

15 33. The matte film of claims 1-22 wherein the microstructured layer comprises the reaction product of a polymerizable resin composition having a refractive index of less than about 1.60.

20 34. The matte film of claim 33 wherein the microstructured layer comprises silica nanoparticles.

35. The matte film of claim 33 wherein the microstructured layer comprises a urethane acrylate.

25 36. The matte film of any of the previous claims wherein the microstructures are free of matte particles.

37. The matte film of any of the previous claims wherein the microstructured layer is microreplicated.

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