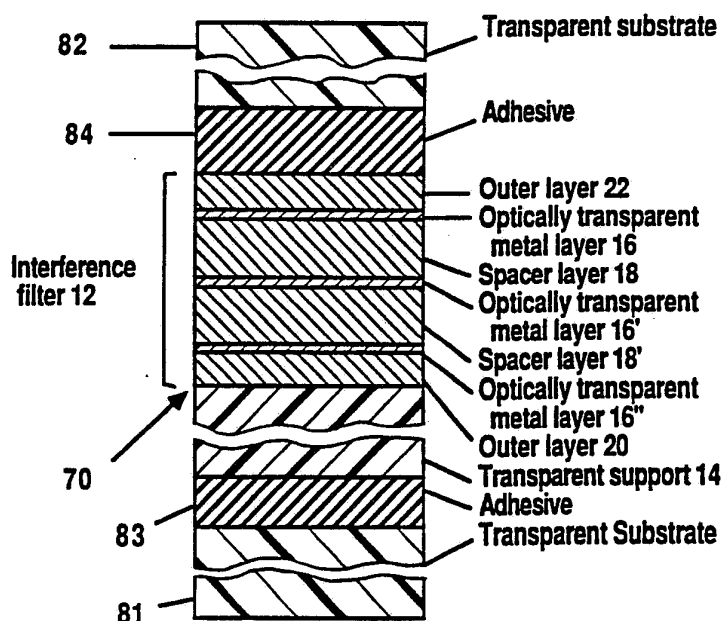




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(21) International Application Number: PCT/US89/00274 (22) International Filing Date: 23 January 1989 (23.01.89) (71) Applicant: SOUTHWALL TECHNOLOGIES, INC. [US/US]; 1029 Corporation Way, Palo Alto, CA 94303 (US). (72) Inventors: MEYER, Stephen, F. ; 1550 Medford Drive, Los Altos, CA 94022 (US). HOOD, Thomas, G. ; 2230 Pacific Avenue, No. 104, San Francisco, CA 94115 (US). (74) Agents: BENZ, William, H. et al.; Irell & Manella, 545 Middlefield Road, Suite 200, Menlo Park, CA 94025 (US).		(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (European patent), DK, FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent). Published <i>With international search report.</i>

(54) Title: MULTILAYER HEAT-REFLECTING COMPOSITE FILMS AND GLAZING PRODUCTS CONTAINING THE SAME

**(57) Abstract**

Visually transparent, preferably color corrected, infra-red reflecting films (80) are disclosed for solar heat control. The films employ Fabry-Perot sandwich interference filters (12) which are characterized by having two or more transparent layers (16, 16', 16'') of sputter-deposited metal such as silver separated by dielectric spacer layers (18, 18') and optionally boundary layers (20, 22). Methods for producing these materials by sputtering techniques as well as glazing materials (81-84) incorporating these films are disclosed, as well. In preferred embodiments, these films are laminated into glazing structures (81-84).

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MULTILAYER HEAT-REFLECTING COMPOSITE FILMS
AND GLAZING PRODUCTS CONTAINING THE SAME

10

Background of the Invention

1. Field of the Invention

15 This invention relates to heat-reflecting films. More particularly, it relates to composite films comprising a series of dielectric and metal layers so as to create an infrared reflecting interference filter and to the use of such films in window glazing materials.

20

2. Description of the Prior Art

In the 1890s, Fabry and Perot developed an interferometer consisting of a pair of parallel-sided, half-silvered mirrors separated by a nonabsorbing layer.
25 This device had the property of preferentially passing energy of certain wavelengths and reflecting energy of other wavelengths. An embodiment of this principle known as the Fabry-Perot sandwich consists of two more or less transparent metal layers separated by a
30 dielectric spacer layer. (See, for example, Knittl, Zdenek, OPTICS OF THIN FILMS, John Wiley & Sons, Ltd., London, 1976, at page 284.) Other filter products known as "induced transmission filters" have been constructed

of metal-dielectric sandwiches for use in window glazing structures. One such structure is described in USP 4,337,990 of Fan (July 6, 1982) as consisting of a transparent substrate, overlayered with a phase matching layer, a single metallic silver layer and an outer antireflection layer, with the three overlayers constituting a transparent heat reflector. While generally effective, products of this general structure suffer from the disadvantage that to achieve high levels of heat reflection they must have relatively thick metal layers such as 15 to 25 nm in thickness which tend to have low transmittances of visible radiation, as well.

Another system which used a Fabry-Perot approach to achieve heat reflection while transmitting visible radiation is shown in USP 3,682,528 of Apfel and Gelber (August 8, 1972). In this system, thinner layers of metal are employed but it is taught that to obtain such layers of an optically suitable metal, in particular silver, it is necessary to first lay down a thin "nucleation" precoat layer of nickel by vacuum deposition and then apply the silver to it, again by vacuum deposition methods. It is further taught that the deposited silver must then receive a thin postcoat layer of vapor-deposited nickel if another layer is to be applied over it. These extra coatings with nickel are time consuming and economically unattractive. This patent also discloses a filter having two silver layers but shows that each silver layer must be accompanied by one or two nickel layers and suggests only durability advantages to this more involved structure. The substrate upon which this multilayer heat-reflecting film was constructed most commonly was glass. In one aspect this invention provides an improved version of

Fabry-Perot-based glazings which need not contain these added protective layers.

It is also recognized that a wavelength selective filter can be achieved with a stack of alternating high/low index of refraction dielectrics. This would work but would require a large number of layers and be prohibitively expensive. This would not have the capability of low emissivity either.

In preferred embodiments, this invention avoids other difficulties found in the application of the Fabry-Perot approach to glazing products. While as a general class these materials perform the task of heat rejection with admirable efficiency, in some settings they present a strong color cast to their reflection when viewed from the incident light direction. This strong color is often objected to by some consumers. It is a preferred object of this invention to correct this failing in heat reflective glazings.

Another desired property of reflective glazing is that the appearance does not change as a function of viewing angle. This absence of angle sensitivity has not been easily achievable with prior materials used in Fabry-Perot configurations.

In studying glazing materials employing these heat-reflecting filters we have discovered a number of configurations for plate glass and anti-lacerative glass which optimize the effectiveness of the filter systems and/or simplify their fabrication. These glass configurations find application in automotive and architectural settings. In some automotive settings, there is a desire to reflect as much heat as possible, but this must be done within the confines of various regulations setting light transmission limits and the

like. For example, in the United States, automotive windshields must have a transmission of visible light of at least 70% at normal incidence. The present invention can serve these needs.

5

Summary of the Invention

It is a general object of this invention to provide an improved glazing materials employing a Fabry-Perot interference filter. In some embodiments, these Fabry-Perot filters are characterized by a simpler construction than materials employed heretofore. In other embodiments which are often preferred, this filter is constructed such that, when laminated into a sandwich structure, it does not substantially alter the color of incident light reflected from its surface and is thus relatively color neutral.

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It is a further general object of this invention to provide an improved transparent Fabry-Perot filter stack which will selectively reflect heat, that is, infrared radiation, while giving high transmission of the visible wavelengths preferably with a color-neutral appearance.

20

It is also an object to provide filter stacks which are designed to take into consideration the optical properties of the substrate (for example, glass or plastic) upon which they are deposited or to which they are laminated, and incorporate these substrates into an overall product having the desired wavelength selectivity, color neutrality and high visible transmission and uniform color reflection.

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It is also an object in certain embodiments of this invention to provide a heat-reflecting,

color-neutral transparent film which is plastic backed and has enhanced durability and scratch resistance.

It is an additional object to provide glazing structures incorporating these heat-reflecting, color-neutral filters and/or transparent films.

It is a further object of this invention to provide glass-filter composites which offer optimal heat-rejection characteristics.

It has now been found that these and other related objects are achieved by employing in such films a Fabry-Perot filter incorporating a plurality and preferably three or more layers of transparent metal separated from one another by spacer layers of dielectric. In preferred embodiments, the spacer layers are sputter-deposited inorganic oxides. In other preferred embodiments, the metal layers are directly contiguous to the spacer layers.

Thus in one aspect this invention involves improved transparent, infrared reflecting composite films including a transparent metal layer-dielectric layer Fabry-Perot interference filter deposited on or adhered to a transparent support, wherein the improvement involves employing as the interference filter a multilayer stack including at least two and preferably three separate discrete continuous sputter-deposited transparent metal layers separated from one another by discrete continuous sputter-deposited layers of dielectric. Preferably, the metal layers and dielectric layers are directly contiguous to one another.

In another aspect this invention involves visually transparent, color-corrected infrared reflecting composite films comprising a transparent

support having adhered to one surface thereof two or more sequential interference filters each of the filters comprising a cavity defined by a continuous spacer layer of dielectric sandwiched between continuous discrete
5 transparent metal layers.

In further aspects this invention involves methods of producing such films by sputter-deposit techniques.

This invention can be embodied in many forms.
10 It can take the form of glass or plastic-supported sheets which may be interposed or laminated within or applied to transparent window glazing materials. It may take the form of a thin metal-dielectric multilayer sandwich film laid down directly onto a glazing material
15 substrate. In such applications the films may contain additional layers such as hardcoats.

Detailed Description of the Invention

Brief Description of the Drawings

In the drawings:

Figs. 1A and 1B are schematic cross-sectional views of two simple heat-reflecting filters of this invention employing two and three transparent layers of
25 metal, respectively;

Fig. 2 is a schematic cross-sectional view of a simple four-metal-layer heat reflector film of this invention;

30 Fig. 3 is a schematic cross-sectional view of a heat reflector film of this invention, such as shown in Fig. 1, having a physical protection layer covering its Fabry-Perot filter;

Fig. 4 is a schematic cross-sectional view of a heat reflector film of this invention, such as shown in Fig. 1, having an optional hardcoat layer on its transparent support and adhered to an additional transparent substrate via its filter layer stack which could serve as window glazing;

Fig. 5 is a schematic cross-sectional view of a filter as shown in Fig. 1 interposed between two rigid substrates such as glass.

Fig. 6 is a schematic cross-sectional view of a product as shown in Fig. 5 additionally including an antilacerative plastic layer for use in windshields and the like.

Fig. 7 is a schematic cross-sectional view of a film such as shown in Fig. 1 adhered to an additional transparent substrate via its support layer. This too could serve as window glazing;

Fig. 8 is a cross-sectional view of a laminated window glazing in which a film of the invention is laminated between two sheets of transparent substrate;

Figs. 9a, b and c are three cross-sectional views illustrating three film materials prepared in the Example;

Fig. 10 is a graph illustrating for comparison purposes the performance of a prior art reflecting film;

Fig. 11 is a graph illustrating the performance of a reflecting film having two transparent metal layers;

Fig. 12 is a graph illustrating the improved performance of a reflecting film of this invention having three transparent metal layers;

Fig. 13 is an expanded-scale graph illustrating the spectral properties (transmittance, reflectance, and absorption) of an excellent laminated product incorporating a reflecting film having three
5 transparent metal layers;

Fig. 14 is a color coordinant chart showing the color properties of filters of this invention using the CIE L*a*b* system; and

Fig. 15 is a cross-sectional view of a
10 flexible film-substrated filter of this invention employed as a suspended film in a double-pane window glazing structure.

Description of Preferred Embodiments

15

Definitions

As used in this specification and the appended claims, the following terms have defined meanings:

"Color neutral" and "color neutrality" are
20 used herein in the normally accepted sense. That is, these terms mean that a laminated product of this invention has a reflectivity which is substantially invariant as a function of wavelength throughout the visible part of the spectrum and preferably independent
25 of the angle of incidence. In preferred embodiments, the laminated product has a neutral transmitted color. This will follow if there is no wavelength-selective absorption.

"Visible radiation" or "light" means
30 electromagnetic radiation having a wavelength of from 380 nanometers to 750 nanometers. (CIE Standard)

"Infrared radiation" or "heat" means electromagnetic radiation having a wavelength above 750 nanometers.

5 "Transparent" means having the property of transmitting visible radiation unless otherwise stated.

"Tvis" or "Tv" or "Transmittance visible" each refer to a measure of transmittance over the visible wavelength. It is an integrated term covering the area under the transmittance vs. wavelength curve throughout the visible wavelengths. (1931 CIE Illuminant C Standard). In automotive windshield glazing, Tvis should be 70% or greater.

10 "Tsol" or "Ts" or "Transmittance solar" each refer to a measure of transmittance over all solar energy wavelengths. (ASTM E 424A) It is an integrated term covering the area under the transmittance vs. wavelength curve for both visible and infrared wavelengths. In heat reflecting films and glazings incorporating them it is a primary goal to decrease Tsol while maintaining Tvis as high as possible.

15 "SC" or "Shading Coefficient" is an accepted term in the field of architecture. It relates the heat gain obtained when an environment is exposed to solar radiation through a given area of opening or glazing to the heat gain obtained through the same area of 1/8 inch single pane clear glass. (ASHRAE Standard Calculation Method) The clear glass is assigned a value of 1.00. An SC value below 1.00 indicates better heat rejection than single pane clear glass. A value above 1.00 would be worse than the baseline clear single pane. A similar term is "Rsol" or "reflectance, solar", which is measure of total reflectance over the solar energy wavelength.

5 "Transparent metal layers" are homogeneous coherent metallic layers composed of silver, gold, platinum, palladium, aluminum, copper or nickel and alloys thereof of a thickness which permits substantial transparency.

"Sputter deposit" or "sputter-deposited" refers to the process or the product of the process in which a layer of material is laid down by the use of a magnetron sputterer.

10 "Dielectrics" are nonmetallic materials which are transparent to both visible and infrared radiation. Generally, these materials are inorganic oxides but other materials such as organic polymers may be included as well.

15 "Contiguous" has its usual meaning of being in actual contact, i.e. of being adjoining. From time to time the somewhat redundant term "directly contiguous" is used for emphasis or clarification and has an identical meaning.

20 A "spacer layer" is a dielectric layer located between and contiguous with two transparent metal layers. In Fig. 1, 18 is a spacer layer.

A "boundary layer" is a layer contiguous with one and not two transparent metal layers. In Fig. 1, 20 and 22 are boundary layers.

Description of Filters

30 The present invention involves heat reflecting filters. A basic embodiment of these filters is shown as film 10 in Fig. 1A and as film 24 in Fig. 1B. Films 10 and 24 include a multilayer interference filter 12 directly adhered to a transparent support 14. Filter 12 operates according to the Fabry-Perot principle and

includes two or three transparent metal layers 16, 16' and 16" separated by spacer layers 18 and 18' and bonded by two outer or boundary layers 20 and 22. Thus, it presents one or two cavities between metal layers. Fig. 2 shows a three-cavity film 25.

In preferred embodiments of this filter, the transparent metal layers are sputter-deposited. In addition, the spacer and boundary layers can be directly contiguous with the transparent metal layers. No nucleation layers are required when the transparent metal layers are sputter deposited. Nucleation layers may be present if desired, however.

As will be seen with reference to Figs. 1A, 1B and 2, two, three or more than three transparent metal layers such as 16, 16', 16" and 16"', each separated from one another by a spacer layer such as 18, 18' and 18" can be employed. In theory, there is no limit to the number of transparent metal layers that can be used in these sandwich filters. In practice, however three to five transparent metal layers are preferred, with three transparent metal layers being more preferred.

The thickness of the various layers in the filter should be controlled to achieve an optimum balance between desired infra-red reflectance and desired visible radiation transmittance. The ideal thicknesses can also depend upon the nature of the transparent metal and dielectric employed.

Each of the transparent metal layers 16, 16' and 16" is from about 4 to about 40 nanometers (nm) in thickness, with the total thickness of metal generally being from about 12 to about 80 nm. With silver and silver alloyed with up to about 25% w of gold, which constitute preferred transparent metals, excellent

results are obtained with three or four layers of metal, each from 4 to 17 nm in thickness especially from about 5 to about 13 nm.

5 In Figs. 1A and 1B, the transparent metal layers are depicted as of equal thickness. This is not a requirement of the present invention. Best results have been achieved with three-layer systems when the middle of the three metal layers is about 5% to 15%, especially about 10% thicker than each of the outer
10 layers.

The metal layers can be deposited by vapor deposition methods, electron-beam deposition, and the like. Magnetron sputtering is the preferred deposition method, but any methods which can deposit 10 nm layers
15 with 2-3% accuracy in theory can be used.

The spacer layers, e.g., 18 and 18', between the transparent metal layers, e.g., 16, 16' and 16", can be the same or different and are each between about 30 and about 200 nm in thickness. The preferred
20 thicknesses selected within this range will depend upon the index of refraction of the dielectric employed. Index of refraction values can be from about 1.4 to 2.7. In a general relationship, thicker layers are called for with low index material while thinner layers are used
25 with higher index material. Spacer layers are preferably from about 50 to about 110 nm and especially from about 70 to about 100 nm in thickness for dielectrics having an index of refraction of from about 1.75 to about 2.25. Materials having an index of
30 refraction within this range include the inorganic dielectrics such as metallic and semimetallic oxides, for example zinc oxide, indium oxide, tin oxide, titanium dioxide, silicon oxide, silicon dioxide,

bismuth oxide, chromium oxide, as well as other inorganic metal compounds and salts, for example zinc sulfide and magnesium fluoride and mixtures thereof. Of these materials, preference is given to zinc oxide, indium oxide, tin oxide and mixtures thereof and titanium dioxide.

With materials having indices of refraction in the 1.4 to 1.75 range, spacer thicknesses are somewhat thicker. Suitable thicknesses in this embodiment are from about 75 to about 200 nm with thicknesses from about 100 to about 175 nm being preferred. Materials having these indices of refraction include hydrocarbon and oxyhydrocarbon organic polymers (1.55-1.65 index of refraction) and fluorocarbon polymers (1.35-1.45 index of refraction).

With materials having indices of refraction in the 2.25 to 2.75 range, spacer thicknesses are somewhat thinner. Suitable thicknesses in this embodiment are from about 30 to about 90 nm with thicknesses from about 30 to about 80 nm being preferred. Materials having these indices of refraction include lead oxide, aluminum fluoride, bismuth oxide and zinc sulfide.

Other typical inorganic dielectrics and their indexes of refraction are listed in sources such as Musikant, Optical Materials, Marcel Dekker, New York, 1985, pp. 17-96, and may be used.

As will be described below, the inorganic metallic and semimetallic oxide dielectrics can be conveniently and preferably deposited by reactive sputtering techniques, although, if desired, chemical vapor deposit and other physical vapor deposition methods can be employed to apply the dielectric layers.

Filters 12, 24 and 25 in Figs. 1A, 1B and 2 are depicted with two boundary layers 20 and 22. These layers provide physical protection to the metal layers beneath them and also serve to reduce visual reflections off of the metal surface to which they are contiguous. It is preferred to have a symmetric sandwich with boundary layers on both outside surfaces. This will give rise to a series of two or more sequential Fabry-Perot interference filters each of the filters comprising a continuous discrete sputter-deposited solar transparent metal layer directly sandwiched between continuous layers of dielectric.

However, if desired, one or both of the boundary layers can be omitted. The boundary layers can be the same or different dielectric and can be identical to or different than the dielectric making up the spacers. The same preferences for materials recited for the spacer apply to the boundary layers and, for simplicity, it is preferred if the boundary layers and the spacer layers are all made of the same materials and if they are all sputter-deposited.

The thicknesses of the boundary layers range from about 20 nm to about 150 nm. Boundary layers are preferably from about 25 to about 90 nm and especially from about 30 to about 70 nm in thickness for dielectrics having an index of refraction of from about 1.75 to about 2.25. With materials having indices of refraction in the 1.4 to 1.75 range, preferred thicknesses are from about 30 to about 140 nm and especially from about 45 to about 100 nm. If, as shown in Fig. 2, three or more transparent metal layers are employed, the boundary layers will remain substantially unchanged.

To sum up the geometry of the presently preferred filters, they have 7 layers arranged in a stack as follows:

5 Boundary dielectric
 Metal layer I
 Spacer layer I
 Metal layer II
 Spacer layer II
 Metal layer III
10 Boundary dielectric

 In this preferred configuration the three metal layers are preferably silver and total from 25 to 35 nm in thickness with metal layer II being 110% $\pm$ 5% of the metal layers I or III. The boundary layers and
15 spacer layers are preferably indium oxide with boundary layer thicknesses of from 30 to 40 nm and spacer thicknesses of from 60 to 80 nm.

 In a five-layer film, metal layer II and spacer II might be omitted.

20

Supporting the Filter

 In each of Figs. 1 through 6, the Fabry-Perot type filter is shown directly adhered to a transparent support 14. This support is shown in section because it
25 is many times as thick as the filter. This thick support is essential to the practice of this invention. The filter itself is at most only a few hundred nanometers thick and thus can have only minimal physical strength without the added support. Support 14 can be
30 selected from among the rigid and nonrigid but minimally stretchable transparent solids which can withstand the conditions of sputter deposition. Glass, both float or plate glass and laminated glass and especially low iron

float glass, and rigid plastics, such as poly(carbonate) and poly(acrylate) in thicknesses from about 50 mils to about 5 cm or more are representative examples of rigid supports. Poly(ester)s including poly(ethylene terphthalate) and other terphthalate ester polymers, poly(urethanes), cellulose ester polymers, acrylic polymers, and poly(vinyl fluoride)s from about 1 or 2 mils to about 50 mils in thickness are representative examples of nonrigid, minimally stretchable films which may be employed. Poly(esters) and in particular poly(ethylene terphthalates) such as the DuPont "Mylars" are a preferred group of film supports.

The filter 12 is directly adhered to the support 14. This can be carried out by sequentially applying the various layers of the filter directly to the support. If the layers are applied by sputter deposition, this can involve first sputter depositing a boundary layer, then a transparent metal layer, a spacer layer, etc.

The macroscale transparent layers, be they a plastic or glass transparent support or an additional component (such as a glass layer laminated to a plastic supported film), do contribute to the performance and visual optics of the final product as will be shown in the examples.

Optical Properties

In some settings, the desired optical properties include maximum rejection (reflection) of heat (infrared wavelengths) with only less attention being paid to the amount of visible light transmitted or reflected. In other applications specific degrees of visible light transmittance must be attained to meet

government regulations, for example, in auto windshields the T_{vis} must be 70% or greater. Fig. 13 illustrates an excellent reflectance curve for such a product. In this product, reflectance is substantially constant at about 10% (i.e., the reflectance curves is substantially flat throughout the wavelengths between 350 nm and 700 nm. This means that the reflectance off of this product would be neutral in color without the strong tint that can be found objectionable. In this product, the reflectance increases substantially at the wavelengths outside the visible range to achieve good thermal rejection.

As previously noted, the present invention permits one to control the color of reflectance off of the filter. In many cases the property is used to attain color neutrality. With colored light this means a colored reflection or with white light a neutral reflection. This feature can be quantitated by the CIE $L^*a^*b^*$ 1976 color coordinate system, in particular the ASTM 308-85 method.

Using the $L^*a^*b^*$ system the property is shown by values for a^* and b^* near 0 for example a^* from -4 to +1 and b^* from -2 to +2 when using an Illuminant A light source. Fig. 14 is a $L^*a^*b^*$ color coordinant chart which shows the desired color coordinates and defines the desired color space.

This neutral color can also be illustrated by the shape of the absorbance/reflectance vs. wavelength curve. As shown in Fig. 13, products of this invention can achieve excellent constant low reflectances throughout the visible spectrum. One can judge the quality of a product's color neutrality by the flatness

of the reflectance curve over the visible spectrum as shown in that figure.

In general, it will be observed that when the multimetal layer films of this invention are laminated to or between glass and/or plastic layers the overall optical properties are different than the properties observed with the unlaminated films. One achieves optical properties approaching the optimum in ways not easily achieved by less complicated filter stacks. In particular, one can achieve laminated filter products having high T_{vis}/T_{sol} selectivity, neutral color, excellent heat rejection, high T_{vis} , high R_{sol} and an emissivity of less than 0.1.

Incorporation into Glazing Structures

As may be seen by referring to Figs. 3 through 9, the multi-metal layer films of this invention may, if desired, contain a number of optional layers and may be incorporated into a great variety of glazing structures for architectural and transportation system uses. In Fig. 3 a film 30 is shown containing an optional protection layer 32 over filter 12. This layer 32 can typically be a hardcoat, such as a silicon-containing coating which is applied as a liquid and thereafter cured with heat and/or plasma or corona discharge to yield a hard scratch-resistant overcoating. Typical hardcoats are the cured products resulting from heat or plasma treatment of a.) a hydrolysis and condensation product of methyltriethoxysilane; b.) mixtures of poly(silicic acid) and copolymers of fluorinated monomers with compounds containing primary and secondary alcohol groups as described in U.S. Patent Nos. 3,429,845 and 3,429,845, respectively. Other hardcoat

layers are described in U.S. Pat. Nos. 3,390,203; 3,514,425; and 3,546,318. These hardcoat layers have thicknesses in the range of a few to a few hundred microns.

5 In Fig. 4, a preferred configuration 40 for employing the films of this invention is depicted. In this embodiment, the filter 12 is deposited on a support 14 as already described. When the support 14 is a flexible plastic it can carry a previously applied
10 hardcoat 42 for scratch resistance. The filter side of the film is then adhered to a transparent substrate 46 such as another film of flexible plastic or a layer of glass or rigid plastic, or the like using an optically acceptable adhesive 44 such as poly(vinyl butyral),
15 ionomer resin, poly(urethane) resin, or polyvinyl chloride resin. Although not wishing to be limited to a particular adhesive, preference is given to the commonly used glass adhesive, poly(vinyl butyral).

The configuration shown in Fig. 4 is of
20 special interest in areas where the film comprises a filter 12 supported on plastic sheet 14 and this is applied to a surface such as the inside surface of a sheet of glass or other rigid material. This can be used as architectural glass, as automotive windshields
25 (when the glass is a suitable tempered or laminated safety glass), automotive side or rear window glass (again with proper tempering, etc), as aircraft canopies, and the like. In these applications, the substrate 46 is the "outside" surface and support 14
30 can, if desired, be selected to provide antilacerative properties to the resulting final product, as is disclosed in U.S. Pat. No. 3,900,673 which is incorporated herein by reference both for its teachings of antilacer-

ative coatings and for its teachings of the fabrication of safety glass structures.

5 Fig. 5 shows a variation 50 of the product of Fig. 1. Embodiment 50 includes a filter 12 deposited on support 14 as previously described and this combination is attached via adhesive 51 to additional transparent layer 52. If layers 14 and 52 are both glass a very durable product results.

10 Fig. 6 depicts a variation 60 of the product of Fig. 5 in which layers 14 and 52 are both glass. Embodiment 60 includes an antilacerative coating 62 adhered to the inside surface of support 14 with adhesive layer 61.

15 Turning to Fig. 7, another embodiment 70 of the invention is depicted in which the film is adhered to a transparent substrate 72 with an adhesive 71, this time through the transparent support 14. This embodiment has the disadvantage that the filter 12 is potentially physically accessible so that it can be physically damaged if great care is not taken. This can
20 of course be corrected by placing this surface in the interior of a double pane glass unit, or by providing other suitable protection.

25 Fig. 8 shows yet another embodiment 80. This embodiment 80 includes filter 12 deposited on transparent support (e.g., plastic film) 14. The filter and support are then laminated between two transparent substrates 81 and 82 using adhesive layers 83 and 84, respectively. This configuration has the advantage,
30 when 81 and 82 are glass, of presenting two glass surfaces.

The film products of the invention can also be used in nonlaminated structures, as shown in Fig. 15.

-21-

In the figure, window unit 90 contains a sheet of film 10 stretched under tension between glass panes 65 and 64. 66 and 66' are air voids and 68 and 68' are spacer plugs for holding the film in proper position and properly under tension. This general window structure in which the present filters may be used and the materials and methods of its manufacture are shown in U.S. Patent No. 4,335,166.

An unexpected advantage of the films of the present invention which employ multiple transparent metal layers is their superior efficiency when laminated to a transparent substrate in the configurations shown in Figs. 4, 5, 6, 7 or 8.

In these configurations, the multiple transparent metal layer filters of this invention offer special advantages and efficiencies. When a transparent support-backed single metal layer sandwich filter (i.e. an induced transmission filter) is laminated directly to a second sheet of transparent substrate to give a support-filter-substrate configuration, the filter undergoes a pronounced drop in efficiency. Fig. 9 illustrates that for a single metal layer filter this drop in efficiency is quite pronounced.

Fig. 10 depicts the transmission and reflectance of visible and infra-red wavelengths by a one metal layer filter with and without lamination to a second transparent layer. In the case shown, this second layer is a second layer of plastic support. By difference, the energy absorbed by this filter with and without lamination is shown as well. Line T is the transmittance curve for the un laminated film. T_L is the transmittance curve for the laminated film. R and R_L are the reflectance curves. A and A_L are the absorption curves

before and after lamination respectively. This filter has a 4 mil poly(ethylene terphthalate) (PET) backing having a directly deposited 46 nm thick indium oxide dielectric boundary layer; an 11.8 nm thick layer of sputter-deposited silver topped with another 46 nm thick indium oxide boundary layer. The layer to which this film is laminated is a second sheet of the PET.

As can be seen, the lamination causes transmittance in the visible region to drop markedly while substantially increasing transmittance of energy in the infra-red region. The T_{vis} value for the filter drops from 82% to 70% when it is laminated. As the same time T_{sol} only drops from 62% to 55%. This illustrates that the filter is not preferentially passing visible wavelengths with the efficiency it did before lamination. This film when laminated provides a Shading Coefficient of 0.67. This is little better than conventional green-tinted glass.

Turning to Fig. 11, comparable curves are presented for a filter of the invention having two metal layers. This filter uses the same materials and the same lamination layer used in the filter characterized in Fig. 8. The filter layers are 35nm of dielectric, 10.7 nm of silver, 75nm of dielectric, 10.7 nm of silver and 40 nm of dielectric. The curves are identified as in Fig. 10. One advantage is clear from the curves. In the infra-red region, this filter is much more efficient and does not change appreciably when laminated. When T_{vis} and T_{sol} and SC values are determined it is seen that the drop in T_{vis} is much less pronounced and in fact, relatively less or the same than the drop in T_{sol} . (T_{vis} went from 76% to 70%; T_{sol} went from 45% to 40%.)

The SC value for the laminated material is a superior 0.53.

In Fig. 12 the same data are presented for a filter of this invention having three sputter-deposited transparent metal layers. This filter uses the same materials used in the filters characterized in Figs. 10 and 9 in a 35 nm dielectric / 7 nm silver / 65 nm dielectric / 10 nm silver / 70 nm dielectric / 9 nm silver / 35 nm dielectric structure. With this filter, the drop in T_{vis} is relatively less than the drop in T_{sol} so that the efficiency of the filter was substantially unchanged by lamination. (T_{vis} went from 74% to 70% and T_{sol} went from 42% to 38%.) Fig. 13 is an expanded-scale plot of the spectral properties of a 7-layer (3-metal-layer) filter of this configuration repeated with greater precision and confirming the excellent spectral properties which are obtained.

Methods of Preparation

The films of this invention are prepared by laying down a series of uniform continuous layers of metal and dielectric in sequence on a support. These layers can be deposited by physical vapor deposition methods such as thermal evaporation, molecular beam epitaxy, ion-assisted vapor deposition, sputtering and the like; and chemical vapor deposition and plasma assisted vapor deposition methods. The metal layers are preferably laid down using magnetron sputtering. This technique can also be used to lay down the dielectric layers if they are of the inorganic oxide type which is preferred. Importantly, this technique can achieve the desired direct contiguous deposit of the various layers

upon one another and upon the support layer without resort to nucleation layers and the like.

5 This technique and apparatus suitable for carrying out the production of the present materials are both described in detail in U.S. Patent No. 4,204,942 of Charroudi (May 27,1980).

10 Chemical coating or vapor deposition can be used to deposit the dielectric materials. If these methods are used, conventional techniques of thermal evaporation, electron beam evaporation and chemical vapor deposition and the like known to those of skill in the art will be employed.

Examples

15

Seven multilayer filter stacks were prepared on plastic substrates. For purposes of the example they were denominated samples A-G. These materials were then adhered to glass layers or laminated between glass
20 layers. In some cases the final products were designed to have anti-lacerative properties.

Design Materials

25

Substrate

30 Substrate poly(ethylene terphthalate) (ICI 393, 4 mil) with a clear polysiloxane hardcoat was used for the anti-lacerative coatings, coated on the non-hardcoat side. Four mils was used to achieve anti-lacerative properties. ICI 393 was selected because it maximized the adhesion of hardcoat. Encapsulated coatings were made on a different (no hardcoat) 4 mil polyester (American Hoechst 4600).

Encapsulated anti-lacerative samples were made by laminating an uncoated piece of ICI 393 onto an encapsulated sample.

5 Glass

3 mm clear float glass was used for all laminations. In several later repeats, low iron glass laminations were prepared which showed several percentage points improvement in R_{sol} .

10

Adhesive

15 mil and 30 mil Monsanto PVB were used for all sputtered film laminations for which data are presented. 15 mil and 30 mil DuPont PVB was examined and found to be optically similar. The transmission spectra of laminations without sputtered coatings was measured to determine the variability of absorption with lamination temperature. Laminations were made at 280°F and 300°F.

20

Sputtered Coating

Indium oxide and silver were used as dielectric and metal respectively. The coatings were laid down in a magnetic sputtering apparatus.

25

The thickness of the filter layers in samples A-G was as shown in Table 1.

30

Table 1

Layer, thickness, nm

<u>Sample</u>		<u>Layer</u>						
		D ₁	M ₁	D ₂	M ₂	D ₃	M ₃	D ₄
5	A	35	10	70	11	70	10	35
	B	33	10	67	11	67	10	33
	C	31	10	63	11	63	10	31
(all prepared with hardcoated substrate)								
10	D	35	10	70	11	70	10	35
	E	33	10	66	11	66	10	33
	F	31	10	62	11	62	10	31
	G	29	10	58	11	58	10	29
(all prepared without hardcoat on substrate)								
15	D ₁ = dielectric 1 M ₁ = metal 1, etc.							

20 These seven filter stacks were then incorporated into glazing structures as shown in Fig. 9. A, B and C were laminated into structures as shown in Fig. 9B. D, E, F and G were made up into 9A and 9C type structures.

25 In addition to these samples, three comparative samples of three composite laminates were provided. One was a glass / 30 ml PVB / glass composite that had no sputtered filter coating and was intended to simulate current laminated windshields. The second was a anti-lacerative version like 9B, different only in
 30 having no sputtered film. The third was a sample of "Easy-Eye" brand, absorbing glass made up into a glass/PVB/glass geometry. These samples were also measured.

Visible transmission and reflection values were measured on a Spectrogard using Illuminant "A" for the A-G materials with and without lamination and for the three comparative materials.

5

Observations

The results of the color measurements are given in Table 2. These results show that Tvis values of greater than 70% can be achieved with color neutrality using the present invention.

10

15

20

25

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Table 2

	Sample	Tvis, %	Rsol, %	Color Properties of Reflected Light		
				L	a*	b*
5	A*	72.6	36.7	33.25	5.47	6.72
	B*	71.5	35.4	34.59	6.86	7.29
	C*	70.3	37.0	33.6	6.45	5.44
10	A	73.8	24.1	33.04	0.55	1.16
	B	71.8	23.3	33.15	-1.19	1.87
	C	72.8	23.5	33.27	-1.11	1.65
15	D*	76.5		33.82	8.44	-6.9
	E*	75.9		34.68	8.27	-5.11
	F*	75.6		36.6	6.96	1.56
	G*	74.9	37.6	36.84	6.19	0.12
20	D	73.0	29.3	34.61	-3.28	1.42
	E	71.5	29.8	34.57	-3.26	1.0
	F	71.9	29.9	33.34	-3.11	1.1
	G	71.9	32.1	34.36	+4.81	1.12
25	Encap- sulated	84.0	7.1	33.46	- .82	-0.36
	Antila- cerative	83.7	8.5	34.76	-2.05	-3.08
	Easy Eye	75.4	6.0	31.98	-2.62	-1.05

*Before lamination

30

These results also showed that the lamination of the films of this invention into composites gave improved color performance. Materials which were not acceptable from a color point of view before lamination

were acceptable thereafter. The color properties are also shown in color charts such as Fig. 14.

Fig. 14 shows an L*a*b* color coordinate system and shows the general colors it represents together with the a* and b* values for materials of this invention before and after lamination as taken from Table 1. As can be seen, the color properties became more neutral (that is, move closer to the 0,0 point of the coordinate system) with lamination.

Additionally, when the reflection off of materials of this invention was inspected at a variety of angles, the materials were observed to have minimal angle sensitivity. That is, the color of the reflection did not change with the angle.

Although this invention has been described with reference to certain preferred embodiments, these are not to be construed as limitations upon the invention's scope which is as defined by the following claims:

What is claimed is:

1. In a transparent, infrared reflecting
composit film including a transparent metal
5 layer-dielectric layer filter adhered to one side of a
transparent support, the improvement comprising
employing as the transparent metal layer-dielectric
layer filter a visible light-transmitting
infrared-reflecting Fabry-Perot interference filter
10 which includes at least two separate discrete continuous
sputter-deposited transparent metal layers separated
from one another by a discrete continuous spacer layer
of sputter-deposited inorganic metal oxide, compound or
salt dielectric wherein each transparent metal layer is
15 continguous with and directly adherent to the adjacent
spacer layer of dielectric without an intervening
nucleation layer.

2. The improved composite film of claim 1
20 wherein the dielectric is sputter deposited.

3. The improved composite film of claim 1
wherein the support is plastic.

25 4. The improved composite film of claim 3
additionally comprising a protective layer adhered to
the side of the support which does not have the
transparent metal layer-dielectric layer filter adhered
thereto.

30

5. A transparent, infrared reflecting
composite film comprising a transparent support having
adhered to one surface thereof the first layer of a

five-layer interference filter, each of the five layers comprising a continuous discrete sputter-deposited layer directly contiguous with its adjacent layers, the first, third and fifth layers being dielectric layers and the
5 second and fourth layers being transparent metal layers.

6. A visually transparent, infrared reflecting composite film comprising a transparent support having adhered to one surface thereof an
10 interference filter comprising two or more continuous discrete sputter-deposited transparent metal layers each of which is directly sandwiched between continuous layers of dielectric.

15 7. A visually transparent, infrared reflecting composite film comprising a transparent support having adhered to one surface thereof an interference filter having a plurality of continuous directly continuous stacked layers, said layers
20 comprising:
a. a dielectric layer,
b. a discrete sputter-deposited transparent metal layer,
c. one or more pairs of layers, each pair
25 comprising
a dielectric spacer layer and
a discrete sputter-deposited transparent metal layer, and
d. a dielectric outer layer.

30 8. The composite film of claim 7 wherein the metal layers each are from 4 to 40 nm in thickness and the dielectric layers each are from 40 to 200 nm in

thickness and the metal layers each comprise metal selected from the group consisting of silver, gold, platinum, palladium, aluminum, copper and nickel and alloys thereof.

5

9. The composite film of claim 8 wherein the metal layers each comprise silver and each are from 4 to 17 nm in thickness and the dielectric layers each have an index of refraction of from about 1.75 to about 2.25 with the spacer layers having a thickness of from 70 to 100 nm and outer layers having a thickness of from about 30 nm to about 70 nm.

10

10. A process for preparing a transparent, infrared reflecting composite film including a transparent metal layer-dielectric layer Fabry-Perot interference filter adhered to a transparent support, comprising the steps of

15

a. directly sputter-depositing upon the transparent support a discrete continuous first outer layer of dielectric,

20

b. directly sputter-depositing upon the first layer a discrete continuous first transparent metal layer,

25

c. directly sputter-depositing upon the first transparent metal layer a discrete continuous spacer layer of dielectric,

d. directly sputter-depositing upon the spacer layer a second discrete continuous transparent metal layer, and

30

e. directly sputter-depositing upon the second metal layer a second layer of dielectric.

11. The process of claim 10 comprising the additional steps of repeating steps c and d thereby forming a filter having three discrete metal layers.

5 12. In a transparent, infrared reflecting composite film including a transparent metal layer-dielectric layer filter adhered to a transparent support, the improvement comprising employing as the filter a Fabry-Perot interference filter made up of a
10 multilayer stack including at least three separate discrete continuous transparent metal layers separated from one another by discrete continuous layers of dielectric.

15 13. The improved composite film of claim 12 wherein the multilayer stack additionally comprises a separate and discrete continuous boundary layer of dielectric.

20 14. The improved composite film of claim 12 wherein the multilayer stack additionally comprises two separate and discrete continuous boundary layers of dielectric.

25 15. The improved composite film of claim 12 wherein in the multilayer stack, the transparent metal layers are contiguous with and directly adherent to the dielectric layers without intervening nucleation layers.

30 16. The improved composite film of claim 12 wherein the metal and dielectric layers are sputter-deposited.

17. The improved composite film of claim 16 wherein the support is plastic.

5 18. The improved composite film of claim 12 additionally comprising a hard coat layer adhered to the side of the support which does not have the filter adhered thereto.

10 19. A transparent, infrared reflecting composite film comprising a transparent support having adhered to one surface thereof the first layer of a seven layer interference filter each of the seven layers comprising a continuous discrete sputter-deposited layer directly contiguous with its adjacent layers, the first,
15 third, fifth and seventh layers being dielectric layers and the second, fourth and sixth layers being transparent metal layers.

20 20. A glazing material comprising a transparent structural sheet member having two sides and a surrounding edge, said sheet member having adhered to one of its sides a color-corrected infrared-reflecting composite, said composite itself comprising three or more separate discrete continuous transparent metal
25 layers bounded by and separated from one another by discrete continuous transparent dielectric layers.

30 21. The glazing material of claim 20 wherein the metal layers each comprise silver and each are from 4 to 17 nm in thickness and the dielectric layers each have an index of refraction of from about 1.75 to about 2.25 with spacer layers having a thickness of from 70 to

100 nm and boundary layers having a thickness of from about 30 nm to about 70 nm.

22. A window glazing material product
5 comprising the glazing material of claim 21 wherein the sheet member is plastic sheet, wherein the composite is directly adhered to the surface of the plastic and wherein the glazing material is adhered to a transparent substrate comprising glass.

10

23. A window glazing product comprising the glazing material of claim 20 wherein the sheet member is plastic sheet, wherein the composite is adhered to the surface of the plastic and wherein the glazing material
15 is laminated between two parallel sheets of plastic or glass.

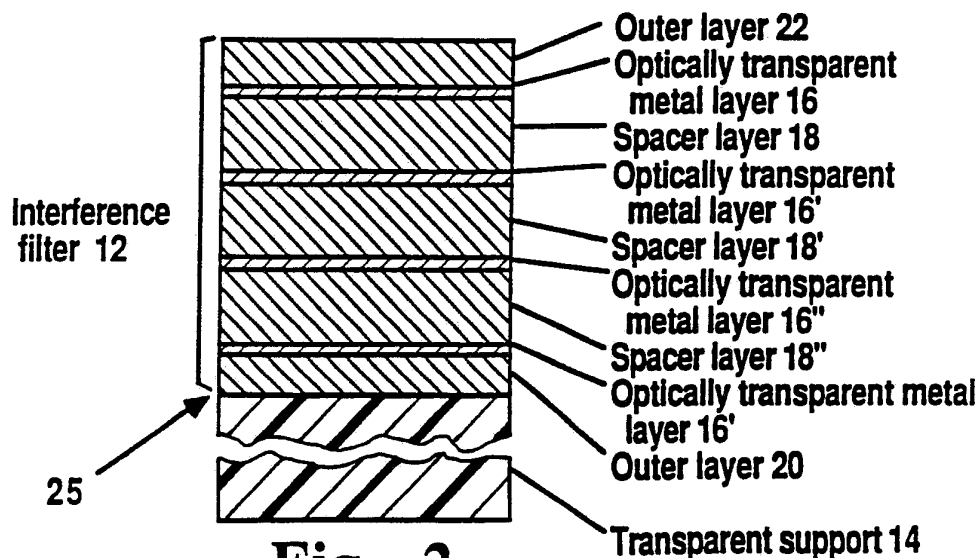
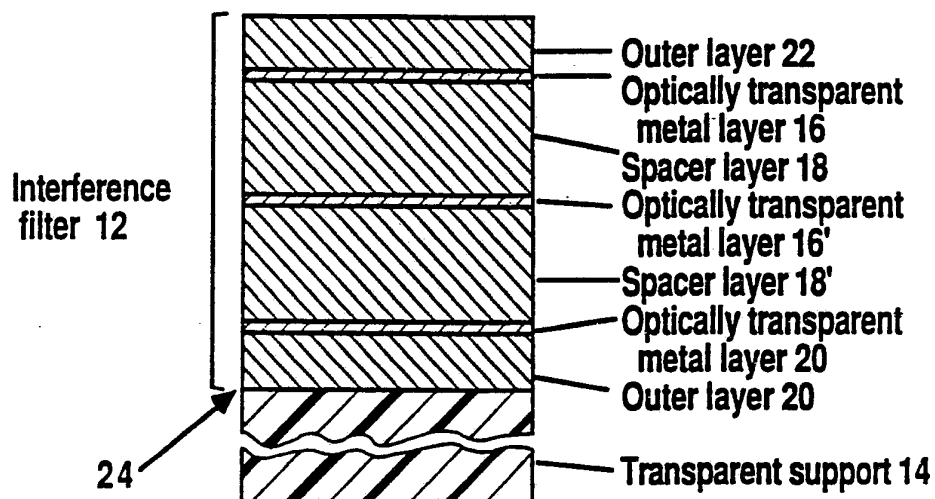
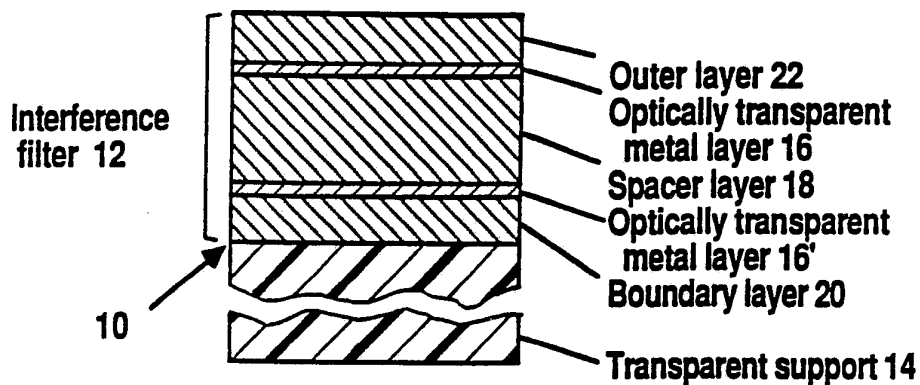
24. The window glazing product of claim 23 wherein the parallel sheets are low iron glass.

20

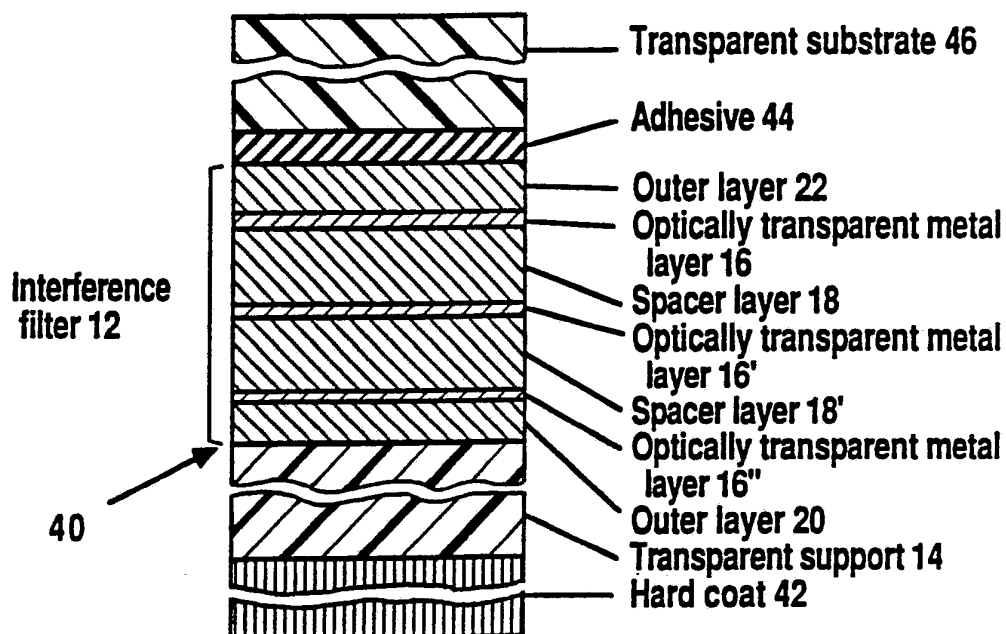
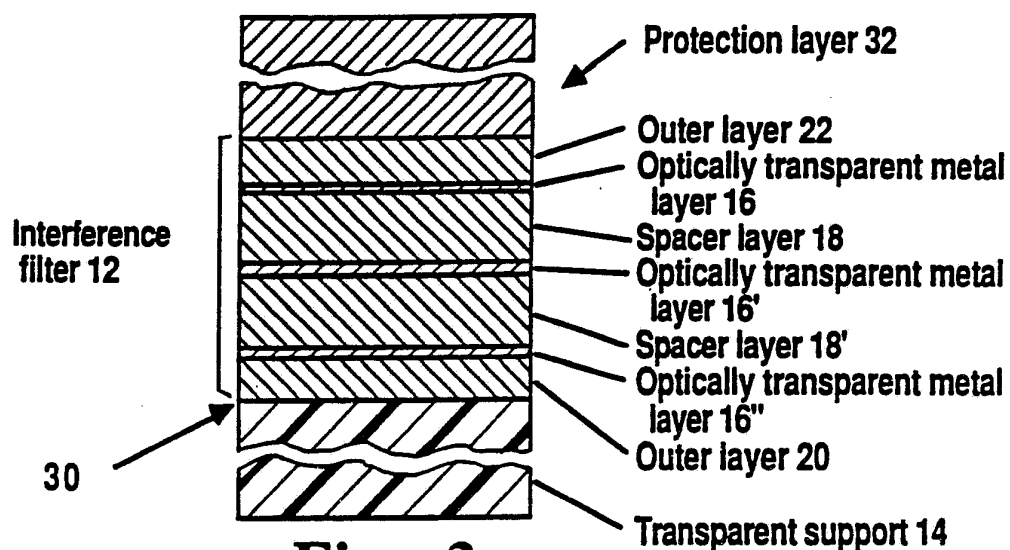
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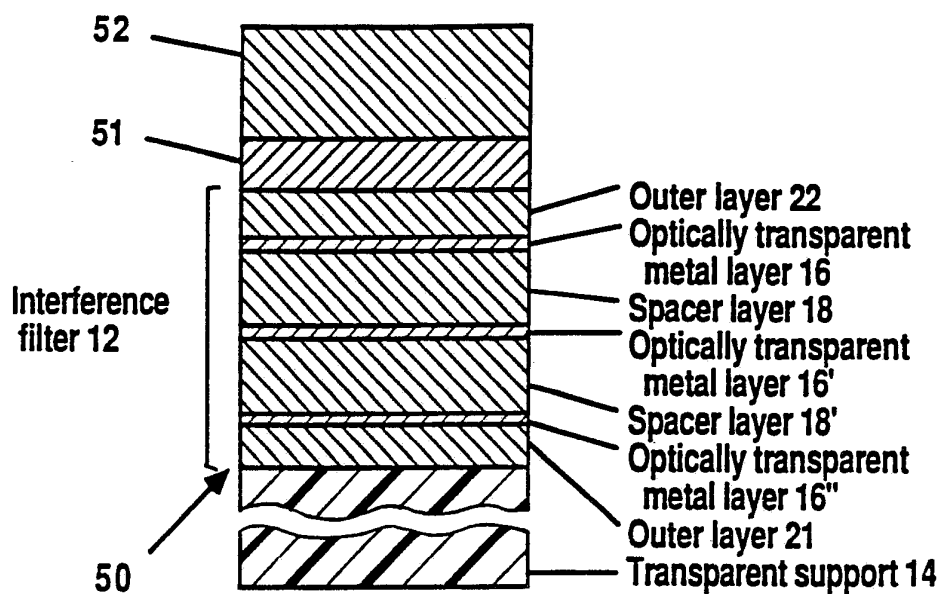
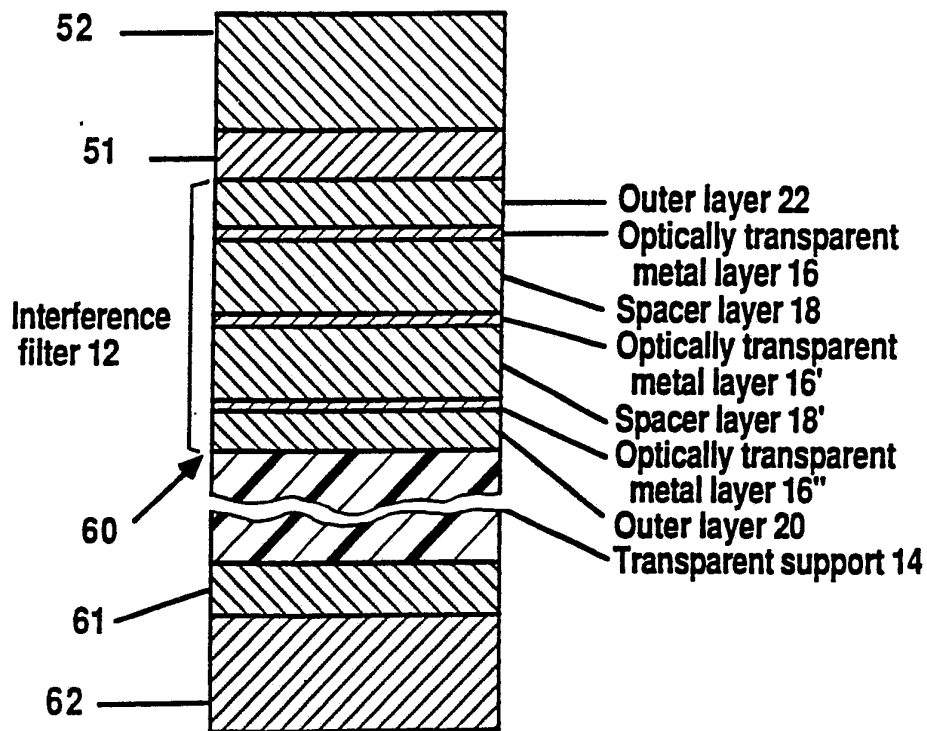


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**Fig. 5****Fig. 6****SUBSTITUTE SHEET**

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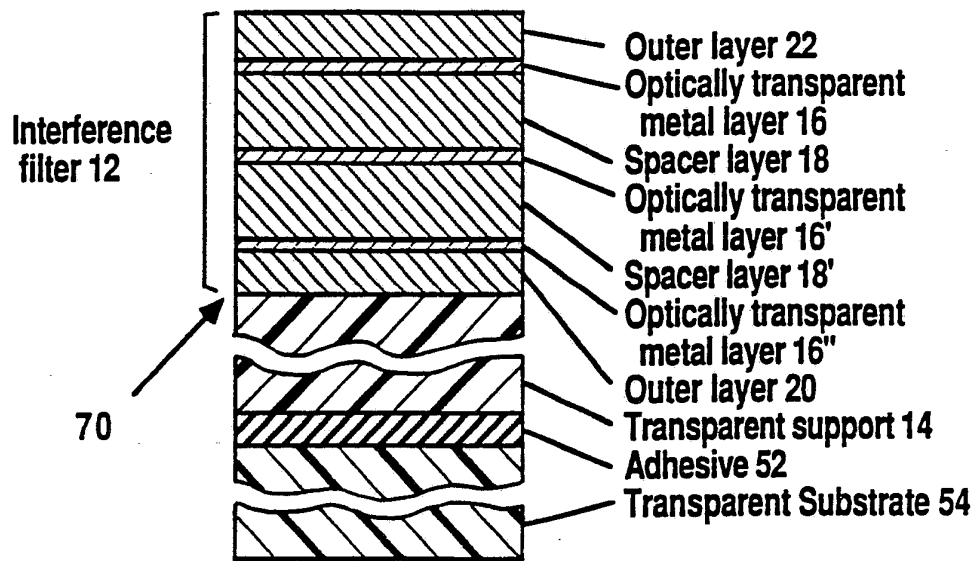


Fig. 7

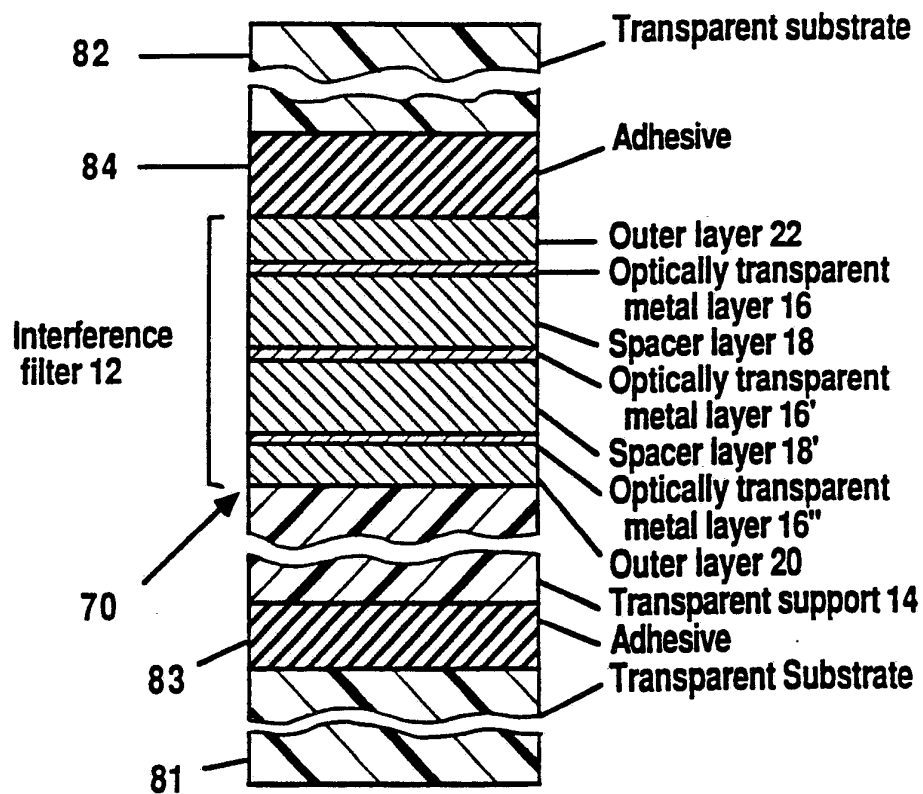
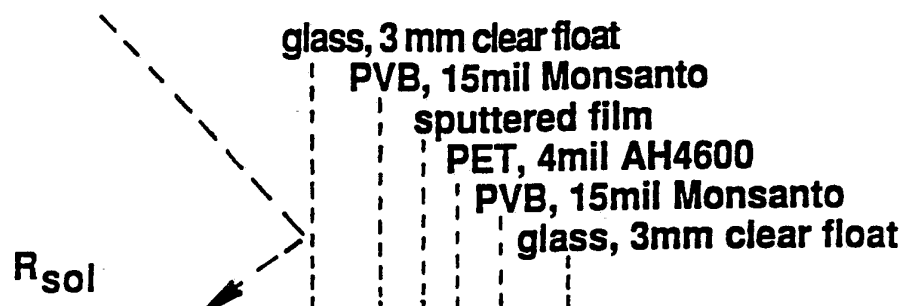
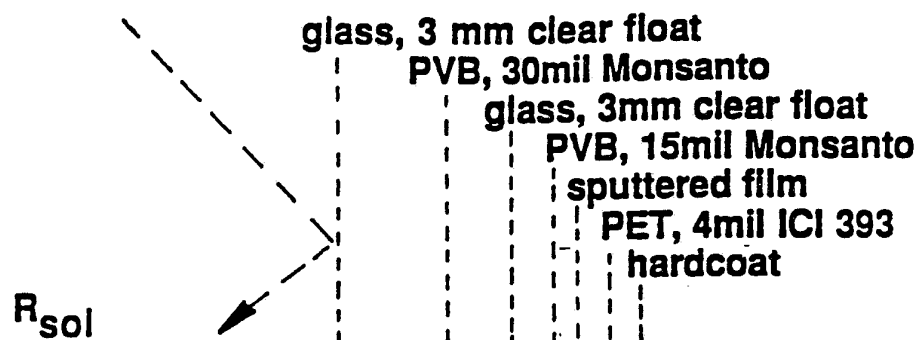
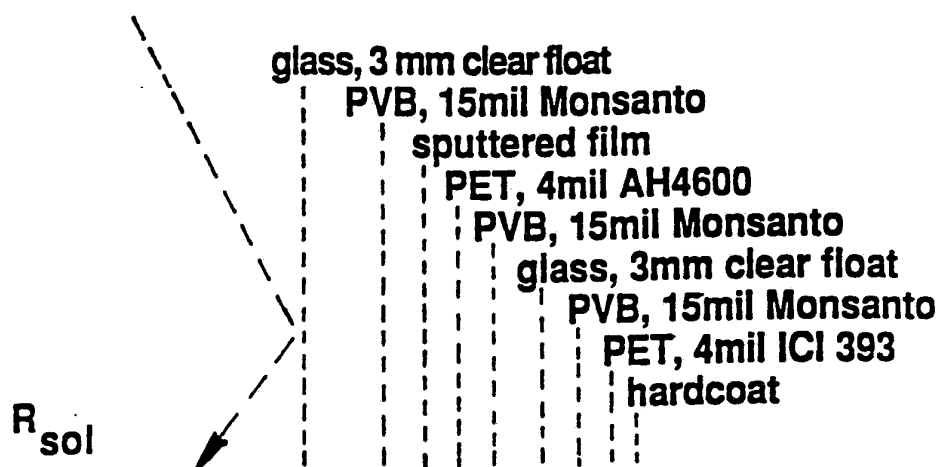
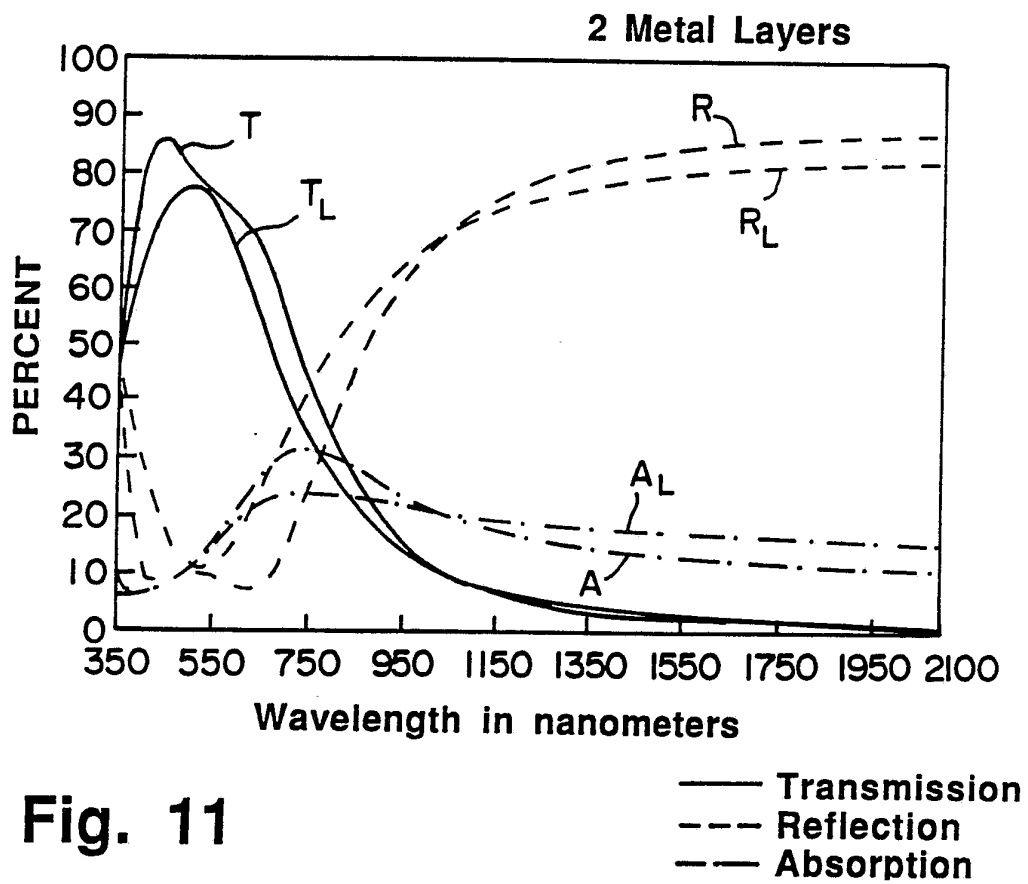
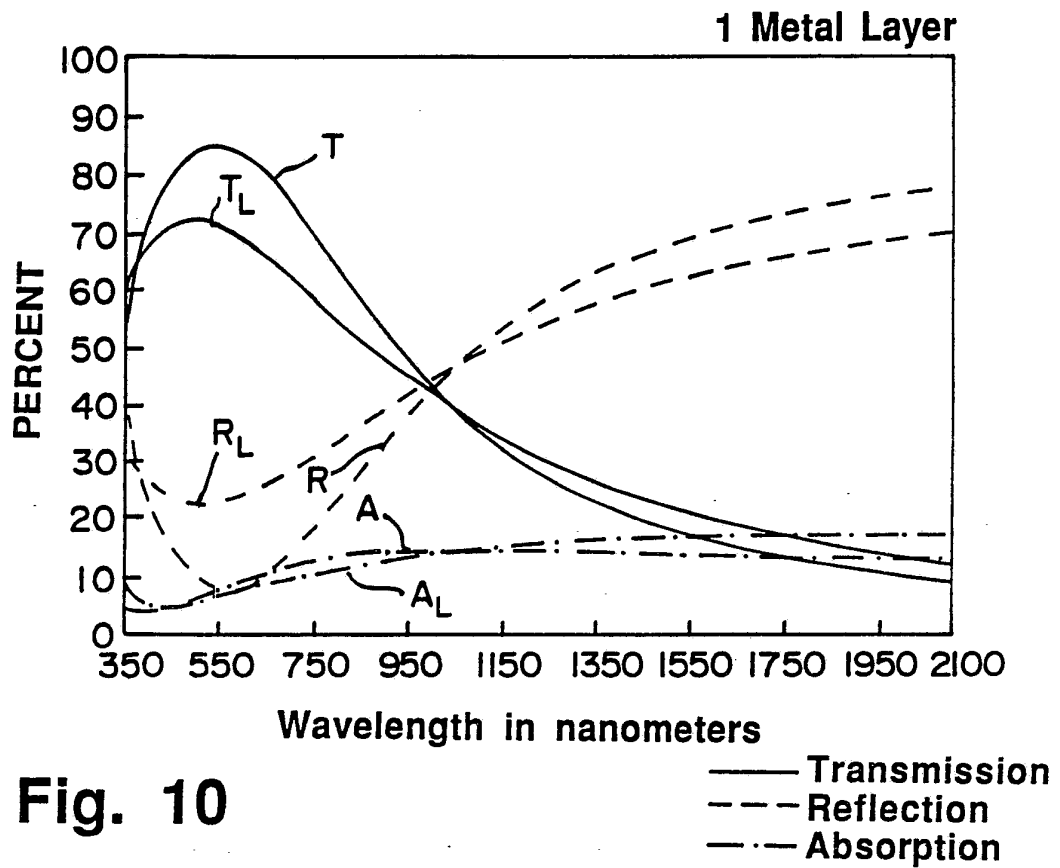


Fig. 8

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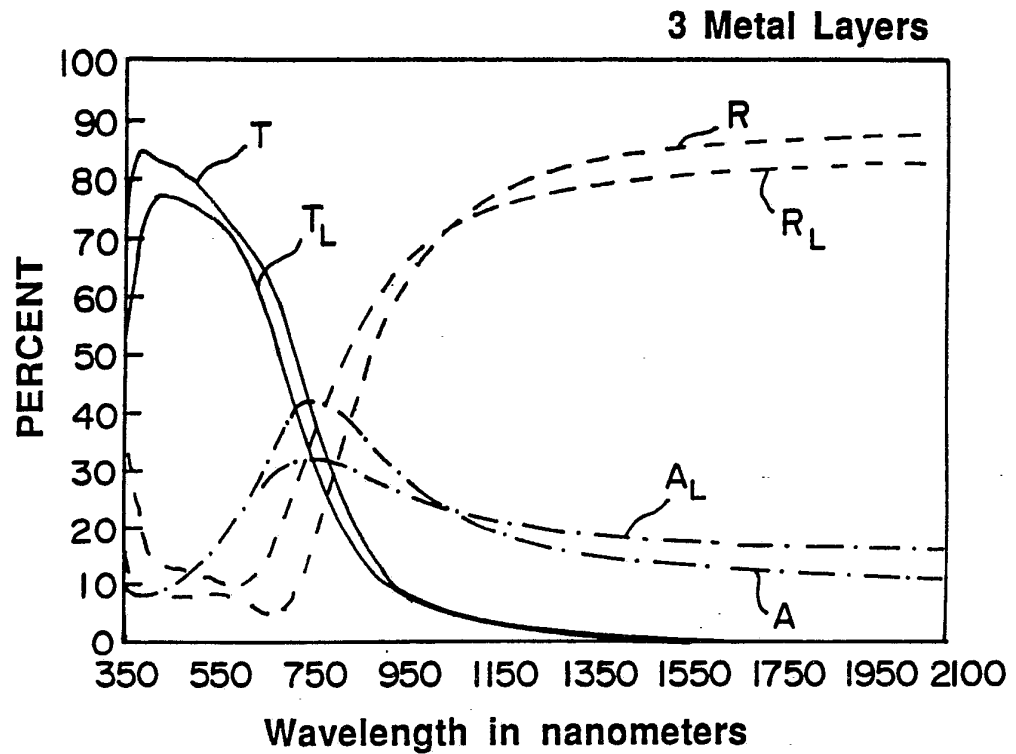
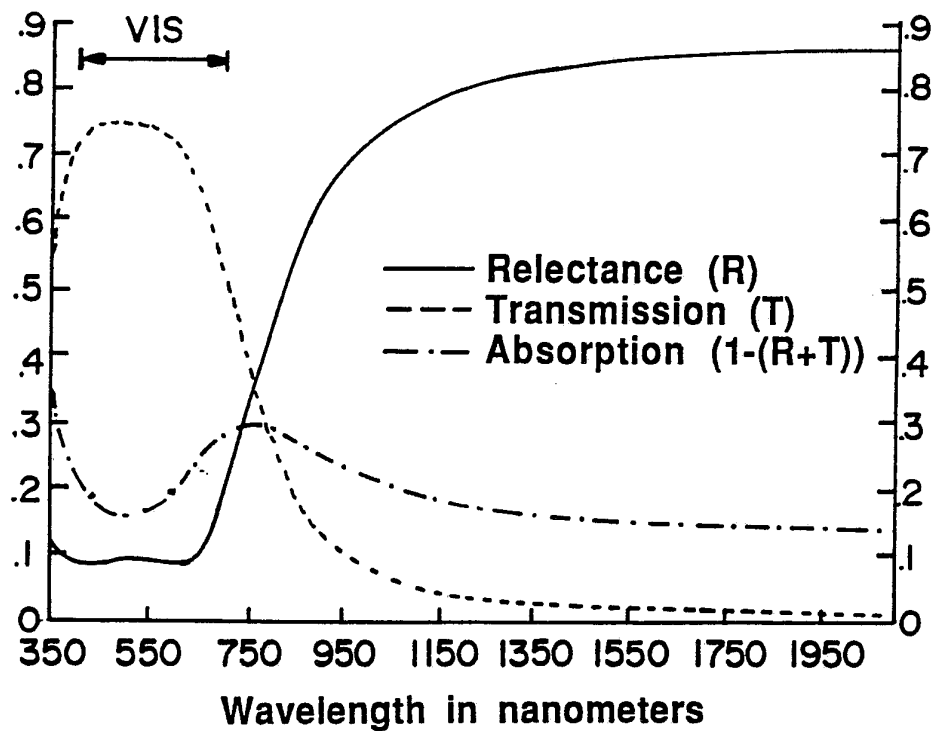
Encapsulated**Fig. 9A****Anti-lacerative****Fig. 9B****Encapsulated anti-lacerative****Fig. 9C****Structures of Examples****SUBSTITUTE SHEET**

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**Fig. 12****Fig. 13****SUBSTITUTE SHEET**

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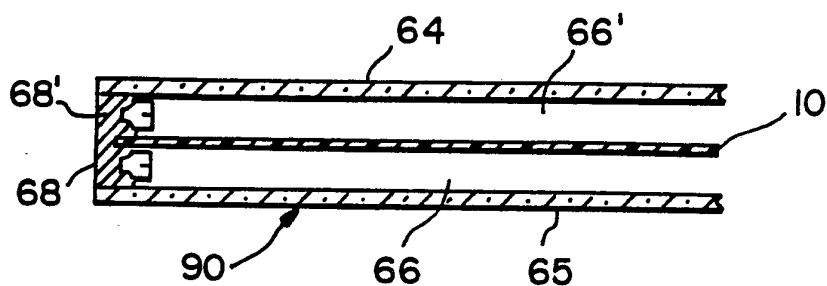


Fig. 15

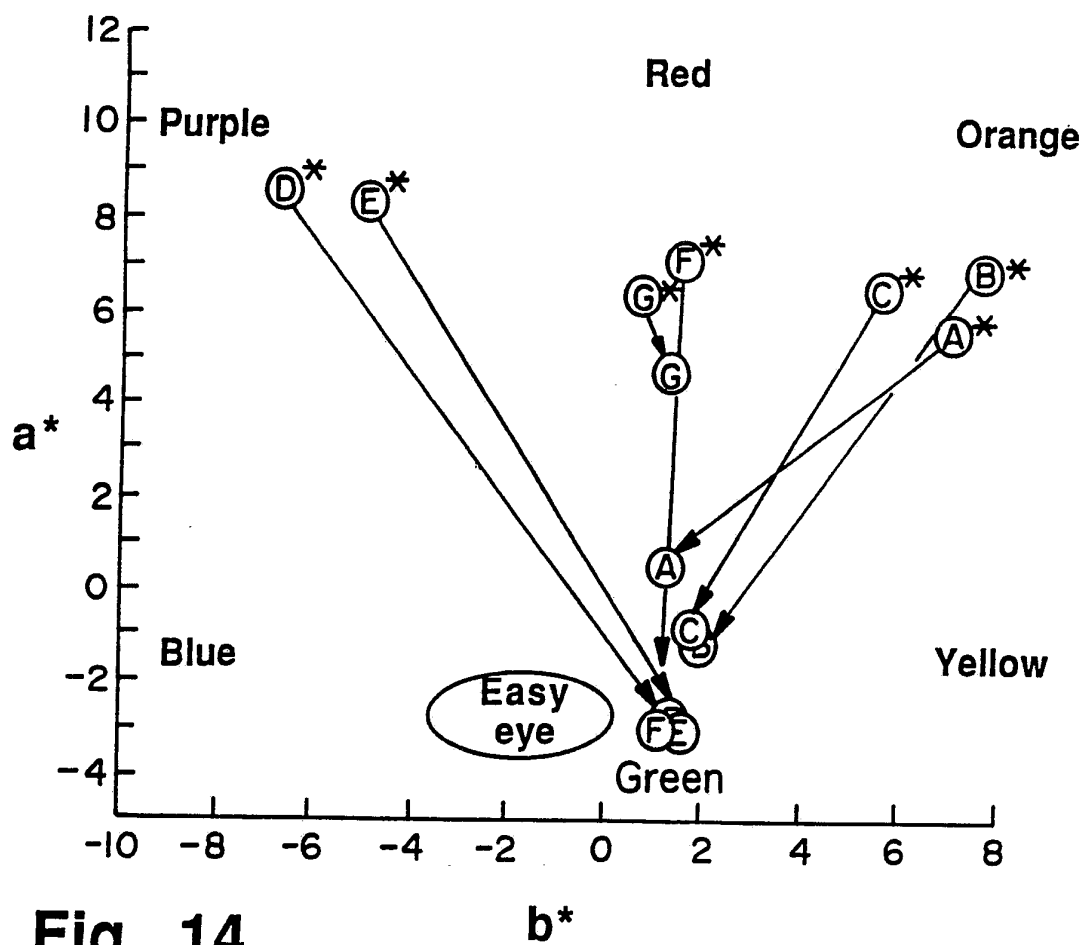


Fig. 14

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/00274

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(4): G02B 1/10; C23C 14/34.		
U.S.Cl.: 350/1.7; 204/192.27.		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.Cl.	350/1.7; 204/192.27	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X, E	US, A, 4799745 (S.F. MEYER ET AL) published 24 January 1989, see claims 1-25.	1-24
A	US, A, 3846152 (H. FRANZ) published 05 November 1974, see fig. 3; col. 2, lines 57-66; col. 6, lines 40-45.	1-24
A	US, A, 3682528 (J.H. APFEL ET AL) published 08 August 1972, see fig. 1; col. 4, lines 17-29.	1-24
* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document 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 "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		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
11 April 1989	02 JUN 1989	
International Searching Authority	Signature of Authorized Officer	
ISA/US	DAVID J. EDMONDSON	