the wavelengths of visible light spectrum and therefore can induce higher haze (i.e., > 4%) to reduce display quality.

SUMMARY

[0009] A subwavelength structured surface gradient solution is therefore desired. Preferably, the solution provides a relatively low reflection (i.e., average reflection over the visible range less than, less than 2.0 (in some embodiments, less than 1.5, or even less than 1.0) percent) and durable characteristics to enhance the viewing quality of display devices.

[0010] ~~In one aspect, t~~The present disclosure describes a material comprising sub-micrometer particles dispersed in a polymeric matrix, the material having a thickness, at least first and second integral regions across the thickness, the first region having the outer major surface wherein at least the outer most sub micrometer particles are partially conformally coated by (and optionally covalently bonded to) the polymeric matrix, wherein the first and second regions have first and second average densities, respectively, and wherein the first average density is less than the average second density. In one aspect, the present disclosure describes a material comprising sub-micrometer particles dispersed in a polymeric matrix, the material having a thickness, at least first and second integral regions across the thickness, the first region having the outer major surface, wherein at least the outer most sub-micrometer particles are partially conformally coated by the polymeric matrix, wherein the first and second regions have first and second average densities, respectively, and wherein the first average density is less than the average second density, and wherein, the difference between the first and second average densities is in a range from 0.1 g/cm^3 to 0.8 g/cm^3. In some embodiments, the difference between the first and second average densities is in a range from 0.1 g/cm3 to 0.8 g/cm3 (in some embodiments, 0.2 g/cm3 to 0.7g/cm3, or even 0.3 g/cm3 to 0.6 g/cm3). In some embodiments, the second region is substantially free of closed porosity (i.e., free of than closed pores greater than 200 nm (in some embodiments, greater than 150 nm, 100 nm, or even greater than 50 nm) in diameter). In some embodiments, the sub-micrometer particles each have an outer surface, and wherein at least 50 (in some embodiments, at least 60, 70, 75, 80, 90, 95, 99, or even 100) percent by volume of the sub-micrometer particles have their outer surface is free of fluorine. In some embodiments, the material having a Steel Wool Scratch Test value of at least 1 (in some embodiments, of at least 2, 3, 4, or even 5). In some embodiments, the sub-micrometer particles dispersed in the polymeric matrix has an average particle size, and the first region has a thickness less than (in some embodiments equal to; in some embodiments, greater than; in some embodiments, at least twice; in some embodiments three to five times) the average particle size of the sub-micrometer particles.

[0011] The present disclosure describes a material comprising sub-micrometer particles dispersed in a polymeric matrix, the material having a thickness, at least first and second integral regions across the thickness, wherein the first and second regions have first and second densities, respectively, and wherein the first average density is less than the second average density, and wherein the material having a Steel Wool Scratch Test value of at least 1 (in some embodiments, of at least 2, 3, 4, or 5). ~~In another aspect, the present disclosure describes a material comprising sub-micrometer particles dispersed in a polymeric matrix, the material having a thickness, at least first and second integral regions across the thickness, wherein the first and~~

~~second regions have first and second densities, respectively, wherein the first average density is less than the second average density, wherein the first region having an outer major surface, wherein at least the outer most sub-micrometer particles are partially conformally coated with the polymeric matrix, and wherein the material having a Steel Wool Scratch Test value of at least 1.~~ In some embodiments, the first region having the outer major surface wherein at least the outer most sub-micrometer particles are partially conformally coated with the polymeric matrix. In some embodiments, the sub-micrometer particles are covalently bonded to the polymeric matrix. In some embodiments, the second region is substantially free of closed porosity. In some embodiments, the sub micrometer particles each have an outer surface, and wherein at least 50 (in some embodiments, at least 60, 70, 75, 80, 90, 95, 99, or even 100) percent by volume of the sub micrometer particles have their outer surface is free of fluorine. In some embodiments, the sub micrometer particles dispersed in the

[0017] Articles described herein can be used, for example, for creating high performance, low fringing, antireflective optical articles. When a functional layer is disposed on a layer of material described herein, articles described herein may have, for example, further desired optical properties.

[0018] Embodiments of articles described herein are useful for numerous applications including display applications (e.g., liquid crystal displays (LCD), light emitting diode (LED) displays, or plasma displays); light extraction; electromagnetic interference (EMI) shielding, ophthalmic lenses; face shielding lenses or films; window films; antireflection for construction applications; and construction applications or traffic signs. Articles described herein are also useful for solar applications (e.g., solar films). They may also be useful, for example, as the front surface of solar thermal hot liquid/air heat panels or any solar energy absorbing device; for solar thermal absorbing surfaces having micro- or macro-columns with additional nano-scale surface structure; for the front surface of flexible solar photovoltaic cells made with amorphous silica photovoltaic cells or CIGS photovoltaic cells; and for the front surface of a film applied on top of flexible photovoltaic cells.

[0019a] In another aspect, the present disclosure describes a method of making a material of any preceding claim, the method comprising: providing a free radical curable layer having sub-micrometer particles dispersed therein; and actinic radiation curing the free radical curable layer in the presence of a sufficient amount of inhibitor gas, to inhibit the curing of a major surface region of the layer to provide a layer having a bulk region with a first degree of cure and a major surface region having a second degree of cure, wherein the first degree of cure is greater than the second degree of cure, and wherein the material having a structured surface that includes a portion of the sub-micrometer particles. ~~nanostructured material made according to the method as described above.~~

Listing of Exemplary Embodiments

[0019] Various exemplary embodiments of the present disclosure are further illustrated by the following listing of embodiments, which should not be construed to unduly limit the present disclosure:

[0020] 1A. A material comprising sub-micrometer particles dispersed in a polymeric matrix, the material having a thickness, at least first and second integral regions across the thickness, the first region having the outer major surface, wherein at least the outer most sub-micrometer particles are partially conformally coated by and, wherein the first and second regions have first and second average densities, respectively, and wherein the first average density is less than the second average density.

[0021] 2A. The material of Embodiment 1A , wherein, the difference between the first and second average densities is in a range from 0.1 g/cm^3 to 0.8 g/cm^3 (in some embodiments, 0.2 g/cm^3 to 0.7 g/cm^3, or even 0.3 g/cm^3 to 0.6g/cm^3).

[0022] 3A. The material of any preceding Embodiment A, wherein the second region is free of substantially closed porosity.

[0023] 4A. The material of any preceding Embodiment A, wherein at least the outer most sub-micrometer particles are covalently bonded to the polymeric matrix.

[0024] 5A. The material of any preceding Embodiment A, wherein the sub-micrometer particles each have an outer surface, and wherein at least 50 (in some embodiments, at least 60, 70, 75, 80, 90, 95, 99, or even 100) percent by volume of the sub-micrometer particles have their outer surface is free of fluorine.

[0025] 6A. The material of any preceding Embodiment A having a Steel Wool Scratch Test value of at least 1 (in some embodiments, of at least 2, 3, 4, or even 5).

[0026] 7A. The material of any preceding Embodiment A, wherein at least a portion of the polymer matrix is made from a prepolymer comprising free radically curable prepolymer.

Claims

1. A material comprising sub-micrometer particles dispersed in a polymeric matrix, the material having a thickness, at least first and second integral regions across the thickness, the first region having the outer major surface, wherein at least the outer most sub-micrometer particles are partially conformally coated by the polymeric matrix, wherein the first and second regions have first and second average densities, respectively, and wherein the first average density is less than the average second density~~.~~, and

~~2. The material of claim 1,~~ wherein, the difference between the first and second average densities is in a range from 0.1 g/cm^3 to 0.8 g/cm^3.

~~3~~2. The material of ~~either~~ claim 1 ~~or 2~~, wherein the second region is free of substantially closed porosity.

~~4~~3. The material of ~~any preceding~~either claim 1 or 2 having a Steel Wool Scratch Test value of at least 1.

~~5~~4. The material of any preceding claim, wherein at least the outer most sub-micrometer particles are partially conformally coated by and covalently bonded to the polymeric matrix.

~~6~~5. The material of any preceding claim, wherein at least a portion of the polymer is made from a prepolymer comprising free radically curable prepolymer.

~~7~~6. The material of claim ~~6~~5, wherein at least a portion of the prepolymer comprises at least one of a monomeric or oligomeric multifunctional (meth)acrylate.

~~8~~7. The material of claim ~~6~~5, wherein at least a portion of the prepolymer comprises at least one of a monomeric or oligomeric difunctional (meth)acrylate.

~~9~~8. The material of claim ~~6~~5, wherein at least a portion of the prepolymer comprises at least one of a monomeric or oligomeric monofunctional (meth)acrylate.

~~10~~9. The material of claim ~~6~~5, wherein at least a portion of the prepolymer comprises a mixture of mutifuctional, difuctional, and monofunction (meth)acrylates.

~~11~~10. The material of any one of claims ~~6~~5 to ~~10~~9, wherein the prepolymer composition has a functionality of 1.25 to 2.75.

~~12~~11. The material of any preceding claim, wherein the sub-micrometer particles comprise surface modified sub-micrometer particles.

~~13~~12. The material of any preceding claim, wherein the sub-micrometer particles have sub-micrometer particle sizes of at least 5 nm to 1000 nm.

~~14~~13. The material of any preceding claim, wherein the sub-micrometer particles comprise silica.

~~15~~14. The material of any preceding claim, wherein the sub-micrometer particles have particle sizes in a range from 5 nm to 10 micrometer.

~~16~~15. The material of any preceding claim, wherein there is an average spacing between the protruding sub-micrometer particles in a range from 40 nm to 300 nm.

~~17~~16 A method of making a material of any preceding claim, the method comprising:

providing a free radical curable layer having sub-micrometer particles dispersed therein; and

actinic radiation curing the free radical curable layer in the presence of a sufficient amount of inhibitor gas, to inhibit the curing of a major surface region of the layer to provide a layer having a bulk region with a first degree of cure and a major surface region having a second degree of cure, wherein the first degree of cure is greater than the second degree of cure, and wherein the material having a structured surface that includes a portion of the sub-micrometer particles.

~~18~~17. The method of claim ~~17~~16, wherein the inhibiting gas has an oxygen content is 100 ppm to 100,000 ppm.

~~19~~18. The method of either claim ~~17~~16 or ~~18~~17, wherein all actinic radiation curing is conducted in a single chamber.

~~20~~19. The method of any one of claims ~~17~~16 to ~~19~~18, wherein a portion of the actinic radiation curing is conducted in a first chamber having a first inhibitor gas and a first actinic radiation level, and a portion of the actinic radiation curing is conducted in a second chamber having a second inhibitor gas and a second actinic radiation level, wherein the first inhibitor gas has a lower oxygen content than the second inhibitor gas, and wherein the first actinic radiation level is higher than the second actinic radiation level.

~~21~~20. The method of claim ~~20~~19, wherein the first inhibitor gas has an oxygen content in a range from 100 ppm to 100,000 ppm, and wherein the second inhibitor gas has an oxygen content in a range from 100 ppm to100,000 ppm.

~~22~~21. The method of either claim ~~20~~ 19 or ~~21~~20, wherein final curing of the free radical curable layer is conducted in the second chamber.

~~23~~22. The method of any one of claims ~~17~~ 16 to ~~22~~21, wherein a portion of the actinic radiation curing is conducted in a first chamber having a first inhibitor gas and a first actinic radiation level, and a portion of the actinic radiation curing is conducted in a second chamber having a second inhibitor gas and a second actinic radiation level, wherein the first inhibitor gas has a higher oxygen content than the second inhibitor gas, and wherein the first actinic radiation level is lower than the second actinic radiation level.

~~24~~23. The method of claim ~~23~~22, wherein the first inhibitor gas has an oxygen content in a range from 100 ppm to 100,000 ppm, and wherein the second inhibitor gas has an oxygen content in a range from 100 ppm to 100,000 ppm.

~~25~~24. The method of either claim ~~23~~ 22 or ~~24~~23, wherein final curing of the free radical curable layer is conducted in the second chamber.

~~26. A material comprising sub-micrometer particles dispersed in a polymeric matrix, the material having a thickness, at least first and second integral regions across the thickness, wherein the first and second regions have first and second average densities, respectively, wherein the first average density is less than the second average density, wherein the first region having an outer major surface, wherein at least the outer most sub-micrometer particles are partially conformally coated with the polymeric matrix, and wherein the material has a Steel Wool Scratch Test value of at least 1.~~

~~27. The material of claim 26, wherein the sub-micrometer particles are covalently bonded to the polymeric matrix.~~

~~28. The material of either claim 26 or 27, wherein, the difference between the first and second average densities is in a range from 0.1 g/cm^3 to 0.8 g/cm^3.~~

29. The material of any one of claims 26 to 28, wherein the second region is free of substantially closed porosity.

30. The material of any one of claims 26 to 29, wherein at least a portion of the polymer is made from a prepolymer comprising free radically curable prepolymer.

31. The material of claim 30, wherein at least a portion of the prepolymer comprises at least one of a monomeric or oligomeric multifunctional (meth)acrylate.

32. The material of claim 30, wherein at least a portion of the prepolymer comprises at least one of a monomeric or oligomeric difunctional (meth)acrylate.

33. The material of claim 30, wherein at least a portion of the prepolymer comprises at least one of a monomeric or oligomeric monofunctional (meth)acrylate.

34. The material of claim 33, wherein at least a portion of the prepolymer comprises a mixture of nutifuctional, difuctional, and monofunction (meth)acrylates.

35. The material of any one of claims 30 to 34, wherein the prepolymer composition has a functionality of 1.25 to 2.75.

36. The material of any of claim 26 to 35, wherein the sub-micrometer particles comprise surface modified sub-micrometer particles.

37. The material of any one of claims 26 to 36, wherein the sub-micrometer particles have particle sizes of at least 5 nm to 1000 nm.

38. The material of any one of claims 26 to 37, wherein the sub-micrometer particles comprise silica.

39. The material of any one of claims 26 to 38, wherein the sub-micrometer particles have sub-micrometer particle sizes in a range from 5 nm to 10 micrometer.

40. The material of any one of claims 26 to 39, wherein there is an average spacing between the protruding sub-micrometer particles in a range from 40 nm to 300 nm.

41. The material of any one of claims 26 to 40, wherein the material further comprises an outer layer comprising agglomerates of silica nanoparticles, the silica nanoparticles having an average particle diameter of 40 nanometers or less, said agglomerates comprising a three-dimensional porous network of silica nanoparticles, further wherein the silica nanoparticles are bonded to adjacent silica nanoparticles.

42. A method of making a material of any one of claims 26 to 41, the method comprising:

providing a free radical curable layer having sub-micrometer particles dispersed therein; and

actinic radiation curing the free radical curable layer in the presence of a sufficient amount of inhibitor gas, to inhibit the curing of a major surface region of the layer to provide a layer having a bulk region with a first degree of cure and a major surface region having a second degree of cure, wherein the first degree of cure is greater than the second degree of cure, and wherein the material having a structured surface that includes a portion of the sub-micrometer particles.

43. The method of claim 42, wherein the inhibiting gas has an oxygen content is 100 ppm to 100,000 ppm.

44. The method of either claim 42 or 43, wherein all actinic radiation curing is conducted in a single chamber.

45. The method of any one of claims 42 to 44, wherein a portion of the actinic radiation curing is conducted in a first chamber having a first inhibitor gas and a first actinic radiation level, and a portion of the actinic radiation curing is conducted in a second chamber having a second inhibitor gas and a second actinic radiation level, wherein the first inhibitor gas has a lower oxygen content than the second inhibitor gas, and wherein the first actinic radiation level is higher than the second actinic radiation level.

46. The method of claim 45, wherein the first inhibitor gas has an oxygen content in a range from 100 ppm to 100,000 ppm, and wherein the second inhibitor gas has an oxygen content in a range from 100 ppm to100,000 ppm.

47. The method of either claim 45 or 46, wherein final curing of the free radical curable layer is conducted in the second chamber.

48. The method of any one of claims 42 to 47, wherein a portion of the actinic radiation curing is conducted in a first chamber having a first inhibitor gas and a first actinic radiation level, and a

portion of the actinic radiation curing is conducted in a second chamber having a second inhibitor gas and a second actinic radiation level, wherein the first inhibitor gas has a higher oxygen content than the second inhibitor gas, and wherein the first actinic radiation level is lower than the second actinic radiation level.

49. The method of claim 48, wherein the first inhibitor gas has an oxygen content in a range from 100 ppm to 100,000 ppm, and wherein the second inhibitor gas has an oxygen content in a range from 100 ppm to 100,000 ppm.

50. The method of either claim 48 or 49, wherein final curing of the free radical curable layer is conducted in the second chamber.

51. The method of any one of claims 17 to 25 or 42 to 50, further comprising contacting the layer with a coating composition comprising: a) 0.5 to 99 wt. % water b) 0.1 to 20 wt. % silica nanoparticles having an average particle diameter of 40 nm or less, c) 0 to 20 wt. % silica nanoparticles having an average particle diameter of 50 nm or more, wherein the sum of b) and c) is 0.1 to 20 wt. %; d) a sufficient amount of an acid having a pKa of < 3.5 to reduce the pH to less than 5; e) 0 to 20 percent by weight of a tetraalkoxysilane, relative to the amount of the silica nanoparticle; and

drying to provide a silica nanoparticle coating on the layer.

52. A nanostructured material made according to the method of claim 51.