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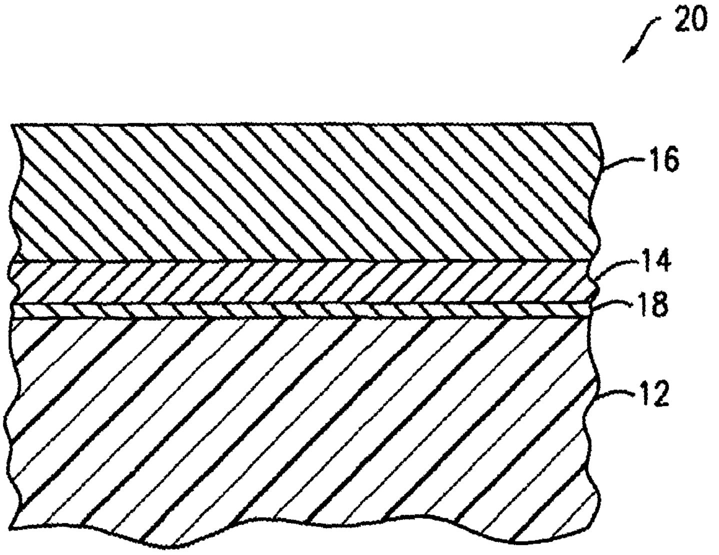
(54) Title: ROBUST HIGHLY REFLECTIVE OPTICAL CONSTRUCTION



(57) Abstract: An optical construction (20) comprises an optically transmissive substrate (12), an optional adhesion-promoting layer (18) comprising an oxide form of at least one metal or metalloid deposited onto the surface of the optically transmissive substrate (12), a reflective layer (14) composed of a highly reflective metal overlaying the adhesion-promoting layer (18), and a protective layer (16) composed of a parylene polymer film bonded to the reflective m etal layer (14).

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ROBUST HIGHLY REFLECTIVE OPTICAL CONSTRUCTION

Field of the Invention

The present invention relates to optical constructions, and more particularly to optical constructions having an optically transmissive substrate material coated with a robust highly reflective optical layer.

Background of the Invention

Optical components such as waveguides are generally designed to confine and direct the propagation of light waves for many applications. In applications that rely on the reflection and transmission of light, significant gains in performance can be made when highly reflective materials are used in combination with optically transmissive materials. For example, a step-index fiber optic is composed of a thin strand of concentric layers of optically transmissive materials- a central optical medium (i.e., the core) and a surrounding optical medium (i.e., the cladding), the latter having a lower index of refraction. Light is channeled through the core. During transmission, the light often travels to the boundary of the core and cladding, where it is reflected back towards the core by total internal reflection. However, total internal reflection is not total, as some of the light is lost, for example, due to scatter induced by imperfections within the core or at the core/cladding boundary.

To reduce this loss, a reflective layer can be applied over the surface of the cladding along the length of the fiber optic. The reflective layer significantly increases the amount of light directed back to the core and improves the overall light transmission through the fiber optic.

Ideally, the reflective layer used in optical components should possess a high reflectance characteristic over a broad spectrum of light and over all incidence angles of reflectance. Silver is one metal known to possess a high reflectance value. Silver has a reflectance of about 98% over the entire visible light spectrum at normal incidence. Silver also sustains a high reflectance of about 96% for off-normal light at near grazing incidence angles. In comparison, aluminum, a more commonly used reflective-layer material, possesses a reflectance of about 93% at normal incidence. The reflectance of aluminum drops precipitously to 75% for light at grazing incidence angles.

Although silver possesses excellent optical characteristics, there are several problems associated with the use of the reflective metal. Silver has a tendency to undesirably tarnish when exposed to the atmosphere, especially in the presence of corrosive gases and contaminants, including sulfur dioxide, hydrogen sulfide, nitrogen dioxide, ozone, hydrogen chloride, chlorine, and organic acids. It is known that long-term performance of silver coatings is rarely, if ever, guaranteed by commercial coating facilities based on the aggressive nature of silver tarnishing brought on by ordinary exposure to the environment, along with the lack of suitably available protective measures which have been successfully tested under corrosive conditions.

Further, silver's adherence to optically transmissive substrate materials, including glass or polymeric materials such as polymethyl methacrylate, is moderate at best. Polymethyl methacrylate is a low-cost acrylic resin frequently used in the fabrication of optical components.

For the foregoing reasons, there is a need for an optical construction having a highly reflective coating that adheres favorably to a range of optically transmissive materials and that possesses improved resistance against corrosion and tarnishing to provide improved optically effective performance and longer lasting operating life.

Summary of the Invention

The present invention is generally directed to an optical construction for optical components such as hollow and solid waveguides, solid and hollow light pipes, fiber optics, prisms, microstructured sheets, curved mirrors (ellipsoidal, parabolic, etc.), plano mirrors, and other optics having topographic forms. The optical construction of the present invention is designed to maintain high optical performance and light transmission through the optical component in the presence of potentially corrosive substances including sulfur dioxide, hydrogen sulfide, nitrogen dioxide, ozone, hydrogen chloride, chlorine, organic acids and the like, which are present in the atmosphere at least in trace amounts.

The optical construction of the present invention is especially useful in optical components where a highly reflective surface composed of a metal such as silver is desired. The optical construction is further adapted to provide favorable durability and preservation of the highly reflective surface in the optical component without measurably degrading the total reflectance qualities of the optical component.

In one aspect of the invention, the optical construction generally comprises an optically transmissive substrate adapted for efficiently channeling light therethrough with a highly reflective layer composed of a highly reflective metal deposited on the surface of the substrate, and bonded thereto. Overlying the highly reflective metal layer and firmly adherently bonded thereto is a protective layer comprised of a parylene polymer film.

The parylene polymer protective layer as used in the present invention serves to isolate the reflective layer from exposure to external elements such as ambient atmosphere, corrosive substances, salt, humidity and the like. Such external elements can cause the destruction and degradation of the metal reflective layer over time through tarnishing, breakdown, delamination, or discoloration, resulting in the loss of its reflectivity. The parylene polymer protective layer further improves the reflective layer's resistance to mechanical deformation and delamination as indicated by a tape-pull test described hereinafter.

Optionally, the optical construction of the present invention can further include an adhesion-promoting layer applied between the surface of the substrate and the reflective layer to strengthen the bond therebetween. The adhesion-promoting layer as used in the present invention significantly improves the adhesion between the functional reflective metal layer and the optically transmissive substrate for improved resistance against delamination where the reflective layer physically separates from the optically transmissive substrate resulting in degraded performance and reduction in reflectivity. Further, the adhesion-promoting layer promotes uniformity and consistency in reflective properties of the reflective layer along the substrate/reflective layer interface.

In an alternative form of the invention, a waveguide structure such as a fiber optic, comprising an optically transmissive glass or polymer material, is coated with an adhesion-promoting layer of the oxide form of a metal or metalloid. A silver reflective layer is applied in contact with the adhesion-promoting layer. A protective layer of a parylene polymer film is applied over the silver reflective layer to prevent the silver from losing its high reflective luster or from delaminating or degrading due to corrosive agents in the environment such as ambient air. The preferred form of the invention forms a robust highly reflective parylene/silver/metal-oxide/waveguide structure with improved performance qualities including longer operating life.

Brief Description of the Drawings

Various embodiments of the invention are described in detail below with reference to the drawings, in which like items are identified by the same reference designation, wherein:

Figure 1 is a cross sectional view of an optical construction having a highly reflective layer illustrative of one embodiment of the present invention;

Figure 2 depicts a schematic diagram of a parylene vacuum evaporation deposition reactor system for depositing a parylene polymer film to make an optical construction in accordance with the principles of the present invention;

Figure 3 is a cross sectional view of an optical construction having a highly reflective layer illustrative for a second embodiment of the present invention;

Figure 4 is a cross sectional view of an optical construction having a highly reflective layer illustrative for a third embodiment of the present invention;

Figure 5 is a cross sectional view of a fiber optic waveguide comprising the optical construction in accordance with the present invention;

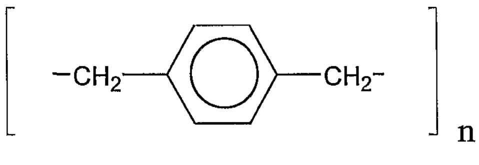
Figure 6 is a graph plotting the silver corrosions rates for various samples exposed in the presence of ambient air; and

Figure 7 is a graph plotting the silver corrosion rates for various samples exposed in the presence of an ammonium sulfide solution.

Description of the Invention and Preferred Embodiments

The present invention is generally directed to an optical construction and a method of making such optical constructions. The optical construction of the present invention includes a substrate, a highly reflective layer, an optional adhesion-promoting layer in contact between the substrate and the reflective layer, and a protective layer comprising a parylene polymer film overlaying the reflective layer. The optical construction of the present invention provides favorable optical qualities with improved adherence of the reflective layer to the substrate and improved resistance to corrosion and tarnishing for a longer operating life. The substrate material can be selected from the group consisting of glass and organic polymer-based materials such as polymethyl methacrylate (PMMA), for example.

In the present invention, the parylene polymer film, useful as a protective layer, has the following polymer repeat unit structure:



where "n" indicates the number of repeating units in the structure. The parylene polymer coating may be exemplified in three forms or variations, with each comprising varying degrees of chlorination. The three forms include parylene N as shown above with no chlorine atoms, parylene C which is produced from the same monomer as parylene N and is further modified by the substitution of a chlorine atom for one of the aromatic hydrogens, and parylene D which is produced from the same monomer as parylene N and is further modified by the substitution of two chlorine atoms for two of the aromatic hydrogens.

With reference to Figure 1, there is depicted an optical construction illustrative for one embodiment of the present invention. We note that the thickness of the corresponding elements in the construction are not drawn to scale, and is shown for illustrating the general structure and relationships thereof. The optical construction denoted herein by reference numeral 10, can be applied for the fabrication of a range of optical components where a highly reflective surface composed of a metal such as silver, is desired.

The optical construction 10 generally comprises an optically transmissive substrate 12 for efficiently transmitting and directing light therethrough, a reflective layer 14 preferably composed of a highly reflective metal such as silver vapor-deposited on the surface of the optically transmissive substrate 12, and a protective layer 16 preferably composed of a parylene polymer film. Preferably, the surface of the substrate 12 is optically smooth and substantially free from optical imperfections to provide the highest specular reflectance. The surface of the substrate 12 can be optionally treated to promote adhesion with the reflective layer 14 including, but not limited to, plasma treatment as described in U.S. Pat. No. 5,982,546, the content of which is incorporated herein by reference to the extent that there is no conflict.

The optically transmissive substrate used for fabricating optical components such as fiber optic waveguides can be selected from a range of materials depending, for example, on the application, the desired performance characteristics, the cost, and the characteristics of the transmitted light. The optically transmissive substrate 12 can be composed of glass or polymer material. The polymer materials can include organic polymers such as polyhydrocarbons, polyoxyhydrocarbons, polysulfohydrocarbons, and fluorocarbon and fluorohydrocarbon materials, as well. Representative organic polymers include polyesters such as poly(ethyleneterephthalate) and poly(butyleneterephthalate), polyacrylates and methacrylates such as poly(methylmethacrylate) (PMMA), poly(methacrylate), and poly(ethylacrylate), copolymers such as poly(methylmethacrylate-co-ethylacrylate) and polycarbonates. Fluorocarbon polymers such as TEFLON and the various fluorohydrocarbon polymers known in the art can be used as well. More preferably, the polymer material is PMMA.

Other polymers can be used as optically transmissive substrate materials, particularly in applications where low birefringence is desired. Such polymers include CR-39 allyl diglycol carbonate resin marketed by PPG Industries of Pittsburgh, Pennsylvania; OZ-1000 cycloaliphatic acrylic resin marketed by Hitachi Chemical Co., Ltd. of Tokyo, Japan; CALIBRE 1080 DVD polycarbonate resin marketed by Dow Engineering Plastics of Midland, Michigan; MAKROLON DP1-1265 polycarbonate resin marketed by Bayer Corporation of Pittsburgh, Pennsylvania; PLEXIGLAS VOD-100 acrylic molding resin marketed by ATOFINA Chemicals, Inc. of Philadelphia, Pennsylvania, TOPAS cyclo-olefin copolymer resin marketed by Ticona of Summit, New Jersey; ZEONEX cyclo-olefin polymer resin marketed by Nippon Zeon Co., Ltd of Tokyo, Japan; and the like.

Although not a limitation to the application of this invention, the plastic or polymer material can be clear, transparent, and optically transmissive. When used in context of plastic or polymer materials, the terms “clear”, “transparent”, and “optically transmissive” means a plastic or polymer that, in its configuration of use, exhibits transmission over a desired range of wavelengths. The polymer-based substrates themselves are commercially available or can be prepared by various art-known processes and do not, in and of themselves, constitute an aspect of this invention. The polymer substrates can be formed into solid bodies, sheets, films, or coatings applied or laminated onto nonpolymeric surfaces such as metal and glass.

The reflective layer 14 of the optical construction 10 shown in Figure 1 is preferably made up of one or more functional metals that possess high reflectance values such as silver, copper, gold, palladium, iridium, rhodium, combinations in the form of alloys thereof, and the like. Among these metals, copper, silver, and gold are preferred, with silver being the most preferred metal for the visible range of light. The reflective layer 14 comprising a metal or an alloy of metals, can be deposited onto the optically smooth surface of the optically transmissive substrate 12 through conventionally known deposition methods such as cathode sputtering, vacuum evaporation or vapor-phase deposition techniques for a thickness ranging from about 100 to 10,000 Å, preferably 500 to 3,000 Å, and more preferably from about 1000 to 3,000 Å. Individual metals can be used, or a plurality of layers of different metals or layers of alloys of these metals can be used, if desired.

In another embodiment of the present invention, the reflective layer 14 of the optical construction 10 is enclosed and sealed from ambient by the protective layer 16 for optimal protection against corrosion and tarnishing. The protective layer 16, in the form of a parylene polymer film, is vapor deposited on the surface of the reflective layer 14 distal from the optically transmissive substrate 12. The parylene polymer protective layer 16, as applied, forms a continuously uniform coating as will be further described.

The parylene polymer film of the protective layer 16 can be composed of parylene N, parylene C, parylene D, or combinations or mixtures thereof. The parylene polymer film can be composed of an interpolymer of monomers of parylene variants of varying mixture ratios. The thickness of the parylene polymer film of the protective layer 16 is preferably at least 0.0001", more preferably in the range of from about 0.001 to 0.0001". We note that the actual thickness of and the mixture ratios of the variants in the parylene polymer protective layer can be adjusted according to the application, requirements, the reflective layer metal used, the desired effect, the duration of effect, and the types of expected contaminant exposures and the like, and may be readily determined by one skilled in the art.

The parylene polymer film can be optionally processed using suitable annealing or heat-treatment techniques to improve the chemical resistance and durability of the coating as will be described. The term "annealing" or "heat-treating" as used herein refers to any processes for treating a substance or material with heat followed by cooling to modify or alter the structural properties of the treated substance or material.

In accordance with the present invention, the parylene polymer film is applied through a coating process using conventionally known vapor phase deposition or vacuum evaporation deposition techniques. It is understood that the present invention can utilize any suitable commercially available method for applying parylene polymer on a surface as known by one skilled in the art.

As an illustrative example, one process for applying a parylene polymer coating is described in U.S. Pat. No. 3,342,754, the disclosure of which is hereby incorporated by reference in its entirety to the extent that no conflict exists. It is understood that the invention is not limited to the use of this process.

With reference to Figure 2, a general schematic diagram of a basic parylene vacuum evaporation deposition reactor system 40 for carrying out the vacuum evaporation deposition process described in U.S. Pat. No. 3,342,754, is shown. As noted above, there are many known systems and processes known in the art for applying a polymer film on a substrate. The following description of system 40 provides an illustration of the process that may be used for coating a substrate with a parylene polymer layer. The system 40 can be constructed using commercially available components and parts as known by those skilled in the art.

With further reference to Figure 2, the system 40 comprises a vaporization chamber 42, a cracking chamber 44, a deposition chamber 46, and a vacuum pump

48. The vacuum pump 48 operates to evacuate the air from the interior of the system 40. The vaporization chamber 42 is adapted to heat a sample of the di-p-xylylene dimer under vacuum at an elevated temperature sufficient to vaporize the dimer. Under vacuum conditions, the vaporized dimer radiates in all directions within the chamber 42.

The vaporized dimer proceeds to the cracking chamber 44 where the dimmer is heated to a temperature of less than 700°C, preferably between 450°C and 700°C, and more preferably at about 680°C for a sufficient time at a pressure such that the vapor pressure is below 1.0 mm Hg, to form a parylene diradical monomer of parylene.

The parylene diradical monomer proceeds to the deposition chamber 46 where the diradical monomer condenses and polymerizes at a temperature of less than 200°C, preferably below the ceiling condensation temperature of the parylene diradical monomer, and more preferably at room temperature on the cooler surface of the reflective metal-coated optically transmissive substrate. The condensation of the diradical monomer yields a tough, linear, non-fluorescent polymer. The vacuum pump 48 is connected to the system 40 to ensure that the process is carried out in an evacuated atmosphere for optimal processing.

The vacuum evaporation technique of depositing parylene polymer provides several advantages. The first is that the room temperature deposition process enables a range of substrates to be coated with parylene polymer films. The second is the formation of a highly conforming and uniformly continuous coating on substrates with complex shapes. The third is the capability to form very thin coating layers while remaining continuous and uniform for precise coating control.

With particular reference to Figures 1 and 2, the overall process of making the optical construction of the present invention will now be described. In a preferred form of the optical construction 10, the construction is formed by vapor depositing a silver layer 14 onto the optically smooth surface of a PMMA-based optically transmissive substrate 12. The reflective metal-coated optically transmissive substrate is placed into the deposition chamber 46 of the reactor 40, and suitably positioned for exposing the outer surface of the reflective silver metal 14 to the parylene diradical monomer flow. The parylene vacuum evaporation process produces a parylene polymer protective layer 16 of sufficient thickness on the surface of the silver metal layer 14. The thickness of the deposited parylene polymer protective layer 16 can be determined while in the deposition chamber 46 using any one of various optical methods known in the art. Alternatively, the thickness of the parylene polymer protective layer 16 can be determined after the article is removed from the deposition chamber 46.

The above deposition process can be repeated at least once using the same or a different parylene variant (i.e., parylene N, parylene C, parylene D, and/or mixtures thereof) to produce a multilaminate parylene polymer coating on the surface of the reflective silver layer 14 as will be further described hereinafter. The deposition chamber 46 is sealed from ambient air and the atmosphere of the chamber 46 is evacuated with the vacuum pump 48. Alternatively, the atmosphere in the deposition chamber 46 can be substituted at ambient pressure with an inert gas such as helium, argon or nitrogen.

We have discovered that by annealing the deposited parylene polymer protective film in the protective layer at an elevated temperature for a sufficient time, and allowing them to cool, a substantially improved chemically resistant parylene polymer barrier is formed. We have also discovered that the physical barrier and mechanical properties of the parylene polymer coating are greatly improved after the annealing thermal treatment. The annealing temperature can be at least 120°C, preferably from about 120°C to 220°C and the annealing time may range from about 1 hour to five (5) days. The annealing process can be carried out under suitable atmospheric conditions including, but not limited to vacuum, inert gas, and normal ambient atmosphere. The annealing conditions can be varied as required by the thermal mass of the substrate, the maximum substrate temperature rating, and the like, as may be determined by those skilled in the art.

The parylene polymer film can be annealed immediately after the completion of the parylene deposition process. The annealing process is preferably conducted in a vacuum, or in the presence of at least one inert gas such as helium, argon, nitrogen, and the like, at atmospheric pressure. The optimal annealing conditions may differ slightly between each variant of the parylene polymer. We further note that the annealing process may be utilized on each parylene polymer protective layer individually as applied during the vapor deposition process, or on the parylene polymer protective layer as a whole after applying more than one parylene polymer layer.

In another embodiment of the present invention as shown in Figure 3, there is provided an optical construction 20 which is not drawn to scale, comprising an optically transmissive substrate 12 as described above and a thin adhesion-promoting layer 18 comprising the oxide form of at least one metal or metalloid that is applied to the substrate surface using conventional deposition processes such as vacuum evaporation, cathode sputtering, electron beam evaporation, and the like. The adhesion-promoting layer 18 is applied to the substrate 12 prior to the application of the reflective layer 14. Details describing the use of aluminum oxides for enhancing the adhesion of silver to glass substrates, is found in Hass et al., *Applied Optics*, 14, 2639 (1975), the content of which is incorporated herein by reference.

The reflective layer 14 comprising a highly reflective metal such as silver is deposited, using methods described above including electron beam evaporation, onto the surface of the adhesion-promoting layer 18 for a thickness sufficient to form an opaque, highly reflective surface at the interface between the substrate 12 and the reflective layer 14. Finally, the surface of the reflective layer 14 is coated with a protective layer 16 comprising a parylene polymer film preferably using the vacuum evaporation deposition or suitable process as described above.

As noted above, the adhesion-promoting layer 18 preferably comprises the oxide form of at least one metal or metalloid that is sufficient to bond the metal atoms of the reflective layer 14 to the smooth surface of the optically transmissive substrate 12. Preferably, the thickness of the adhesion-promoting layer 18 can range from about 10 to 1000Å, and more preferably about 300 Å. The use and application of metal- and metalloid-based oxides (collectively referred hereinafter as "metal oxides") as adhesion promoting materials between a metal and a polymer substrate is further described in U.S. Pat. Nos. 5,589,280 and 5,902,634, the pertinent teachings of both are incorporated herein by reference to the extent that there is no conflict.

For most applications, any of the adhesion-promoting materials selected should be as nearly colorless as possible, at least in the amounts found effective to provide reliable adhesion. An adhesion-promoting material that imparts a visually detectable color to the substrate 12 under the desired illuminant not only reduces the efficiency of reflection by absorbing light passing to and from the reflective layer 14 but also changes the color value of the light rays directed at the reflective layer 14 through the substrate 12. We note that the adhesion-promoting material, in addition to promoting adhesion of the metallic reflective layer 14 to the substrate 12, must resist corrosion to maintain its optical qualities. We further note that the selection of the materials for the adhesion-promoting layer must also take into account the effects of the relative expansion coefficients in order to preclude undesirable effects including delamination resulting from cyclic temperature changes.

In one embodiment of the present invention, the adhesion-promoting layer 18 which is positioned between the optically transmissive substrate 12 and the reflective layer 14, is composed of the oxide form of one or more metals including, but not limited to, hafnium, zirconium, tantalum, titanium, niobium, silicon, tungsten, aluminum, vanadium, molybdenum, chromium, tin, antimony, indium, zinc, bismuth, cadmium, nickel and the like.

Generally, the method for producing the adhesion-promoting layer 18 is to deposit the metal oxide via cathode sputter deposition, electron beam evaporation deposition or any suitable process for depositing metal oxides. The metal oxides are preferably deposited in the oxidized mode, which may be achieved for example by sputtering in the presence of an excess of oxygen so that the metal is fully oxidized, to attain the desired adhesion promotion.

Since some of the metals considered here for the adhesion-promoting layer 18 exhibit substantial absorption in their metal state (i.e., >3% absorption at thicknesses less than 20 Å), it is advantageous to deposit them as oxides. Similarly, it may also be advantageous to up-oxidize the metal layers fully or partially after their deposition.

Referring to Figure 4, an optical construction is depicted for a third embodiment of the invention. The optical construction denoted herein as reference numeral 30 is similar to the optical construction 20 of Figure 3 previously described above. We again note that the thickness of the corresponding elements in the construction are not drawn to scale, and is shown for illustrating the general structure and relationships thereof. In the present embodiment, the optical construction 30 includes a protective layer 16 that is composed of a multilaminate structure with each layer being composed of a distinct parylene polymer selected from the group consisting of parylene N, parylene C, parylene D and combinations or mixtures thereof. The multilaminate form of the protective layer 16 provides benefits of each parylene variant and/or mixtures of parylene variants for improved compatability with the reflective metal layer, chemical resistance and the like.

The protective layer 16 includes first parylene film 17 composed of a first parylene variant or mixtures of parylene variants. The first parylene film 17 is deposited on the reflective layer 14 using one of the suitable deposition methods described above. The protective layer 16 further includes a second parylene film 19 composed of a second parylene variant or mixtures of parylene variants overlaying the surface of the first parylene film 17 distally from the reflective layer 14. The actual thickness of each parylene variant layer can be adjusted according to the application, requirements, the reflective layer metal, the desired effect, the duration of effect, and the types of expected contaminant exposures and the like, and may be readily determined by one skilled in the art.

In one embodiment, the first parylene film 17 is composed of parylene C, and the second parylene film 19 is composed of parylene D. We have determined from experimental results that when parylene C was deposited as a protective layer directly on the silver reflective layer, the change in silver reflectance at the parylene/silver interface, was observed to be within the noise of the experimental data. The findings indicated that there is little or no reactivity between parylene C and silver.

We have further determined from experimental results that when parylene D was deposited on the silver layer as a protective layer, the silver reflectance at the parylene/silver interface, was measurably diminished or degraded. Since parylene D is known to possess an average chlorine content of two chlorine atoms per monomer unit, we theorize that the presence of unbonded or trapped chlorine in the parylene polymer film may be reacting with the silver. Although the findings indicated that there may be some reactivity between parylene D and silver, parylene D is a suitable candidate for use as part of the protective layer. Parylene D is known to have a lower gas permeability value than parylene C for better exposure protection of the silver reflective layer. The silver/parylene C/parylene D laminate combination provides an effective protective layer, which possesses the low reactivity with silver of parylene C, and the low gas permeability of parylene D.

In yet another embodiment, the transitioning of the deposition of parylene films from one parylene variant to another, can be made gradually to form a transitional interlayer (not shown) between the first and second parylene polymer layers. As the deposition of the parylene variants transitions, the vapor flow of the first parylene polymer is gradually reduced while the vapor flow of the second parylene polymer is ramped up in proportion to the corresponding reduction of the first parylene polymer vapor flow. This action produces a graded interface between the pure parylene polymer layers and forms an interpolymer with improved adhesion therebetween. We note that the resulting parylene polymer layer can be annealed or heat-treated as desired to modify the properties of layer as described above.

It is understood that the actual thickness of the interlayer can be adjusted according to the application, requirements, the desired effect, the duration of effect, and the types of expected contaminant exposures and the like, and may be readily determined by one skilled in the art.

Referring to Figure 5, a fiber optic waveguide is depicted for one illustrative embodiment of the present invention. The fiber optic waveguide denoted generally by reference numeral 50, generally comprises an elongated cylindrical body having concentric layers of glass for channeling light therethrough. The fiber optic waveguide 50 of Figure 5 comprises a core 52 composed of an optically transmissive glass or polymer material, a cladding 54 composed of an optically transmissive glass or polymer material with a lower refractive index than the core 52, a reflective layer 58 with an optional adhesive-promoting layer 56 interposed between the reflective layer 58 and the cladding 54, and a parylene polymer protective layer 60 overlaying the reflective layer 56. The fiber optic 50 includes the optical construction of the present invention where the cladding 54 establishes the optically transparent substrate. The fiber optic 50 can be fabricated from any commercially available fiber optic waveguide while using the above-described techniques for applying the reflective layer, the optional adhesion-promoting layer, and parylene polymer layer, all onto the surface of the cladding 54.

EXAMPLE 1

Experimental Tests

We obtained samples of optical quality polymethyl methylacrylate (PMMA) substrates with a reflective index of 1.49 for testing. An aluminum oxide coating was evaporatively applied to one set of samples using conventional electron beam evaporation deposition process to form an adhesion-promoting layer. The aluminum oxide source having a purity of 99.999 %, was obtained from Cerac of Milwaukee, WI. The aluminum oxide was deposited using a flow of 21.8 % O_2/Ar at a total pressure of $2\text{x}10^{-4}$ Torr. The deposition rate was set at approximately 1 Å per second to produce a final thickness of about 300 Å.

A layer of silver metal was applied to the surface of each sample substrate using a conventional electron beam evaporation deposition process. The silver metal source having a purity of 99.999 %, was obtained from Cerac. The silver layer was applied at a thickness of 1,000 Å at a deposition rate of from about 1.2 to 7.3 Å per second. The average deposition rate was about 3 Å per second.

Parylene D and C were each obtained from Paratronix, Inc. of Attleboro, MA. The parylene polymers were applied to the samples using chemical deposition processes resulting in a coating of about 0.0005". The degree of protection the parylene polymer layer provided was measured by the changes in reflectance of the silver layer through the substrate. Reflectance measurements were made using a MacBeth Color-Eye 7000 spectrometer with a spectral range of from about 360 to 750 nm. Measurements at the interface were made through the PMMA substrate and will include any absorption due to the PMMA or interference effects from the first surface reflectance.

Accelerated silver tarnishing was induced by placing the sample in a sealed 200 mm diameter Pyrex glass desiccator containing normal ambient air and a evaporation dish holding 2 cc of ammonium sulfide (20 % aqueous solution) in 18 cc of deionized water. The ammonium sulfide was obtained from Strem Chemicals of Newburyport, MA. The samples of substrates were positioned 4 cm above the solution with the silver layer side exposed to the solution. The silver reflectance was measured as a function of the exposure time in the desiccator chamber. The ammonium sulfide solution generated hydrogen sulfide as the primary corrosion agent. We had observed that elemental sulfur had deposited on the desiccator walls after long exposure times. Ammonium sulfide solution is known to be one of the most aggressive tarnishing agent of silver. See, Dar-Yuan Song et al., *Applied Optics* 24 (8), 1164 (1985).

Ambient Air Results

In order to estimate the rate of silver corrosion in ambient air for an unprotected sample, the reflectance of a silver coated PMMA sample was measured periodically when exposed to the ambient air of the laboratory. The change in reflectance of the silver surface and the silver/PMMA interface as measured through the optically transmissive PMMA substrate was recorded for each sample. The reflectance was measured using light with a wavelength of about 550 nm extending over a period of about 70 days. The points were plotted and linear regression analysis was executed to generate a graph depicted in Figure 6.

With reference to Figure 6, the graph shows that the ambient air exposure resulted in tarnish rates of about 6.3×10^{-2} %/day for the silver surface, and about 2.2×10^{-2} %/day for the silver/PMMA interface. We believe that the lower tarnish rate at the interface as compared to the silver surface can be explained in that the diffusion of corrosion agents through the silver layer, or less likely, through the much thicker PMMA substrate was slower. Included in the graph are reflectance measurements for samples (control) that had been stored in 3M Corrosion Control Absorber Paper (CPAP), an anticorrosion paper product of Minnesota Mining and Manufacturing Co. of St. Paul, Minnesota. The anticorrosion paper is designed to prevent tarnishing from the presence of air contaminants that cause oxidation and corrosion. When the corrosive elements were removed from the air by the anticorrosion paper, both the silver surface and the silver/PMMA interface showed no measurable change in reflectance. The change of reflectance was less than 3 x 10^{-4} %/day over the 70 day measurement period. Comparing the two sets of data, we can conclude that the changes in silver reflectance were produced by air corrosion alone, and there appeared to be no perceptible interaction of the silver mirror with the PMMA substrate at the interface.

Ammonium sulfide

To test the ability of parylene coatings to inhibit the tarnish of silver, several silver coated PMMA samples were prepared in the manner as described above. The PMMA samples were encapsulated with films of both C and D variants of parylene. The parylene polymer coated PMMA samples were obtained from Paratronix. The film thickness of the parylene coatings was measured to be on average of about 0.00043 of an inch.

Using the test procedure described above, the effectiveness of parylenes coatings C and D were evaluated. Changes in silver reflectance as a function of exposure time in the corrosion chamber were measured and the results are shown in Figure 7. Referring to Figure 7, the samples were each exposed to ammonium sulfide solutions. The corrosion rates were determined from data analyses using linear least-square fits. The corresponding corrosion rates for exposure to ambient air and ammonium sulfide are listed below in Table 1.

Table 1

Silver Tarnish Rates Determined from Reflectance Measurements at 550 nm

Protective Film	Silver Tarnish Rate (%/day at 550 nm)		Corroding Agent
	Ag Surface	Ag/PMMA Interface	
None	0.063	0.022	Air
None	7.1×10^4	5.3×10^3	Ammonium sulfide
Parylene C	4.9	0.50	Ammonium sulfide
Parylene D	0.33	0.17	Ammonium sulfide

Comparing the tarnish rates through the parylene C and D films, we had observed that the tarnish rate for the parylene C was fifteen times higher than the rate for parylene D. Comparing the tarnish rates for parylene protected samples to the unprotected silver samples, we had observed that the tarnish rate was reduced by a factor of 6.9×10^{-5} for the parylene C coating and a factor of 4.6×10^{-6} for the parylene D coating. Assuming that similar corrosion agents are responsible for the ambient air tarnish results, the above tarnish reduction factors can be used to estimate a tarnish rate for parylene polymer protected silver in normal atmospheric air. Applying the tarnish reduction factors to the ambient air data results in an estimated air tarnish rate of about 4.3×10^{-6} %/day for a parylene C protected silver film and an estimated air tarnish rate of about 2.9×10^{-7} %/day for parylene D.

Based on this analysis, either of the parylene variants would protect silver for 50 years with less than a 0.1% change in reflectance.

The measured tarnish rates at the silver/PMMA interface listed in Table 1 are at all times lower that those from the silver surface. This result is expected since there is the added requirement for the corrosion gases to diffuse through the silver layer to reach the silver/PMMA interface.

Silver Adhesion

Parylene C and D films were deposited directly onto PMMA to test the adhesion of these films. Several samples of each variant were tested with SCOTCH tape marketed by Minnesota Mining and Manufacturing. Co., and were observed to be adherent to the substrate with no instances of the parylene film removal by the tape pulls.

Although silver appears to be compatible with PMMA when in direct contact, the adhesion to this material is marginal. SCOTCH tape tests of silver coatings on PMMA consistently removed all of the silver film. Encapsulation of the silver coated PMMA substrates with parylene, as would be done for the final silver coated waveguide structure, does improve the robustness of the silver coating.

Due to the high tensile strengths of the parylene films, silver films on PMMA that have been coated with either parylene C or parylene D will usually pass the SCOTCH tape test without any film delamination. However, in some instances blisters can be seen in the film after the pull test indicating areas where the silver film has detached from the PMMA substrate. The parylene film, however, remains intact and well-bonded to the underlying silver film. These failures confirmed the need to improve the silver/PMMA interfacial bond.

As detailed previously, metal- or metalloid-oxides are known to enhance the adhesion of silver to glass substrates. Alumina was chosen since it is also an excellent candidate for the silver coated waveguide application due to its high transparency throughout the visible spectrum. In order to test alumina as an adhesion layer for silver on PMMA, a 300 Angstrom-thick layer was deposited on PMMA prior to deposition of the silver mirror. SCOTCH tape tests indicate that the alumina interfacial layer improves the silver adhesion. Approximately 80% of the tape pulls resulted in no loss of silver film with 20% of the pulls removing a portion of the silver mirror from the PMMA substrate. Once alumina-bonded silver films were overcoated with parylene C, no removal or delamination of the silver mirror from the substrate was observed from tape test pulls.

Although various embodiments of the invention have been shown and described, they are not meant to be limiting. Those of skill in the art may recognize various modifications to these embodiments, which modifications are meant to be covered by the spirit and scope of the appended claims.

What is Claimed is:

1. An optical construction comprising:

an optically transmissive substrate;

a reflective layer composed of a highly reflective metal overlaying the optically transmissive substrate, and bonded thereto; and

a protective layer composed of a parylene polymer film bonded to the reflective metal layer.

2. The optical construction of Claim 1, further comprising an adhesion-promoting layer deposited between the optically transmissive substrate and the reflective layer for increasing the strength of the bond therebetween.

3. The optical construction of Claim 2, wherein the adhesion-promoting layer is composed of the oxide form of a metal or metalloid.

4. The optical construction of Claim 3, wherein the metal or metalloid of the adhesion-promoting layer is selected from the group consisting of aluminum, hafnium, zirconium, tantalum, titanium, niobium, silicon, tungsten, vanadium, molybdenum, chromium, tin, antimony, indium, zinc, bismuth, cadmium, and nickel.

5. The optical construction of Claim 3, wherein the metal of the adhesion-promoting layer is aluminum.

6. The optical construction of Claim 1, wherein the parylene polymer film comprises at least one layer of a parylene polymer variant.

7. The optical construction of Claim 6, wherein the parylene polymer variant is selected from the group consisting of parylene N, parylene C, parylene D, and combinations thereof.

8. The optical construction of Claim 1 wherein the highly reflective metal is selected from the group consisting of silver, copper, gold, palladium, iridium, rhodium, and combinations in the form of alloys thereof.

9. The optical construction of Claim 1, wherein the highly reflective metal is silver.

10. The optical construction of Claim 1, wherein the optically transmissive substrate is composed of glass or a polymer material.

11. The optical construction of Claim 10, wherein the polymer material of the optically transmissive substrate is selected from the group consisting of

polyhydrocarbons, polyoxyhydrocarbons, polysulfohydrocarbons, fluorocarbons and fluorohydrocarbons, polyesters, poly(ethyleneterephthalate), poly(butyleneterephthalate), polyacrylates methacrylates, poly(methylmethacrylate) (PMMA), poly(methacrylate), poly(ethylacrylate), copolymers, poly(methylmethacrylate-co-ethylacrylate), and polycarbonates, and CR-39 allyl diglycol carbonate resin, OZ-1000 cycloaliphatic acrylic resin, CALIBRE 1080 DVD polycarbonate resin, MAKROLON DP1-1265 polycarbonate resin, PLEXIGLAS VOD-100 acrylic molding resin, TOPAS cyclo-olefin copolymer resin, ZEONEX cyclo-olefin polymer resin, and combinations thereof.

12. The optical construction of Claim 10, wherein the polymer material of the optically transmissive substrate is poly(methylmethacrylate).

13. The optical construction of Claim 1, wherein the highly reflective layer comprises a thickness of from about 100 to 10,000 Å.

14. The optical construction of Claim 2, wherein the adhesion-promoting layer comprises a thickness of from about 10 to 1000 Å.

15. The optical construction of Claim 6, wherein the parylene polymer film comprises a layer of parylene C in contact with the reflective layer, and a layer of parylene D in contact with the layer of parylene C.

16. The optical construction of Claim 15, wherein the parylene polymer film further comprises an interlayer of parylene C and parylene D between the layer of parylene D and the layer of parylene C.

17. The optical construction of Claim 1, wherein the protective layer comprises a thickness of from about 0.001 to 0.0001 of an inch.

18. The optical construction of Claim 1, wherein the substrate comprises a fiber optic waveguide.

19. The optical construction of Claim 1, wherein the protective layer composed of the parylene film is annealed or heat-treated.

20. An optical construction comprising:

an optically transmissive substrate;

an adhesion-promoting layer comprising the oxide form of at least one metal or metalloid deposited onto the surface of the optically transmissive substrate;

a reflective layer composed of a highly reflective metal; and

a protective layer composed of a parylene polymer film in bonded contact with the reflective metal layer.

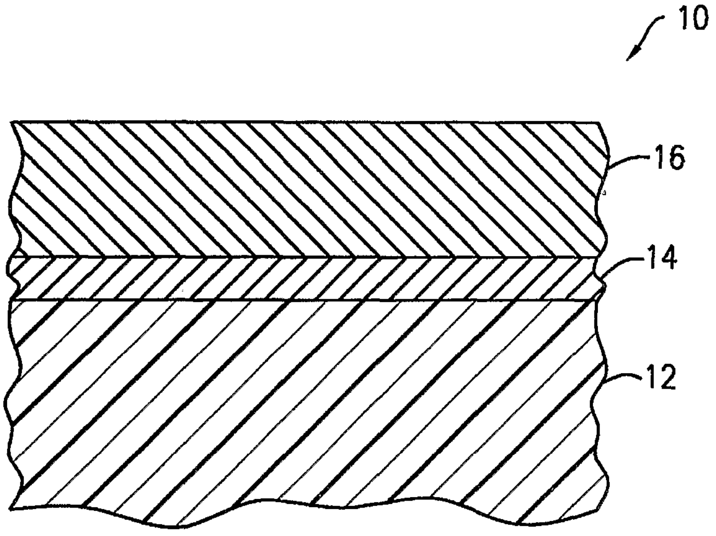
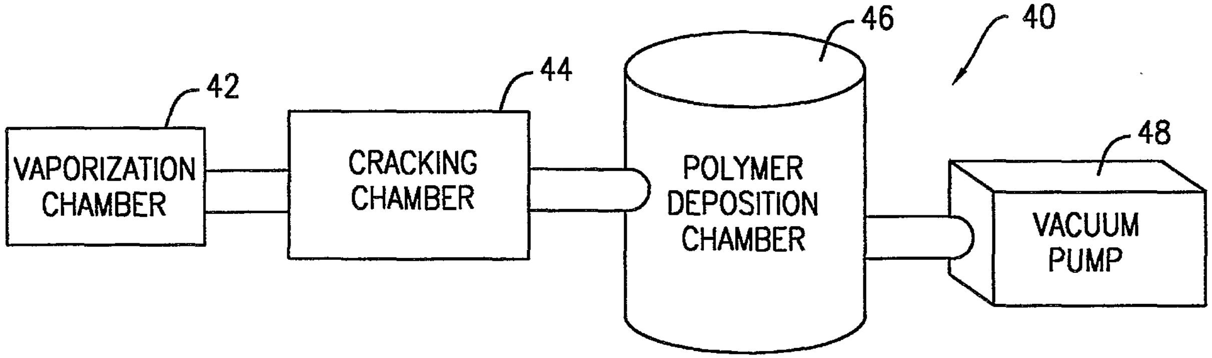


FIG. 1



PARYLENE VACUUM EVAPORATION REACTOR

FIG. 2

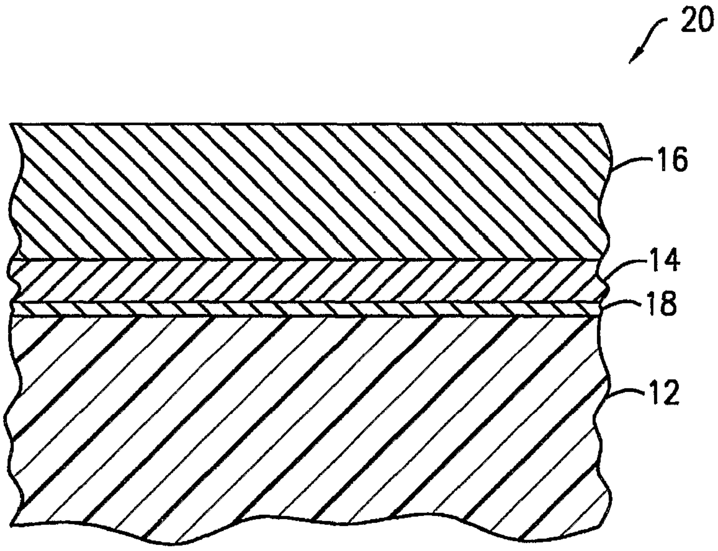


FIG. 3

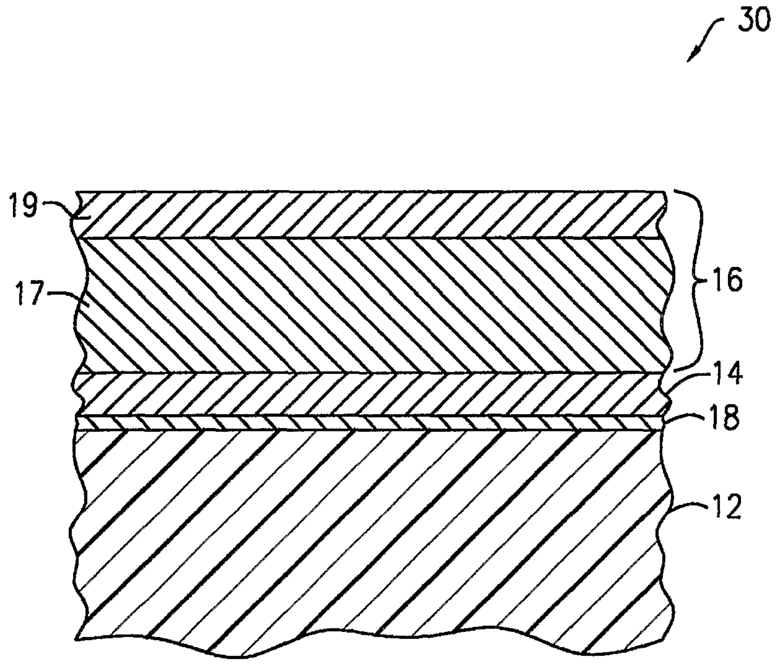


FIG. 4

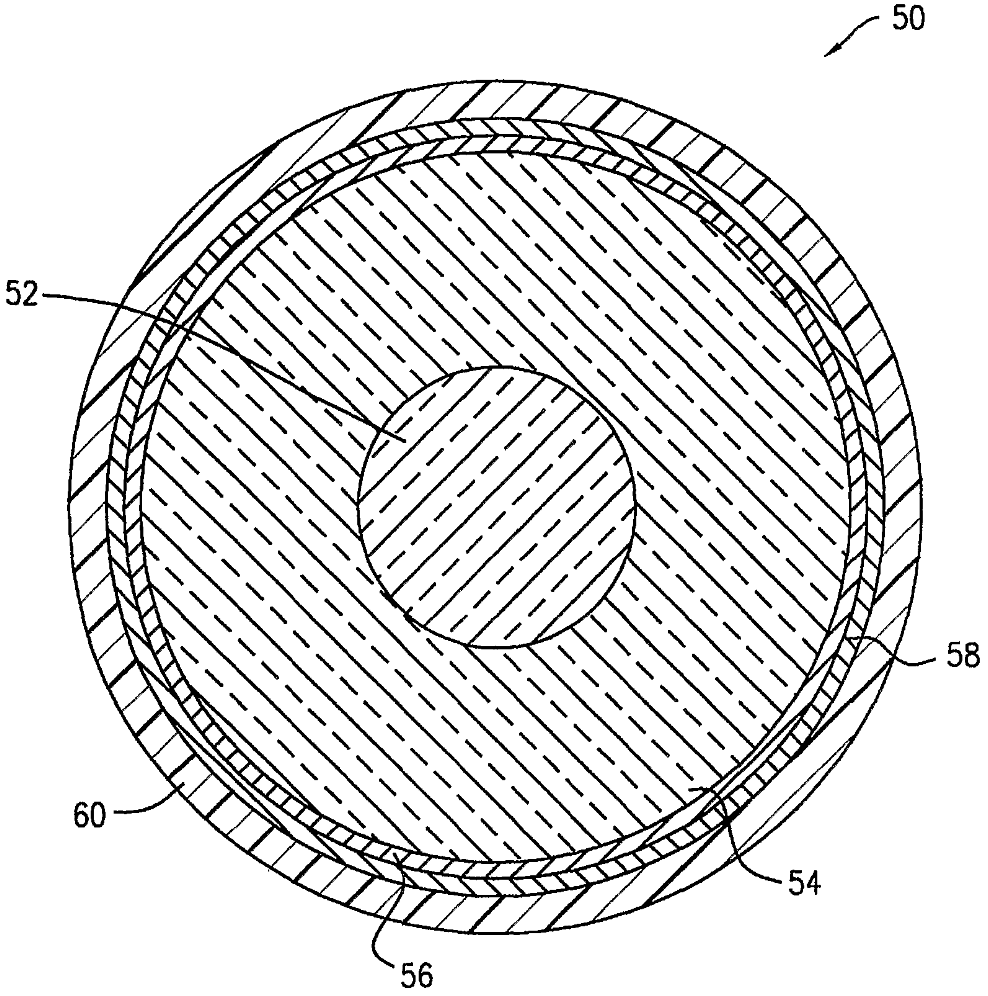


FIG. 5

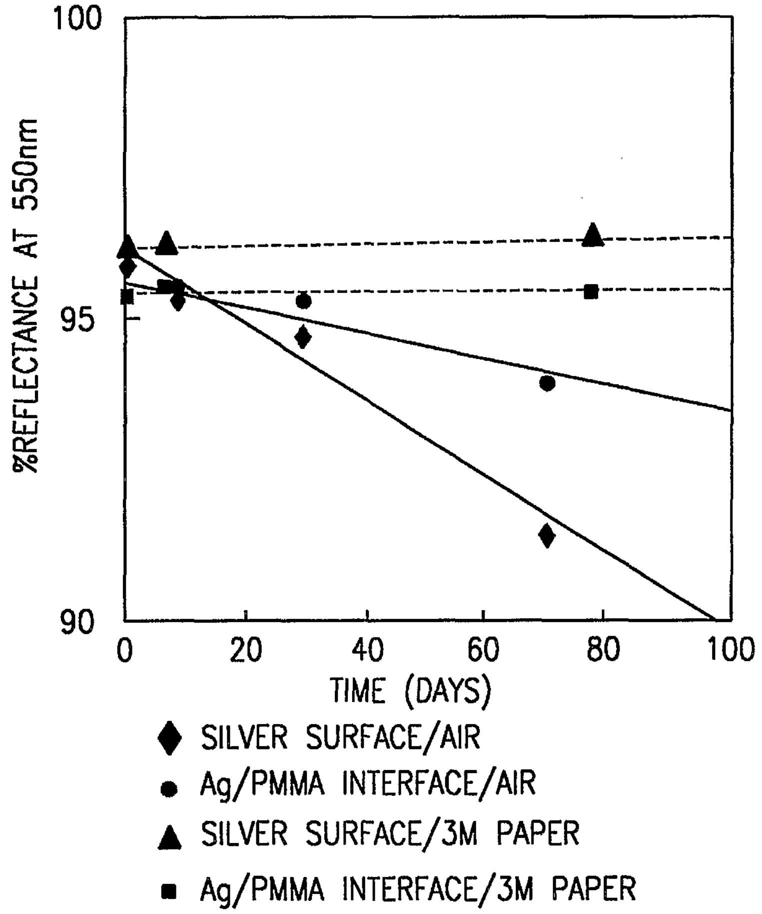

100
95
90
%REFLECTANCE AT 550nm
0
20
40
60
80
100
TIME (DAYS)
♦ SILVER SURFACE/AIR
● Ag/PMMA INTERFACE/AIR
▲ SILVER SURFACE/3M PAPER
■ Ag/PMMA INTERFACE/3M PAPER

FIG. 6

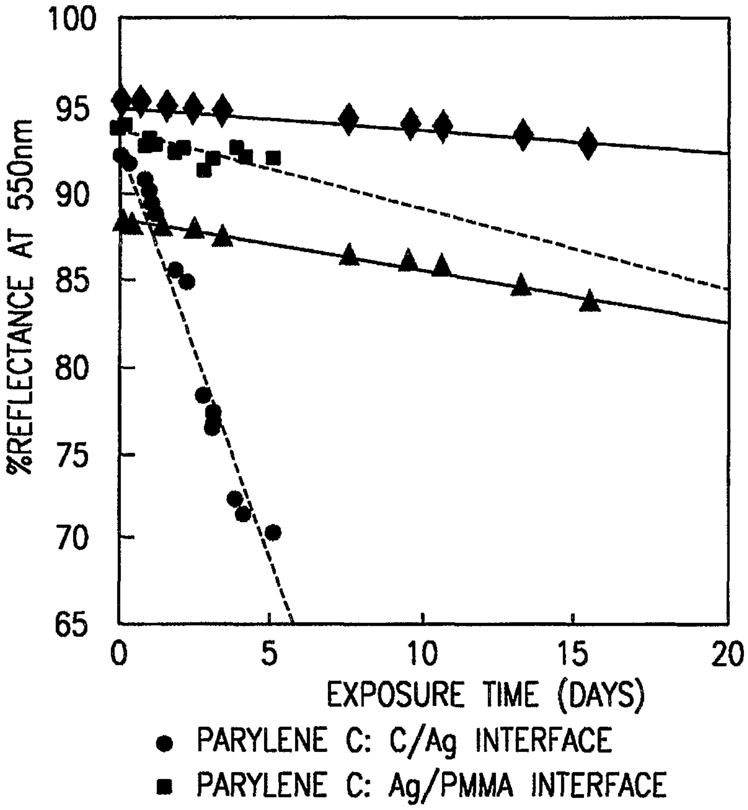

100
95
90
85
80
75
70
65
%REFLECTANCE AT 550nm
0
5
10
15
20
EXPOSURE TIME (DAYS)
● PARYLENE C: C/Ag INTERFACE
■ PARYLENE C: Ag/PMMA INTERFACE
▲ PARYLENE D: D/Ag INTERFACE
♦ PARYLENE D: Ag/PMMA INTERFACE

FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/02559

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :Please See Extra Sheet.
US CL :Please See Extra Sheet.
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)

U.S. : 65/385, 431, 432; 385/100, 101, 123, 126, 128; 428/332, 336, 412, 421, 480, 522

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

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

DERWENT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US 6,261,006 B1 (SELFRIDGE) 17 July 2001.	1-20
A	US 5,253,312 A (PAYNE et al) 12 October 1993.	1-20
Y	FR 2,700,619 A1 (MARI) 22 July 1994, abstract.	1-14, 17-20
Y	EP 412,242 A1 (JOSTAN et al) 13 February 1991, abstract.	1-14, 17-20
A	US 4,762,392 A (YAMAMOTO et al) 09 August 1988.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	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 document 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 30 APRIL 2002	Date of mailing of the international search report 16 MAY 2002
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer RAMSEY ZACHARIA Jean Proctor Paralegal Specialist
Facsimile No. (703) 305-3230	Telephone No. (703) 305-0503

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (7):

B32B 15/08, 15/20, 17/02, 17/10, 27/30, 27/36; G02B 6/02, 6/10, 6/16, 6/18, 6/44

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

65/385, 431, 432; 385/100, 101, 123, 126, 128; 428/332, 336, 412, 421, 480, 522