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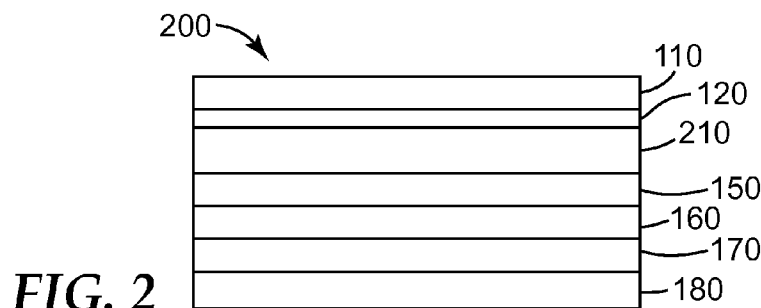
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[Continued on next page]

(54) Title: DURABLE SOLAR MIRROR FILMS

**FIG. 2**

(57) Abstract: The present disclosure generally relates to durable solar mirror films, methods of making durable solar mirror films, and constructions including durable solar mirror films. In one embodiment, the present disclosure relates to a solar mirror film comprising: a weatherable layer having a weatherable layer coefficient of hygroscopic expansion; a reflective layer having a reflective layer coefficient of hygroscopic expansion; and a compliant layer between the weatherable layer and the reflective layer, the compliant layer having a compliant layer coefficient of hygroscopic expansion that is between the weatherable layer coefficient of hygroscopic expansion and the reflective layer coefficient of hygroscopic expansion.



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DURABLE SOLAR MIRROR FILMS

Government License Rights

[0001] The Government of the United States of America has rights in at least some of the inventions described in this Patent Application pursuant to DE-AC36-08GO28308 (CRADA No. 08-316) awarded by the U.S. Department of Energy.

Technical Field

[0002] The present disclosure generally relates to durable solar mirror films, methods of making durable solar mirror films, and constructions including durable solar mirror films.

Background

[0003] Renewable energy is energy derived from natural resources that can be replenished, such as sunlight, wind, rain, tides, and geothermal heat. The demand for renewable energy has grown substantially with advances in technology and increases in global population. Although fossil fuels provide for the vast majority of energy consumption today, these fuels are non-renewable. The global dependence on these fossil fuels has not only raised concerns about their depletion but also environmental concerns associated with emissions that result from burning these fuels. As a result of these concerns, countries worldwide have been establishing initiatives to develop both large-scale and small-scale renewable energy resources. One of the promising energy resources today is sunlight. Globally, millions of households currently obtain power from solar photovoltaic systems.

[0004] In general, concentrated solar technology involves the collection of solar radiation in order to directly or indirectly produce electricity. The three main types of concentrated solar technology are concentrated photovoltaic, concentrated solar power, and solar thermal.

[0005] In concentrated photovoltaic (CPV), concentrated sunlight is converted directly to electricity via the photovoltaic effect. Generally, CPV technology uses optics (*e.g.* lenses or mirrors) to concentrate a large amount of sunlight onto a small area of a solar photovoltaic material to generate electricity. CPV systems are often much less expensive to produce than other types of photovoltaic energy generation because the concentration of solar energy permits the use of a much smaller number of the higher cost solar cells.

[0006] In concentrated solar power (CSP), concentrated sunlight is converted to heat, and then the heat is converted to electricity. Generally, CSP technology uses mirrored surfaces in multiple geometries (*e.g.*, flat mirrors, parabolic dishes, and parabolic troughs) to concentrate sunlight onto

a receiver. That, in turn, heats a working fluid (*e.g.* a synthetic oil or a molten salt) or drives a heat engine (*e.g.*, steam turbine). In some cases, the working fluid is what drives the engine that produces electricity. In other cases, the working fluid is passed through a heat exchanger to produce steam, which is used to power a steam turbine to generate electricity.

[0007] Solar thermal systems collect solar radiation to heat water or to heat process streams in industrial plants. Some solar thermal designs make use of reflective mirrors to concentrate sunlight onto receivers that contain water or the feed stream. The principle of operation is very similar to concentrated solar power units, but the concentration of sunlight, and therefore the working temperatures, are not as high.

[0008] The rising demand for solar power has been accompanied by a rising demand for reflective devices and materials capable of fulfilling the requirements for these applications. Some of these solar reflector technologies include glass mirrors, aluminized mirrors, and metalized polymer films. Of these, metalized polymer films are particularly attractive because they are lightweight, offer design flexibility, and potentially enable less expensive installed system designs than conventional glass mirrors. Polymers are lightweight, inexpensive, and easy to manufacture. In order to achieve metal surface properties on a polymer, thin layers of metal (*e.g.* silver) are coated on the polymer surface.

[0009] One exemplary commercially available solar mirror film is shown schematically in Fig. 1. The solar mirror film 100 of Fig. 1 includes a premask layer 110, a weatherable layer 120 (including, for example, a polymer), a thin, sputter-coated tie layer 140, a reflective layer 150 (including, for example, a reflective metal such as silver), a corrosion resistant layer 160 (including, for example, a metal such as copper), an adhesive layer 170, and a liner 180. The film of Fig. 1 is typically applied to a support substrate by removing liner 180 and placing adhesive layer 170 adjacent to the support substrate. Premask layer 110 is then removed to expose weatherable layer 120 to sunlight.

Summary

[0010] The metalized polymer films used in concentrated solar power units and concentrated photovoltaic cells are subject to continuous exposure to the elements. Consequently, a technical challenge in designing and manufacturing metalized polymer reflective films is achieving long-term (*e.g.*, 20 years) durability when subjected to harsh environmental conditions. There is a need for metalized polymer films that provide durability and retained optical performance (*e.g.*, reflectivity) once installed in a concentrated solar power unit or a concentrated photovoltaic cell. Mechanical properties, optical clarity, corrosion resistance, ultraviolet light stability, and resistance

to outdoor weather conditions are all factors that can contribute to the gradual degradation of materials over an extended period of operation.

[0011] The inventors of the present disclosure recognized that many of the technical problems in forming a durable metalized polymer film capable of long-term outdoor use that retains its optical performance arise from the fundamental mismatch in the physical and chemical nature and properties of metals and polymers. One particular difficulty relates to ensuring good adhesion between the polymer layer and the metal reflective surface. Without good adhesion between these layers, delamination occurs. Delamination between the polymer layer and the reflective layer is often referred to as “tunneling.”

[0012] The inventors of the present disclosure recognized that the delamination typically results from the decreased adhesion between the polymer layer and the reflective layer. This decreased adhesion can be caused by any of numerous factors - and often a combination of these factors. Some exemplary factors that the inventors of the present disclosure recognized include (1) increased mechanical stress between the polymer layer and the reflective layer; (2) oxidation of the reflective layer; (3) oxidation of an adhesive adjacent to the reflective layer; and (4) degradation of the polymer layer (this can be due to, for example, exposure to sunlight). Each of these factors can be affected by numerous external conditions, such as, for example, environmental temperature (including variations in environmental temperatures), thermal shock, humidity, exposure to moisture, exposure to air impurities such as, for example, salt and sulfur, UV exposure, product handling, and product storage.

[0013] One of the most challenging problems is related to stress at the metal/polymer interface. Once the stress becomes too great, buckling can occur, causing the polymer layer to delaminate from the reflective layer. Further, when metalized polymer films are cut, their edges may be fractured and unprotected. Corrosion of metalized polymers begins at their edges, so this combination of fractured, exposed metal edges with the net interfacial stresses listed above can overcome adhesion strength and cause tunneling. The inventors of the present invention recognized the importance of protecting the interface between the polymer layer and the reflective layer – especially along the edges of this interface.

[0014] Two prior art approaches have been used to address these problems. First, a sealing caulk has been applied around the edges of the metalized film. Second, a tape has been wrapped around the edges of the metalized film. Both approaches are effective at minimizing short-term delamination and/or tunneling, if properly applied. However, both approaches disadvantageously reduce the total available reflective area. Also, both approaches disadvantageously introduce a separate material to the front surface of the metalized film, which results in the creation of a ridge or protrusion above and below the plane of the metalized film. These ridges or protrusions are

areas of potential additional stress when the metalized film is exposed to, for example, wind and hail. The additional stress is increased during routine maintenance processes including, for example, cleaning (*e.g.* pressure washing) and handling during application. Also, in order to be effective over the lifetime of the metalized film (*e.g.*, 20 years), the separate material must adhere to the metalized film for the lifetime of the film. These materials have limited ability to do so.

[0015] The inventors of the present disclosure recognized that typical solar mirror films include a polymeric layer having a coefficient of hygroscopic expansion (CHE) on the order of about 30 parts per million (ppm) per percent relative humidity (RH) adjacent to a reflective layer having a CHE of about zero ppm per RH. The inventors of the present disclosure recognized that one way to minimize or eliminate film delamination and/or tunneling involves including in the solar mirror film construction a layer between the reflective layer and the polymer layer that has a CHE that is between the CHE of the prior art weatherable layer and the CHE of the reflective layer. For purposes of clarity, the term “compliant layer” will be used herein to describe the layer positioned between the reflective layer and the weatherable layer and having a CHE between the CHE of the reflective layer and the weatherable layer. Use of the word “compliant” in connection with this layer is not meant to add any requirements to the term layer.

[0016] In some embodiments, the compliant layer has a coefficient of hygroscopic expansion (CHE) less than about 30 parts per million per PPH and greater than about 1 part per million per PPH. In some embodiments, the compliant layer has a coefficient of hygroscopic expansion (CHE) less than about 25 parts per million per PPH and greater than about 3 part per million per PPH. In some embodiments, the compliant layer has a coefficient of hygroscopic expansion (CHE) less than about 20 parts per million per PPH and greater than about 5 part per million per PPH. In some embodiments, the compliant layer has a coefficient of hygroscopic expansion (CHE) less than about 18 parts per million per PPH and greater than about 7 part per million per PPH.

[0017] As such, the solar mirror films of the present disclosure have a reduced stress differential caused by the disparity in CHEs of the polymeric layer and the reflective layer. Elimination or minimization of this stress differential eliminates or minimizes tunneling and results in increased life of solar mirror films. Increased life results in decreased cost of solar power generation, which may lead to faster and/or wider adoption of this form of green energy generation.

[0018] One embodiment of the present disclosure relates to a solar mirror film comprising: a weatherable layer having a weatherable layer coefficient of hygroscopic expansion; a reflective layer having a reflective layer coefficient of hygroscopic expansion; and a compliant layer between the weatherable layer and the reflective layer, the compliant layer having a compliant

layer coefficient of hygroscopic expansion that is between the weatherable layer coefficient of hygroscopic expansion and the reflective layer coefficient of hygroscopic expansion.

[0019] In some embodiments of the solar mirror film, the coefficient of hygroscopic expansion of the compliant layer is less than about 30 ppm per percent RH and greater than zero (0) ppm per percent RH. In some embodiments, the coefficient of hygroscopic expansion of the compliant layer is less than about 28 ppm per percent RH and greater than zero (0) ppm per percent RH. In some embodiments, the coefficient of hygroscopic expansion of the compliant layer is less than about 25 ppm per percent RH and greater than one (1) ppm per percent RH. In some embodiments, the coefficient of hygroscopic expansion of the compliant layer is less than about 25 ppm per percent RH and greater than three (3) ppm per percent RH. In some embodiments, the coefficient of hygroscopic expansion of the compliant layer is less than about 20 ppm per percent RH and greater than five (5) ppm per percent RH. In some embodiments, the coefficient of hygroscopic expansion of the compliant layer is between about 10 ppm per percent relative humidity and about 25 ppm per percent relative humidity. In some embodiments of the solar mirror film, the coefficient of hygroscopic expansion of the compliant layer is between about 15 ppm per percent relative humidity and about 20 ppm per percent relative humidity.

[0020] Some embodiments of the solar mirror film have a reflective layer as the reflective layer. Some embodiments of the solar mirror film include a reflective layer that is at least one of silver, gold, aluminum, copper, nickel, and titanium. Some embodiments of the solar mirror film include a reflective layer whose coefficient of hygroscopic expansion of the reflective layer is between 0 ppm per percent relative humidity and 3 ppm per percent relative humidity.

[0021] Some embodiments of the solar mirror film further include a tie layer between the weatherable layer and the compliant layer or between the compliant layer and the reflective layer (or both). In some embodiments, the tie layer comprises titanium dioxide.

[0022] In some embodiments, the solar mirror film includes a corrosion protective layer adjacent to the reflective layer. In some embodiments, the corrosion protective layer comprises at least one of copper and an inert metal alloy.

[0023] In some embodiments, the solar mirror film includes an adhesive layer adjacent to the reflective layer. In some embodiments, the adhesive is a pressure sensitive adhesive. In some embodiments, the adhesive layer is between the reflective layer and a substrate. In some embodiments, the substrate is one of a photovoltaic solar panel and a concentrated solar power system.

[0024] Another embodiment of the present disclosure relates to a concentrated photovoltaic system including a solar mirror film as described herein, including, but not limited to, any of the embodiments described above.

[0025] Another embodiment of the present disclosure relates to a concentrated solar power system including a solar mirror film as described herein, including, but not limited to, any of the embodiments described above.

[0026] Another embodiment of the present disclosure relates to a reflector assembly including a solar mirror film as described herein, including, but not limited to, any of the embodiments described above.

[0027] Various aspects and advantages of exemplary embodiments of the disclosure have been summarized. The above summary is not intended to describe each illustrated embodiment or every implementation of the present disclosure. The Drawings and the Detailed Description that follow more particularly exemplify the various embodiments disclosed herein. These and various other features and advantages will be apparent from a reading of the following detailed description.

Brief Description of Drawings

[0028] Fig. 1 is a schematic view of a prior art solar mirror film.

[0029] Fig. 2 is a schematic view of one exemplary embodiment of a solar mirror film in accordance with the present disclosure.

[0030] Fig. 3 is a schematic view of another exemplary embodiment of a solar mirror film in accordance with the present disclosure.

[0031] Fig. 4 is a schematic view of another exemplary embodiment of a solar mirror film in accordance with the present disclosure.

Detailed Description

[0032] Some embodiments of the present application relate to the inclusion of a compliant layer having a CHE that is between the CHE of the weatherable layer and the CHE of the reflective layer. In some embodiments, the compliant layer has a CHE of less than 30 ppm per percent RH and greater than zero ppm per percent RH. The compliant layer is positioned between the weatherable layer and the reflective layer of a solar mirror film. The inclusion of the compliant layer lowers the stress differential caused by the disparity in CHEs of the weatherable layer and the reflective layer.

[0033] One exemplary embodiment is shown schematically in Fig. 2. Solar mirror film 200 of Fig. 2 includes a premask layer 110, a weatherable layer 120, a compliant layer 210, a reflective layer 150 (including, for example, a reflective metal such as silver), a corrosion resistant layer 160 (including, for example, a metal such as copper), an adhesive layer 170, and a liner 180. All layers

except the weatherable layer 120, the compliant layer 220, and the reflective layer 150 are optional.

[0034] Another exemplary embodiment is shown schematically in Fig. 3. Solar mirror film 300 of Fig. 3 includes a premask layer 110, a weatherable layer 120, a tie layer 140, a compliant layer 210, a tie layer 220, a reflective layer 150 (including, for example, a reflective metal such as silver), a corrosion resistant layer 160 (including, for example, a metal such as copper), an adhesive layer 170, and a liner 180. All layers except the weatherable layer 120, the compliant layer 220, and the reflective layer 150 are optional.

[0035] Another exemplary embodiment is shown schematically in Fig. 4. Solar mirror film 400 of Fig. 4 includes a premask layer 110, a weatherable layer 120, compliant layer 210, a tie layer 140, a reflective layer 150 (including, for example, a reflective metal such as silver), a corrosion resistant layer 160 (including, for example, a metal such as copper), an adhesive layer 170, and a liner 180. All layers except the weatherable layer 120, the compliant layer 220, and the reflective layer 150 are optional.

[0036] For purposes of clarity, all layers in the various embodiments shown in Figs. 1-4 and described herein are optional except for the weatherable layer, the compliant layer, and the reflective layer. Each layer that could be included in a solar mirror film of the types generally described herein is discussed in detail below.

[0037] Premask Layer

[0038] The premask layer is optional. Where present, the premask protects the weatherable layer during handling, lamination, and installation. Such a configuration can then be conveniently packaged for transport, storage, and consumer use. In some embodiments, the premask is opaque to protect operators during outdoor installations. In some embodiments, the premask is transparent to allow for inspection for defects. Any known premask can be used. One exemplary commercially available premask is ForceField® 1035 sold by Tredegar of Richmond, Virginia.

[0039] Weatherable Layer

[0040] In some embodiments, the weatherable sheet or layer is flexible and transmissive to visible and infrared light. In some embodiments, the weatherable sheet or layer is resistant to degradation by ultraviolet (UV) light. In some embodiments, the phrase "resistant to degradation by ultraviolet light" means that the weatherable sheet at least one of reflects or absorbs at least 50 percent of incident ultraviolet light over at least a 30 nanometer range in a wavelength range from at least 300 nanometers to 400 nanometers. Photo-oxidative degradation caused by UV light (*e.g.*, in a range from 280 to 400 nm) may result in color change and deterioration of optical and mechanical

properties of polymeric films. In some embodiments, the weatherable sheet or layer is generally abrasion and impact resistant and can prevent degradation of, for example, solar assemblies when they are exposed to outdoor elements.

[0041] In some embodiments, the weatherable layer includes one or more organic film-forming polymers. Some exemplary polymers include, for examples, polyesters, polycarbonates, polyethers, polyimides, polyolefins, fluoropolymers, and combinations thereof. Assemblies according to the present disclosure include a weatherable sheet or layer, which can be a single layer (monolayered embodiments) or can include more than one layer (multilayered embodiments).

[0042] A variety of stabilizers may be added to the weatherable sheet to improve its resistance to UV light. Examples of such stabilizers include at least one of ultraviolet absorbers (UVA) (*e.g.*, red shifted UV absorbers), hindered amine light stabilizers (HALS), or anti-oxidants. These additives are described in further detail below. In some of these embodiments, the weatherable sheet need not include UVA or HALS.

[0043] The UV resistance of the weatherable sheet can be evaluated, for example, using accelerated weathering studies. Accelerated weathering studies are generally performed on films using techniques similar to those described in ASTM G-155, "Standard practice for exposing non-metallic materials in accelerated test devices that use laboratory light sources." One mechanism for detecting the change in physical characteristics is the use of the weathering cycle described in ASTM G155 and a D65 light source operated in the reflected mode. Under the noted test, and when the UV protective layer is applied to the article, the article should withstand an exposure of at least $18,700 \text{ kJ/m}^2$ at 340 nm before the b^* value obtained using the CIE $L^*a^*b^*$ space increases by 5 or less, 4 or less, 3 or less, or 2 or less before the onset of significant cracking, peeling, delamination or haze.

[0044] In some embodiments, the weatherable sheet includes a fluoropolymer. Fluoropolymers are typically resistant to UV degradation even in the absence of stabilizers such as UVA, HALS, and anti-oxidants. Some exemplary fluoropolymers include ethylene-tetrafluoroethylene copolymers (ETFE), ethylene-chloro-trifluoroethylene copolymers (ECTFE), tetrafluoroethylene-hexafluoropropylene copolymers (FEP), tetrafluoroethylene-perfluorovinylether copolymers (PFA, MFA) tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride copolymers (THV), polyvinylidene fluoride homo and copolymers (PVDF), blends thereof, and blends of these and other fluoropolymers. Fluoropolymers typically comprise homo or copolymers of TFE, CTFE, VDF, HFP or other fully fluorinated, partially fluorinated or hydrogenated monomers such as vinyl ethers and alpha-olefins or other halogen containing monomers. The CTE of fluoropolymer films is typically high relative to films made from hydrocarbon polymers. For example, the CTE of a

fluoropolymer film may be at least 75, 80, 90, 100, 110, 120, or 130 ppm/K. For example, the CTE of ETFE may be in a range from 90 to 140 ppm/K.

[0045] Weatherable films including fluoropolymer can also include non-fluorinated materials. For example, a blend of polyvinylidene fluoride and polymethyl methacrylate can be used. Useful flexible, visible and infrared light-transmissive substrates also include multilayer film substrates. Multilayer film substrates may have different fluoropolymers in different layers or may include at least one layer of fluoropolymer and at least one layer of a non-fluorinated polymer. Multilayer films can comprise a few layers (*e.g.*, at least 2 or 3 layers) or can comprise at least 100 layers (*e.g.*, in a range from 100 to 2000 total layers or more). The different polymers in the different multilayer film substrates can be selected, for example, to reflect a significant portion (*e.g.*, at least 30, 40, or 50%) of UV light in a wavelength range from 300 to 400 nm as described, for example, in U.S. Patent No. 5,540,978 (Schrenk). Such blends and multilayer film substrates may be useful for providing UV resistant substrates that have lower CTEs than the fluoropolymers described above.

[0046] Some exemplary weatherable sheets comprising a fluoropolymer can be commercially obtained, for example, from E.I. duPont De Nemours and Co., Wilmington, DE, under the trade designation "TEFZEL ETFE" and "TEDLAR", and films made from resins available from Dyneon LLC, Oakdale, MN, under the trade designations "DYNEON ETFE", "DYNEON THV", "DYNEON FEP", and "DYNEON PVDF", from St. Gobain Performance Plastics, Wayne, NJ, under the trade designation "NORTON ETFE", from Asahi Glass under the trade designation "CYTOPS", and from Denka Kagaku Kogyo KK, Tokyo, Japan under the trade designation "DENKA DX FILM."

[0047] Some useful weatherable sheets are reported to be resistant to degradation by UV light in the absence of UVA, HALS, and anti-oxidants. For example, certain resorcinol isophthalate/terephthalate copolyarylates, for example, those described in U. S. Patent Nos. 3,444,129; 3,460,961; 3,492,261; and 3,503,779 are reported to be weatherable. Certain weatherable multilayer articles containing layers comprising structural units derived from a 1,3-dihydroxybenzene organodicarboxylate are reported in Int. Pat. App. Pub. No. WO 2000/061664, and certain polymers containing resorcinol arylate polyester chain members are reported in U. S. Pat. No. 6,306,507. Block copolyestercarbonates comprising structural units derived from at least one 1,3-dihydroxybenzene and at least one aromatic dicarboxylic acid formed into a layer and layered with another polymer comprising carbonate structural units are reported in US Publication No. 2004/0253428. Weatherable sheets containing polycarbonate may have relatively high CTEs in comparison to polyesters, for example. The CTE of a weatherable sheet containing a polycarbonate may be, for example, about 70 ppm/K.

[0048] For some or all of the embodiments of the weatherable sheet or layer described above, the major surface of the weatherable sheet (*e.g.*, fluoropolymer) can be treated to improve adhesion to a pressure sensitive adhesive. Useful surface treatments include, for example, electrical discharge in the presence of a suitable reactive or non-reactive atmosphere (*e.g.*, plasma, glow discharge, corona discharge, dielectric barrier discharge or atmospheric pressure discharge); chemical pretreatment (*e.g.*, using alkali solution and/or liquid ammonia); flame pretreatment; or electron beam treatment. A separate adhesion promotion layer may also be formed between the major surface of the weatherable sheet and the PSA. In some embodiments, the weatherable sheet may be a fluoropolymer that has been coated with a PSA and subsequently irradiated with an electron beam to form a chemical bond between the substrate and the pressure sensitive adhesive; (*see, e.g.*, U. S. Pat. No. 6,878,400 (Yamanaka et al.)). Some useful weatherable sheets that are surface treated are commercially available, for example, from St. Gobain Performance Plastics under the trade designation "NORTON ETFE".

[0049] In some embodiments, the weatherable film is a MOF layer (*see, for example*, U.S. Patent Application Matter No. 69678US002, assigned to the present assignee and incorporated in its entirety herein). In some embodiments, the weatherable film include a blend of PMMA and PVDF (*see, for example*, U.S. Patent Application Matter No. 69680US002, assigned to the present assignee and incorporated in its entirety herein). In some embodiments, the weatherable layer has a CHE that is less than 30 ppm per percent RH (*see above* incorporated patent applications).

[0050] In some embodiments, the weatherable sheet has a thickness from about 0.01 mm to about 1 mm. In some embodiments, the weatherable sheet has a thickness from about 0.05 mm to about 0.25 mm. In some embodiments, the weatherable sheet has a thickness from about 0.05 mm to about 0.15 mm.

[0051] Commercially available weatherable layers have a weatherable layer coefficient of hygroscopic expansion of at least about 30 ppm per percent RH.

[0052] Compliant Layer

[0053] The compliant layer has a coefficient of hygroscopic expansion (CHE) that is between the CHE of the reflective layer and the CHE of the weatherable layer.

[0054] In some embodiments, the compliant layer has a CHE of less than 30 ppm per percent relative humidity and greater than zero ppm per percent relative humidity. In some embodiments of the solar mirror film, the CHE of the compliant layer is less than about 30 ppm per percent RH and greater than zero (0) ppm per percent RH. In some embodiments, the CHE of the compliant layer is less than about 28 ppm per percent RH and greater than zero (0) ppm per percent RH. In some embodiments, the CHE of the compliant layer is less than about 25 ppm per percent RH and

greater than one (1) ppm per percent RH. In some embodiments, the CHE of the compliant layer is less than about 25 ppm per percent RH and greater than three (3) ppm per percent RH. In some embodiments, the CHE of the compliant layer is less than about 20 ppm per percent RH and greater than five (5) ppm per percent RH. In some embodiments, the CHE of the compliant layer is between about 10 ppm per percent relative humidity and about 25 ppm per percent relative humidity. In some embodiments of the solar mirror film, the CHE of the compliant layer is between about 15 ppm per percent relative humidity and about 20 ppm per percent relative humidity.

[0055] In some embodiments, the CHE of the compliant layer is between about 75% and about 25% of the CHE of the weatherable layer. In some embodiments, the CHE of the compliant layer is between about 70% and about 30% of the CHE of the weatherable layer. In some embodiments, the CHE of the compliant layer is between about 60% and about 40% of the CHE of the weatherable layer.

[0056] The compliant layer can be any material that has the desired CHE. In some embodiments, the compliant layer includes one or both of PMMA and PVDF. In some embodiments, the compliant layer includes a multilayer optical film.

[0057] In some embodiments, the compliance layer includes poly(methyl methacrylate) and a first block copolymer having at least two endblock polymeric units that are each derived from a first monoethylenically unsaturated monomer comprising a methacrylate, acrylate, styrene, or combination thereof, wherein each endblock has a glass transition temperature of at least 50 degrees Celsius; and at least one midblock polymeric unit that is derived from a second monoethylenically unsaturated monomer comprising a methacrylate, acrylate, vinyl ester, or combination thereof, wherein each midblock has a glass transition temperature no greater than 20 degrees Celsius. As used herein, the term “block copolymer” refers to a polymeric material that includes a plurality of distinct polymeric segments (or “blocks”) that are covalently bonded to each other. A block copolymer includes (at least) two different polymeric blocks, commonly referred to as the A block and the B block. The A block and the B block generally have chemically dissimilar compositions with different glass transition temperatures. The glass transition temperature can be determined using a method such as Differential Scanning Calorimetry (DSC) or Dynamic Mechanical Analysis (DMA).

[0058] Further, each of the A and B blocks includes a plurality of respective polymeric units. The A block polymeric units, as well as the B block polymeric units, are generally derived from monoethylenically unsaturated monomers. Each polymeric block and the resulting block copolymer have a saturated polymeric backbone without the need for subsequent hydrogenation.

[0059] Alternatively, in some embodiments, the compliance layer includes a block copolymer/homopolymer blend. For example, the compliance layer may include an A-B-A triblock copolymer blended with a homopolymer that is soluble in either the A or B block. Optionally, the homopolymer has a polymeric unit identical to either the A or B block. The addition of one or more homopolymers to the block copolymer composition can be advantageously used either to plasticize or to harden one or both blocks. In preferred embodiments, the block copolymer contains a poly(methyl methacrylate) A block and a poly(butyl acrylate) B block, and is blended with a poly(methyl methacrylate) homopolymer.

[0060] Advantageously, blending poly(methyl methacrylate) homopolymer with poly(methyl methacrylate)-poly(butyl acrylate) block copolymers allows the hardness to be tailored to the desired application. As a further advantage, blending with poly(methyl methacrylate) provides this control over hardness without significantly degrading the clarity or processibility of the overall composition. Preferably, the homopolymer/block copolymer blend has an overall poly(methyl methacrylate) composition of at least 30 percent, at least 40 percent, or at least 50 percent, based on the overall weight of the blend. Preferably, the homopolymer/block copolymer blend has an overall poly(methyl methacrylate) composition no greater than 95 percent, no greater than 90 percent, or no greater than 80 percent, based on the overall weight of the blend.

[0061] Particularly suitable non-tacky block copolymers include poly(methyl methacrylate)-poly(n-butyl acrylate)-poly(methyl methacrylate) (25:50:25) triblock copolymers. These materials were previously available under the trade designation LA POLYMER from Kuraray Co., LTD.

[0062] In some embodiments, the A block component is a thermoplastic material while the B block component is an elastomeric material. As used herein, the term “thermoplastic” refers to a polymeric material that flows when heated and that returns to its original state when cooled back to room temperature. As used herein, the term “elastomeric” refers to a polymeric material that can be stretched to at least twice its original length and then retracted to approximately its original length upon release. In some embodiments, the block copolymer has a multiphase morphology, at least at temperatures in the range of about 20 degrees Celsius to 150 degrees Celsius.

[0063] Additional exemplary compliant layer compositions are described, for example, in Patent Application No. US2011/058209, assigned to the assignee of the present application and the entirety of which is incorporated herein.

[0064] In some embodiments, the compliant layer is visible light-transmissive or optically clear, exhibiting, in some exemplary embodiments, an average radiation transmission over the visible light portion of the radiation spectrum from 380 nm to 780 nm (T_{vis}) of at least about 90%, measured along the normal axis. In some exemplary embodiments the compliant layer exhibits an average radiation transmission of at least 90% over the solar radiation wavelength range from 380

nm to 3,000 nm (T_{solar}). In some embodiments, the compliant layer provides at least one of high optical transmissivity and low haze and yellowing, good weatherability, good abrasion, scratch, and crack resistance during to handling and cleaning, and good adhesion to other layers.

[0065] Inclusion of the compliant layer in the solar mirror film construction can, in some embodiments, be introduced as in-line processes.

[0066] In some embodiments, the compliance layer has a thickness of at least 10 micrometers, at least 50 micrometers, or at least 60 micrometers. Additionally, in some embodiments, the compliance layer has a thickness no greater than 200 micrometers, no greater than 150 micrometers or no greater than 100 micrometers. In some embodiments, the compliance layer has a thickness no greater than 5 micrometers. In some such embodiments, the compliance layer has a thickness of from 0.1 micrometer to 3 micrometers.

[0067] Tie Layer

[0068] In some embodiments, the tie layer(s) include a metal oxide such as aluminum oxide, copper oxide, titanium dioxide, silicon dioxide, or combinations thereof. As a tie layer, titanium dioxide may provide surprisingly high resistance to delamination in dry peel and wet peel testing. Further options and advantages of metal oxide tie layers are described in U.S. Patent No. 5,361,172 (Schissel et al.), incorporated herein by reference.

[0069] In some embodiments, the tie layer has a thickness of equal to or less than 500 micrometers. In some embodiments, the tie layer has a thickness of between about 0.1 micrometer and about 5 micrometers. In some embodiments, the tie layer has an overall thickness of at least 0.1 nanometers, at least 0.25 nanometers, at least 0.5 nanometers, or at least 1 nanometer. In some embodiments, the tie layer has an overall thickness no greater than 2 nanometers, no greater than 5 nanometers, no greater than 7 nanometers, or no greater than 10 nanometers.

[0070] Reflective Layer

[0071] The solar mirror films described herein include one or more reflective layers. Besides providing a high degree of reflectivity, the reflective layer(s) can provide manufacturing flexibility. Optionally, the reflective layer may be applied onto a relatively thin organic tie layer or inorganic tie layer.

[0072] In some embodiments, the reflective layer(s) have smooth, reflective metal surfaces that are specular. As used herein, the term “specular surfaces” refer to surfaces that induce a mirror-like reflection of light in which the direction of incoming light and the direction of outgoing light form the same angle with respect to the surface normal. Any reflective metal may be used for this

purpose, although preferred metals include silver, gold, aluminum, copper, nickel, and titanium. In some embodiments, the reflective layer includes elemental silver.

[0073] The reflective layer has a CHE of about zero ppm per percent RH. In some embodiments, the reflective layer has a CHE of between about zero ppm per percent RH and about 3 ppm per percent RH.

[0074] The reflective layer need not extend across the entire major surface of the compliant layer. In some embodiments, the reflective layer is deposited into the compliant layer. In some embodiments, portions of the compliant layer are masked during the deposition process such that the reflective layer is applied onto only a pre-determined portion of the compliant layer. Exemplary ways of creating a pattern in the reflective layer are described, for example, in matter numbers 69678US002, 69677US002, and 69681US002, all assigned to the present applicant and all incorporated herein in their entirety.

[0075] Application of the reflective layer can be achieved using numerous coating methods including, for example, physical vapor deposition via sputter coating, evaporation via e-beam or thermal methods, ion-assisted e-beam evaporation, electro-plating, spray painting, vacuum deposition, and combinations thereof. The metallization process is chosen based on the polymer and metal used, the cost, and many other technical and practical factors.

[0076] Physical vapor deposition (PVD) of metals is very popular for some applications because it provides the purest metal on a clean interface. In this technique, atoms of the target are ejected by high-energy particle bombardment so that they can impinge onto a substrate to form a thin film. The high-energy particles used in sputter-deposition are generated by a glow discharge, or a self-sustaining plasma created by applying, for example, an electromagnetic field to argon gas.

[0077] In one exemplary method, the deposition process continues for a sufficient duration to build up a suitable layer thickness of the reflective layer.

[0078] The reflective layer is preferably thick enough to reflect the desired amount of the solar spectrum of light. The preferred thickness can vary depending on the composition of the reflective layer. In some exemplary embodiments, the reflective layer is between about 75 nanometers to about 100 nanometers thick for metals such as silver, aluminum, copper, and gold. In some embodiments, the reflective layer has a thickness no greater than 500 nanometers. In some embodiments, the reflective layer has a thickness of from 80 nm to 250 nm. In some embodiments, the reflective layer has a thickness of at least 25 nanometers, at least 50 nanometers, at least 75 nanometers, at least 90 nanometers, or at least 100 nanometers. Additionally, in some embodiments, the reflective layer has a thickness no greater than 100 nanometers, no greater than 110 nanometers, no greater than 125 nanometers, no greater than 150 nanometers, no greater than 200 nanometers, no greater than 300 nanometers, no greater than 400 nanometers, or no greater

than 500 nanometers. Although not shown in the figures, two or more reflective layers may be used.

[0079] Corrosion Resistant Layer

[0080] The corrosion resistant layer is optional. Where included, the corrosion resistant layer may include, for example, elemental copper. Use of a copper layer that acts as a sacrificial anode can provide a reflective article with enhanced corrosion-resistance and outdoor weatherability. As another approach, a relatively inert metal alloy such as Inconel (an iron-nickel alloy) can also be used.

[0081] The corrosion resistant layer is preferably thick enough to provide the desired amount of corrosion resistance. The preferred thickness can vary depending on the composition of the corrosion resistant layer. In some exemplary embodiments, the corrosion resistant layer is between about 75 nanometers to about 100 nanometers thick. In other embodiments, the corrosion resistant layer is between about 20 nanometers and about 30 nanometers thick. Although not shown in the figures, two or more corrosion resistant layers may be used.

[0082] In some embodiments, the corrosion resistant layer has a thickness no greater than 500 nanometers. In some embodiments, the corrosion resistant layer has a thickness of from 80 nm to 250 nm. In some embodiments, the corrosion resistant layer has a thickness of at least 25 nanometers, at least 50 nanometers, at least 75 nanometers, at least 90 nanometers, or at least 100 nanometers. Additionally, in some embodiments, the corrosion resistant layer has a thickness no greater than 100 nanometers, no greater than 110 nanometers, no greater than 125 nanometers, no greater than 150 nanometers, no greater than 200 nanometers, no greater than 300 nanometers, no greater than 400 nanometers, or no greater than 500 nanometers.

[0083] Adhesive Layer

[0084] The adhesive layer is optional. Where present, the adhesive layer adheres the multilayer construction to a substrate (not shown in the figures). In some embodiments, the adhesive is a pressure sensitive adhesive. As used herein, the term “pressure sensitive adhesive” refers to an adhesive that exhibits aggressive and persistent tack, adhesion to a substrate with no more than finger pressure, and sufficient cohesive strength to be removable from the substrate. Exemplary pressure sensitive adhesives include those described in PCT Publication No. WO 2009/146227 (Joseph, et al.), incorporated herein by reference.

[0085] Liner

[0086] The liner is optional. Where present, the liner protects the adhesive and allows the solar mirror film to be transferred onto and another substrate. Such a configuration can then be conveniently packaged for transport, storage, and consumer use. In some embodiments, the liner is a release liner. In some embodiments, the liner is a silicone-coated release liner.

[0087] Substrate

[0088] The films described herein can be applied to a substrate by removing liner 180 (where present) and placing adhesive layer 170 (where present) adjacent to the substrate. Premask layer 110 (where present) is then removed to expose weatherable layer 120 to sunlight. Suitable substrates generally share certain characteristics. Most importantly, the substrate should be sufficiently rigid. Second, the substrate should be sufficiently smooth that texture in the substrate is not transmitted through the adhesive/metal/polymer stack. This, in turn, is advantageous because it: (1) allows for an optically accurate mirror, (2) maintains physical integrity of the metal reflective layer by eliminating channels for ingress of reactive species that might corrode the metal reflective layer or degrade the adhesive, and (3) provides controlled and defined stress concentrations within the reflective film-substrate stack. Third, the substrate is preferably nonreactive with the reflective mirror stack to prevent corrosion. Fourth, the substrate preferably has a surface to which the adhesive durably adheres.

[0089] Exemplary substrates for reflective films, along with associated options and advantages, are described in PCT Publication Nos. WO04114419 (Schripsema), and WO03022578 (Johnston et al.); U.S. Publication Nos. 2010/0186336 (Valente, et al.) and 2009/0101195 (Reynolds, et al.); and U.S. Patent No. 7,343,913 (Neidermeyer), all of which are incorporated in their entirety herein. For example, the article can be comprised in one of the many mirror panel assemblies as described in co-pending and co-owned provisional U.S. Patent Application No. 13/393,879 (Cosgrove, et al.), incorporated herein in its entirety. Other exemplary substrates include metals, such as, for example, aluminum, steel, glass, or composite materials.

[0090] Advantages and embodiments of this disclosure are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this disclosure. These examples are merely for illustrative purposes and are not meant to be limiting on the scope of the appended claims. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the disclosure are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing

measurements. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Also, in these examples, all percentages, proportions and ratios are by weight unless otherwise indicated.

[0091] All references mentioned herein are incorporated by reference.

[0092] Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the present disclosure and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings disclosed herein.

[0093] As used in this specification and the appended claims, the singular forms “a”, “an”, and “the” encompass embodiments having plural referents, unless the content clearly dictates otherwise. As used in this disclosure and the appended claims, the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

[0094] Various embodiments and implementation of the present disclosure are disclosed. The disclosed embodiments are presented for purposes of illustration and not limitation. The implementations described above and other implementations are within the scope of the following claims. One skilled in the art will appreciate that the present disclosure can be practiced with embodiments and implementations other than those disclosed. Those having skill in the art will appreciate that many changes may be made to the details of the above-described embodiments and implementations without departing from the underlying principles thereof. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows. Further, various modifications and alterations of the present invention will become apparent to those skilled in the art without departing from the spirit and scope of the present disclosure. The scope of the present application should, therefore, be determined only by the following claims.

What is claimed is:

1. A solar mirror film comprising:
a weatherable layer having a weatherable layer coefficient of hygroscopic expansion;
a reflective layer having a reflective layer coefficient of hygroscopic expansion; and
a compliant layer between the weatherable layer and the reflective layer, the compliant layer having a compliant layer coefficient of hygroscopic expansion that is between the weatherable layer coefficient of hygroscopic expansion and the reflective layer coefficient of hygroscopic expansion.
2. The solar mirror film of claim 1, wherein the compliant layer coefficient of hygroscopic expansion is less than about 30 ppm per percent relative humidity and greater than about 0 ppm per percent relative humidity.
3. The solar mirror film of claim 1, wherein the compliant layer coefficient of hygroscopic expansion is less than about 28 ppm per percent relative humidity and greater than about 0 ppm per percent relative humidity.
4. The solar mirror film of claim 1, wherein the compliant layer coefficient of hygroscopic expansion is less than about 25 ppm per percent relative humidity and greater than about 1 ppm per percent relative humidity.
5. The solar mirror film of claim 1, wherein the compliant layer coefficient of hygroscopic expansion is less than about 25 ppm per percent relative humidity and greater than about 3 ppm per percent relative humidity.
6. The solar mirror film of claim 1, wherein the compliant layer coefficient of hygroscopic expansion is less than about 20 ppm per percent relative humidity and greater than about 5 ppm per percent relative humidity.
7. The solar mirror film of any of the preceding claims, wherein the compliant layer coefficient of hygroscopic expansion is between about 75% and about 25% of the weatherable layer coefficient of hygroscopic expansion.

8. The solar mirror film of any of the preceding claims, wherein the compliant layer coefficient of hygroscopic expansion is between about 70% and about 30% of the weatherable layer coefficient of hygroscopic expansion.

9. The solar mirror film of any of the preceding claims, wherein the compliant layer coefficient of hygroscopic expansion is between about 60% and about 40% of the weatherable layer coefficient of hygroscopic expansion.

10. The solar mirror film of any of the preceding claims, wherein the reflective layer is a reflective layer.

11. The solar mirror film of any of the preceding claims, wherein the reflective layer comprises at least one of silver, gold, aluminum, copper, nickel, and titanium.

12. The solar mirror film of any of the preceding claims, wherein the reflective layer coefficient of hygroscopic expansion is between 0 ppm per percent relative humidity and 3 ppm per percent relative humidity.

13. The solar mirror film of any of the preceding claims, further comprising:
a tie layer between at least one of the compliant layer and the reflective layer; and
the compliant layer and the weatherable layer.

14. The solar mirror film of claim 13, wherein the tie layer includes titanium dioxide.

15. The solar mirror film of any of the preceding claims, wherein the weatherable layer coefficient of hygroscopic expansion is greater than about 30 ppm per percent relative humidity.

16. The solar mirror film of any of the preceding claims, further comprising:
a corrosion protective layer adjacent to the reflective layer.

17. The solar mirror film of claim 16, wherein the corrosion protective layer comprises at least one of copper and an inert metal alloy.

18. The solar mirror film of any of the preceding claims, further including an adhesive layer adjacent to the reflective layer.

19. The solar mirror film of claim 18, wherein the adhesive layer comprises a pressure sensitive adhesive.

20. The solar mirror film of claim 18 or claim 19, wherein the adhesive layer is between the reflective layer and a substrate.

21. The solar mirror film of any of the preceding claims, further comprising:
a substrate.

22. The solar mirror film of any of the preceding claims, wherein the solar mirror film is incorporated into a reflector assembly.

23. A concentrated solar photovoltaic system, comprising the solar mirror film of any of claims 1-21.

24. A concentrated solar power system, comprising the solar mirror film of any of claims 1-21.

FIG. 1
PRIOR ART

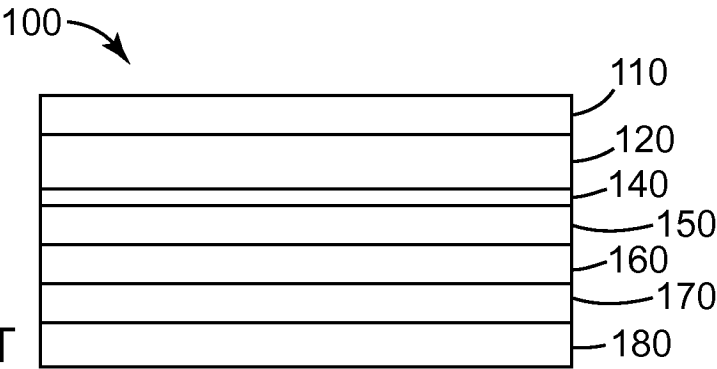


FIG. 2

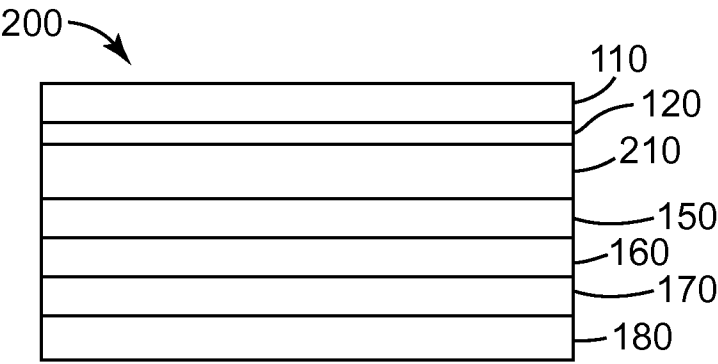


FIG. 3

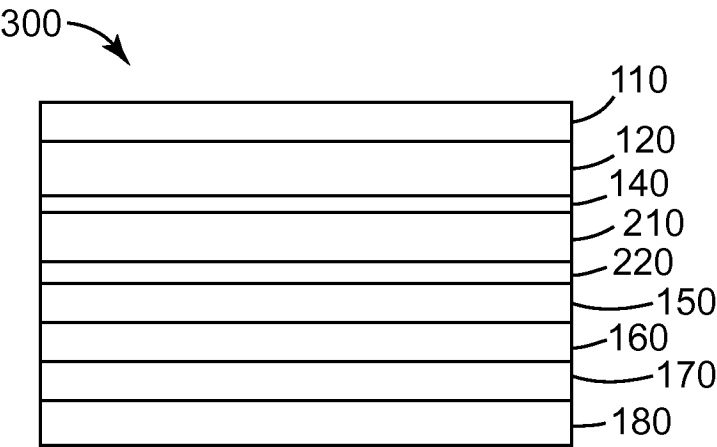
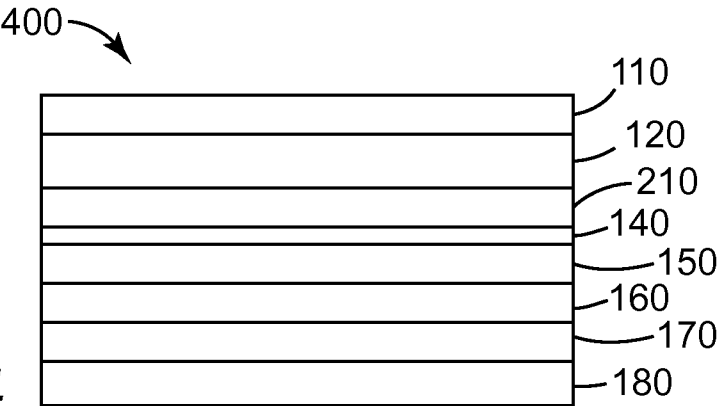


FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2013/038788

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H02N 6/00 (2013.01)

USPC - 136/246

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - H02N 6/00; H01L 31/042; G02B 5/08 (2013.01)

USPC - 136/246, 251, 256, 259; 359/838, 857, 883

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

CPC - G02B 5/08, 5/0808, 23/08 (2013.01)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatBase, Orbit, Google Patents, ProQuest

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006/0181765 A1 (JORGENSEN et al) 17 August 2006 (17.08.2006) entire document	1-7
Y	US 2011/0303277 A1 (NEUMANN et al) 15 December 2011 (15.12.2011) entire document	1-7
A	US 6,120,901 A (OJEDA) 19 September 2000 (19.09.2000) entire document	1-7
A	US 2011/0226234 A1 (DROS et al) 22 September 2011 (22.09.2011) entire document	1-7
A	US 5,361,172 A (SCHISSEL et al) 01 November 1994 (01.11.1994) entire document	1-7

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

13 September 2013

Date of mailing of the international search report

24 SEP 2013

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
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Facsimile No. 571-273-3201

Authorized officer:

Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2013/038788

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 8-24
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.