

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
3 April 2008 (03.04.2008)

PCT

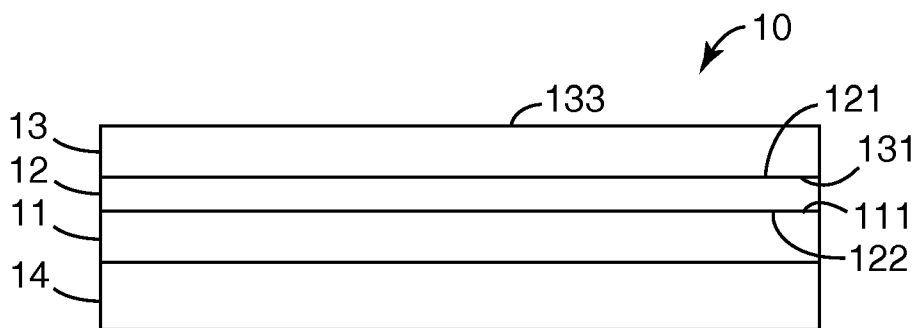
(10) International Publication Number  
**WO 2008/039658 A2**

- (51) International Patent Classification:  
B32B 27/08 (2006.01) C09J 7/02 (2006.01)
- (21) International Application Number:  
PCT/US2007/078732
- (22) International Filing Date:  
18 September 2007 (18.09.2007)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
60/827,133 27 September 2006 (27.09.2006) US
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- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

- Declarations under Rule 4.17:**
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
  - as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- Published:**
- without international search report and to be republished upon receipt of that report

(54) Title: METALLIZED FILMS, ARTICLES, AND METHODS OF MAKING THE SAME



(57) Abstract: Metallized films and articles including a metallized film are disclosed. The metallized films may include multiple layers in which a metal layer is positioned between and in contact with two cross-linked polymeric layers.

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## **METALLIZED FILMS, ARTICLES, AND METHODS OF MAKING THE SAME**

### **BACKGROUND**

Metallized films are widely used to form three-dimensional decorative articles that can be attached to a variety of industrial and consumer items such as motorized vehicles, boats, furniture, building materials, appliances, signs and the like. These decorative or functional articles may be substituted for their metal counterparts resulting in at least one of the following: lighter weight, lower manufacturing costs, better weather resistance, design flexibility, alternative physical or mechanical properties, and sharper detail.

### **SUMMARY**

In one aspect, the present invention provides a metallized film comprising:  
a polymeric primer layer comprising a first polymer at least a portion of which is cross-linked;

a polymeric protective layer comprising a second polymer at least a portion of which is cross-linked; and

a metal layer between the polymeric primer layer and the polymeric protective layer;

wherein the polymeric protective layer has a first outer surface opposite the metal layer and a second outer surface adjacent to the metal layer, wherein the first and second outer surfaces have a respective predetermined surface topography, and wherein (i) the polymeric primer layer has an outer adhesive surface opposite the metal layer or (ii) the metallized film further comprises an adhesive layer on the polymeric primer layer opposite the metal layer, the adhesive layer having an outer adhesive surface opposite the polymeric primer layer.

In some embodiments, at least one predetermined surface topography (e.g., two predetermined surface topographies) is formed by at least partially cross-linking a cross-linkable composition while it is in contact with a textured forming substrate. In some of

these embodiments, the textured forming substrate comprises a release liner. In some of these embodiments, the textured forming substrate comprises a mold.

In some embodiments, the polymeric primer layer has an outer adhesive surface opposite the metal layer. The outer adhesive surface of the polymeric primer layer can be tacky at room temperature (e.g., a pressure sensitive adhesive (PSA)) or become tacky if exposed to heat (e.g., a heat-activatable adhesive). In some embodiments, the outer adhesive surface of the polymeric primer layer is a pressure sensitive adhesive (PSA).

In some embodiments the metallized film further comprises an adhesive layer on the polymeric primer layer opposite the metal layer, the adhesive layer having an outer adhesive surface opposite the polymeric primer layer. The adhesive layer may be, for example, a pressure sensitive adhesive (PSA) layer, a heat-activatable adhesive layer (e.g., a hot-melt adhesive layer), or a combination thereof. In some embodiments, the outer adhesive surface comprises a pressure sensitive adhesive and a hot melt adhesive layer is attached to the outer adhesive surface. In some embodiments, the adhesive layer may be a thermosetting adhesive or a thermosetting PSA. If the adhesive layer comprises a pressure sensitive adhesive (PSA) layer, the metallized film may further comprise a release liner to provide temporary protection to an exposed outer surface of the pressure sensitive adhesive layer.

In some embodiments, at least one outermost surface of the metallized film has topographical features thereon.

In some embodiments, both a first surface of the first polymer and a second surface of the second polymer face the metal layer and have: (i) acidic functional groups on the first and second surfaces, (ii) basic functional groups on the first and second surfaces, (iii) a corona discharge or glow discharge surface treatment, (iv) both (i) and (iii), or (v) both (ii) and (iii).

In some embodiments, the polymeric primer layer, the polymeric protective layer, or both comprise a waterborne polymeric material.

In some embodiments, the first and second polymers are substantially cross-linked throughout a thickness of the polymeric primer layer and the polymeric protective layer.

In some embodiments, the polymeric protective layer comprises a cross-linked polyurethane, a cross-linked polymer or copolymer containing carboxyl groups thereon, a cross-linked polyolefin, a cross-linked ethylene/vinyl acetate/acid terpolymer, or a

combination thereof; and the polymeric primer layer comprises a cross-linked polyurethane, a cross-linked polymer or copolymer containing carboxyl groups thereon, a cross-linked polyolefin, a cross-linked ethylene/vinyl acetate/acid terpolymer, or a combination thereof.

5           In some embodiments, the polymeric protective layer comprises an optically clear cross-linked polyurethane; and the polymeric primer layer comprises a cross-linked ethylene acrylic acid copolymer.

          In some embodiments, the metal layer comprises indium, aluminum, tin, stainless steel, copper, silver, gold, chromium, nickel, alloys thereof, or a combination thereof.

10           In some embodiments, an adherable substrate such as, for example, a thermoformable layer (e.g., polycarbonate layer or polyester layer) or an elastomeric substrate (e.g., a weatherseal substrate) is adhered to the outer adhesive surface.

          Metallized film according to the present invention is useful, for example, in the manufacture of signage, articles having a backlit surface (e.g., backlit signage, vehicle dash gauges and/or mirrors), and/or thermoformable articles.

15           In other aspects, the present invention is directed to methods of preparing metallized films, as well as methods of making articles that include at least one metallized film.

          In another aspect, the present invention provides a method of forming a metallized film, the method comprising the steps of:

20           providing a polymeric protective layer having first and second outer surfaces by a method comprising: forming a rolling bank of a first cross-linkable composition, wherein the rolling bank contacts first and second forming substrates; passing the first and second release liners with the cross-linkable composition therebetween through a nip; at least partially cross-linking the cross-linkable composition to provide a polymeric protective layer; and removing the second liner from the at least partially crosslinked polymeric protective layer to expose the second outer surface;

25           depositing a metal layer over at least a portion of the second outer surface of the polymeric protective layer;

30           applying a second cross-linkable composition over the metal layer;

          at least partially cross-linking the second cross-linkable composition to provide a polymeric primer layer; and

optionally applying an adhesive layer over the polymeric primer layer;  
wherein either (i) the polymeric primer layer has an outer adhesive surface  
opposite the metal layer or (ii) the metallized film comprises the adhesive layer over the  
polymeric primer layer opposite the metal layer, the adhesive layer having an outer  
5 adhesive surface opposite the polymeric primer layer.

In some embodiments, the first and second forming substrates with the first cross-  
linkable composition therebetween are passed through the nip under conditions sufficient  
to provide a substantially void-free layer of the first cross-linkable composition.

10 The following embodiments are applicable to the inventive methods set forth  
hereinabove.

In some embodiments, the corresponding cross-linkable composition comprises a  
two-part-urethane. In some embodiments, the corresponding cross-linkable composition is  
solvent-free.

15 In some embodiments, the method further comprises applying an adhesive layer  
over the polymeric primer layer.

In some embodiments, the method further comprises surface treating the second  
outer surface of the polymeric protective layer, an outer surface of the polymeric primer  
layer, or both using a corona discharge surface treatment, a flame surface treatment, or a  
glow discharge surface treatment.

20 In some embodiments, the method further comprises attaching at least one  
additional layer to an outer surface of the polymeric primer layer opposite the first surface,  
an outer surface of the protective layer opposite the second surface, an outer surface of the  
adhesive layer if present, or a combination thereof. In some embodiments, the at least one  
additional layer comprises a release liner.

25 In some embodiments, the method further comprises providing topographical  
features to one or both outermost surfaces of the metallized film.

In some embodiments, the step of cross-linking the polymeric protective layer  
occurs after the attaching step.

30 In some embodiments, the method further comprises attaching a thermoformable  
layer to the outer adhesive surface to form a thermoformable article. In some  
embodiments, the method further comprises thermoforming the thermoformable article.

In some embodiments, the method further comprises applying graphics to the metallized film.

In some embodiments, the outer adhesive surface comprises a pressure sensitive adhesive.

5 In some embodiments, the polymeric primer layer comprises an outer adhesive surface opposite the metal layer. In some embodiments, the polymeric primer layer comprises a pressure sensitive adhesive layer.

In some embodiments, the method further comprises incorporating the metallized film into indicia (e.g., signage) or backlit indicia (e.g., backlit signage).

10 A variety of film-forming methods, metal deposition methods, coating methods, and/or cross-linking methods may be used in the methods of the present invention.

As used herein:

the prefix "(meth)acryl" includes acryl and/or methacryl;

15 the term "polyurethane" refers generally to a reaction product of at least one polyisocyanate with at least one polyol, polyamine, and/or aminoalcohol unless otherwise specified;

20 the term "predetermined surface topography" refers to a permanent surface topography formed by at least partially crosslinking a cross-linkable composition while it is in contact with a forming substrate having a topographical surface such that the permanent surface topography formed is the mirror image of, or substantially the mirror image of, the topographical surface of the forming substrate, although some minor localized imperfections are permitted;

25 the term "solvent" refers to a volatile liquid component that is non-reactive with components used to form a polyurethane (e.g., non-reactive with either or both of a polyol and polyisocyanate used to make a polyurethane);

the term "solvent-free" means containing less than one weight percent of solvent;

the term "thermosetting" refers to a material that permanently solidifies on being heated at a sufficient temperature or otherwise permanently hardens; and

30 the term "thermoset" refers to a thermosetting material that has been solidified by heating or hardened.

The above summary is not intended to describe each disclosed embodiment or every implementation of the present invention. The detailed description section that follows more particularly exemplifies these embodiments.

5

## BRIEF DESCRIPTION OF THE DRAWINGS

The above aspects may be more completely understood in consideration of the following detailed description of various embodiments in connection with the accompanying drawings, in which:

10

Fig. 1 is a cross-sectional view of an exemplary metallized film of the present invention;

Fig. 2A is a perspective view of an exemplary metal layer suitable for use in an exemplary metallized film of the present invention;

Fig. 2B is a perspective view of another exemplary metal layer suitable for use in an exemplary metallized film of the present invention;

15

Fig. 2C is a perspective view of an exemplary metal layer suitable for use in an exemplary metallized film of the present invention, wherein the exemplary metal layer comprises a discontinuous pattern having at least two separate metal areas;

20

Fig. 3A is a perspective view of an upper surface of an exemplary metal area suitable for use in a metal layer of a metallized film of the present invention, wherein the exemplary metal area comprises a visually continuous, but conductively discontinuous metal area;

Fig. 3B is a cross-sectional view of the exemplary metal area of Fig. 3A;

Fig. 4 is a perspective view of the individual layers in the exemplary metallized film of Fig. 1;

25

Fig. 5 is a cross-sectional view of an exemplary article comprising a metallized film of the present invention;

Fig. 6 is a cross-sectional view of an exemplary article comprising a metallized film adhered to a substrate; and

30

Fig. 7 illustrates an exemplary process useful for preparing an exemplary polymeric protective layer suitable for use with the present invention.

While the invention is amenable to various modifications and alternative forms, specifics thereof have been shown by way of example in the drawings will be described in

detail. It should be understood, however, that the intention is not to limit the invention to the particular embodiments described. To the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the present disclosure.

5

### DETAILED DESCRIPTION

To promote an understanding of the principles of the present invention, descriptions of specific embodiments of the present invention follow and specific language is used to describe the specific embodiments. It will nevertheless be understood that no  
10 limitation of the scope of the present invention is intended by the use of specific language. Alterations, further modifications, and such further applications of the principles of the present invention discussed are contemplated as would normally occur to one ordinarily skilled in the art to which the invention pertains.

An exemplary metallized film of the present invention is provided in Fig. 1. As  
15 shown in Fig. 1, exemplary metallized film 10 comprises at least partially cross-linked polymeric primer layer 11, metal layer 12, at least partially cross-linked polymeric protective layer 13, and adhesive layer 14. In this exemplary embodiment, outer surfaces 121 and 122 of metal layer 12 are in direct contact with second outer surface 131 of polymeric protective layer 13 and outer surface 111 of polymeric primer layer 11  
20 respectively. Further, in this embodiment, adhesive layer 14 is in direct contact with polymeric primer layer 11. Respective first and second outer surfaces 133, 131 of polymeric protective layer 13 bear a predetermined surface topography resulting from manufacture.

It has been discovered that positioning a metal layer between two at least partially  
25 cross-linked layers results in a metallized film having a number of desired properties. In some embodiments, the resulting metallized film has a surprisingly low amount of loss in optical density after stretching. Further, in some embodiments, the resulting metallized film has a surprising increase in surface resistivity after stretching. Isolating and constraining the metal layer between two cross-linked polymeric layers results in a  
30 surprisingly significant improvement in the overall performance properties of the resulting metallized film. Specific properties such as, for example, film elasticity, thermal



degradation, and corrosion resistance, are improved and result in a metallized film with greater robustness in subsequent processing steps, as well as environmental durability.

As used in the present invention, the term "cross-linked" refers to a polymeric material that exhibits what is in effect a high to nearly infinite molecular weight such that the polymeric material resists flowing if mechanically deformed or exposed to high temperatures. The phrase "at least partially cross-linked" refers to a polymeric material or layer of polymeric material, at least a portion of which resists flowing if mechanically deformed or exposed to high temperatures. For example, a relatively thick layer of polymeric material may be at least partially cross-linked such that a first outer surface resists flowing if mechanical deformed or exposed to high temperatures, while an opposite second outer surface exhibits minimal flow resistance if mechanical deformed or exposed to high temperatures.

As illustrated in Fig. 1, metallized films of the present invention may comprise a number of individual layers. A description of individual layers, the overall construction, and various film construction parameters of exemplary metallized films of the present invention is provided below.

*I. Metallized Film Construction and Properties*

The metallized films of the present invention have a unique film structure. A description of each layer of the metallized films of the present invention, as well as exemplary film properties of the resulting metallized film is provided below.

5           *A. Metallized Film Layers*

The metallized films of the present invention comprise one or more of the following individual layers.

*1. Polymeric Protective Layer*

10           The metallized films of the present invention comprise at least one polymeric protective layer, such as exemplary polymeric protective layer 13 of exemplary metallized film 10. The polymeric protective layer covers an adjacent metal layer, providing one or more of the following properties to the resulting metallized film: scratch resistance, impact resistance, water resistance, weather resistance, solvent resistance, resistance to oxidation, and resistance to degradation by ultraviolet radiation. In most embodiments, the  
15           polymeric protective layer completely covers the adjacent metal layer such that no portion of the metal layer is exposed.

            The polymeric protective layer comprises one or more polymeric components, and is at least partially cross-linked. In some embodiments of the present invention, only an outer surface of the polymeric protective layer adjacent the metal layer is cross-linked. In  
20           other embodiments of the present invention, cross-linked polymeric material is essentially distributed throughout an entire thickness of the polymeric protective layer (i.e., the entire polymeric protective layer is subjected to a cross-linking step as opposed to just an outer surface of the polymeric protective layer).

            In other embodiments of the present invention, the degree of cross-linking within  
25           the polymeric protective layer varies to form a cross-linking gradient along a thickness of the polymeric protective layer, wherein an outer surface of the polymeric protective layer adjacent the metal layer has a relatively high degree of cross-linking, and the degree of cross-linking within the polymeric protective layer decreases as the distance from the outer surface of the polymeric protective layer adjacent the metal layer increases. In this  
30           embodiment, an outer surface of the polymeric protective layer opposite the metal layer has the smallest degree of cross-linking, if any, relative to the degree of cross-linking of the outer surface of the polymeric protective layer adjacent the metal layer.

Examples of suitable cross-linkable polymeric components include, but are not limited to, polyurethanes, polymers or copolymers containing polar groups thereon, polyolefins, ethylene/vinyl acetate/acid terpolymers, acrylate-based materials, acid or hydroxyl-functional polyesters, ionomers, fluoropolymers, fluoropolymer/acrylate blends, or any combination thereof.

In some embodiments, the polymeric protective layer comprises a cross-linked polymer or copolymer containing (i) at least one polar group along the polymer chain, (ii) at least one olefinic portion, or (iii) both (i) and (ii). In some embodiments, the polar groups are acids groups, esters thereof, or salts thereof. For example, the polar groups are carboxylic acids, carboxylate esters, or carboxylate salts. Suitable carboxylic acids, carboxylate esters, and carboxylate salts include, but are not limited to, acrylic acid, C<sub>1</sub> to C<sub>20</sub> acrylate esters, acrylate salts, (meth)acrylic acid, C<sub>1</sub> to C<sub>20</sub> (meth)acrylate esters, (meth)acrylate salts, or combinations thereof. Suitable methacrylate and acrylate esters typically contain up to about 20 carbon atoms or up to about 12 carbon atoms (excluding the acrylate and methacrylate portion of the molecules). In some embodiments, the methacrylate and acrylate esters contain about 4 to about 12 carbon atoms.

The olefinic portion of the polymer or copolymer can be formed by free radical polymerization of monomers such as, for example, ethylene, propylene, isobutylene, or combinations thereof. In some embodiments, the olefinic materials include an olefinic monomer having ethylenic unsaturation. For example, reacting a polyethylene oligomer or ethylene monomers with a monomer having a polar group can form a copolymer for use in the polymeric protective layer.

In some embodiments, the copolymer is a reaction product of an olefinic monomer having ethylenic unsaturation with a second monomer selected from (meth)acrylic acid, a C<sub>1</sub> to C<sub>20</sub> (meth)acrylate ester, a (meth)acrylate salt, acrylic acid, a C<sub>1</sub> to C<sub>20</sub> acrylate ester, an acrylate salt, or a combination thereof. The copolymer can be prepared using about 80 to about 99 weight percent of the olefinic monomer and about 1 to about 20 weight percent of the second monomer. For example, the copolymer can be prepared by copolymerizing about 83 to about 97 weight percent of the olefinic monomer and about 3 to about 17 weight percent acrylic acid, a C<sub>1</sub> to C<sub>20</sub> acrylate ester, an acrylate salt, (meth)acrylic acid, a C<sub>1</sub> to C<sub>20</sub> (meth)acrylate ester, a (meth)acrylate salt, or

combinations thereof. In another example, the copolymer contains from about 90 to about 96 weight percent of the olefinic monomer and about 4 to about 10 weight percent acrylic acid, a C<sub>1</sub> to C<sub>20</sub> acrylate ester, an acrylate salt, (meth)acrylic acid, a C<sub>1</sub> to C<sub>20</sub> (meth)acrylate ester, a (meth)acrylate salt, or combinations thereof.

5           When salts of a (meth)acrylate or acrylate group are present in the polymer or copolymer, the positive ion of the salt is typically an alkali metal ion, an alkaline earth metal ion, or a transition metal ion. For example, the positive ion can include, for example, sodium, potassium, calcium, magnesium, or zinc.

10           In some embodiments, the polymeric protective layer includes a copolymer such as, for example, ethylene (meth)acrylic acid or ethylene acrylic acid. Commercially available copolymers suitable for use in the polymeric protective layer include, but are not limited to, copolymers available from Dow Chemical Company (Midland, MI) under the trade designation PRIMACOR such as PRIMACOR 3330, which has 6.5% acrylic acid and 93.5% ethylene; copolymers commercially available from DuPont (Wilmington, DE)  
15           under the trade designation NUCREL such as NUCREL 0403 (a copolymer of ethylene and methacrylic acid); copolymers commercially available under the trade designation ELVALOY (copolymers of ethylene with butyl acrylate, ethyl acrylate, or methyl acrylate); and copolymers commercially available under the trade designation SURYLN (ionomer of ethylene and acrylic acid).

20           In some embodiments, cross-linking of the polymeric protective layer may be achieved by combining reactive component(s) (e.g., monomers) in an appropriate stoichiometric ratio to form an at least partially cross-linkable composition. For example, in the case of an epoxy resin, the inclusion of polyepoxides and/or polyfunctional cross-linkers will typically result in at least partially crosslinked polymeric material. In the case  
25           of a two-part urethane, this may be achieved, for example, by combining at least one of a polyol, polyamine and/or aminoalcohol with at least one polyisocyanate wherein at least one polyol, polyamine, aminoalcohol and/or polyisocyanate has a reactive functionality (e.g., isocyanate group functionality or hydroxyl group or amino group functionality) of at least three.

30           In some embodiments of the present invention, the cross-linkable polymeric components provide a polymeric protective layer that, if elongated, can substantially recovers to an original length (or width) if allowed to relax as long as the yield point of the

polymeric protective layer is not exceeded. Such a polymeric protective layer allows a metal layer thereon to be disrupted during elongation of the polymeric protective layer, but then return to substantially its pre-elongation state once the polymeric protective layer is allowed to relax as long as the yield point of the polymeric protective layer is not  
5 exceeded.

In some embodiments, the polymeric protective layer comprises a cross-linked aliphatic waterborne polyurethane resin. Exemplary aliphatic waterborne polyurethane resins include those described in U.S. Pat. No. 6,071,621 (Falaas et al.), the disclosure of which is incorporated herein by reference. Commercially available aliphatic waterborne  
10 polyurethanes include, but are not limited to, materials sold under the trade designation NEOREZ (e.g., NEOREZ SR 9699, XR 9679, and XR 9603) from DSM (Waalwijk, The Netherlands), and materials sold under the trade designation BAYHDROL (e.g., BAYHYDOL 121) from Bayer Corp. (Pittsburgh, PA). The waterborne polyurethane resins may be formed from various types of polyols such as polyester polyols,  
15 polycarbonate polyols, and the like. The use of a polycarbonate-based polyurethane may be desirable for some applications for better anti-staining properties.

In some embodiments, the polymeric protective layer comprises a cross-linked solvent-based polyurethane resin formed by the reaction of one or more polyols with a polyisocyanate. In some applications, it is desirable for the polyols and the  
20 polyisocyanates to be free of aromatic groups.

In some embodiments, the polymeric protective layer comprises an at least partially cross-linked polyurethane resin formed by the reaction of one or more polyols and/or polyamines and/or aminoalcohols with one or more polyisocyanates, optionally in the presence of non-reactive component(s). In some applications, it is desirable for the  
25 polyols, polyamines, and/or aminoalcohols and the polyisocyanates to be free of aromatic groups. In order to obtain an at least partially cross-linked polymeric protective layer, at least one component (i.e., a polyisocyanate, a polyol, a polyamine, and/or an aminoalcohol) should have a average reactive functionality of greater than 2 (e.g., polyisocyanates having more than two isocyanate groups or polyols, polyamines, and/or  
30 aminoalcohols having more than two isocyanate-reactive groups).

Suitable polyols include, for example, materials commercially available under the trade designation DESMOPHEN from Bayer Corporation (Pittsburgh, PA). The polyols

can be polyester polyols (e.g., DESMOPHEN 631A, 650A, 651A, 670A, 680, 110, and 1150); polyether polyols (e.g., DESMOPHEN 550U, 1600U, 1900U, and 1950U); or acrylic polyols (e.g., DEMOPHEN A160SN, A575, and A450BA/A).

Suitable polyamines include, for example: aliphatic polyamines such as, for example, ethylene diamine, 1,2-diaminopropane, 2,5-diamino-2,5-dimethylhexane, 1,11-diaminoundecane, 1,12-diaminododecane, 2,4- and/or 2,6-hexahydrotoluylendiamine, and 2,4'-diamino-dicyclohexylmethane; and aromatic polyamines such as, for example, 2,4- and/or 2,6-diaminotoluene and 2,4'- and/or 4,4'-diaminodiphenylmethane; amine-terminated polymers such as, for example, those available from Huntsman Chemical (Salt Lake City, UT), under the trade designation JEFFAMINE polypropylene glycol diamines (e.g., JEFFAMINE XTJ-510) and those available from Noveon Corp. (Cleveland, OH) under the trade designation HYCAR ATBN (amine-terminated acrylonitrile butadiene copolymers), and those disclosed in U.S. Pat. No. 3,436,359 (Hubin et al.) and U.S. Pat. No. 4,833,213 (Leir et al.) (amine-terminated polyethers, and polytetrahydrofuran diamines); and combinations thereof.

Suitable aminoalcohols, for example, 2-aminoethanol, 3-aminopropan-1-ol, alkyl-substituted version of the foregoing, and combinations thereof.

Suitable polyisocyanate compounds include, for example: aromatic diisocyanates (e.g., 2,6-toluene diisocyanate; 2,5-toluene diisocyanate; 2,4-toluene diisocyanate; m-phenylene diisocyanate; p-phenylene diisocyanate; methylene bis(o-chlorophenyl diisocyanate); methylenediphenylene-4,4'-diisocyanate; polycarbodiimide-modified methylenediphenylene diisocyanate; (4,4'-diisocyanato-3,3',5,5'-tetraethyl) diphenylmethane; 4,4'-diisocyanato-3,3'-dimethoxybiphenyl (o-dianisidine diisocyanate); 5-chloro-2,4-toluene diisocyanate; and 1-chloromethyl-2,4-diisocyanato benzene), aromatic-aliphatic diisocyanates (e.g., m-xylylene diisocyanate and tetramethyl-m-xylylene diisocyanate); aliphatic diisocyanates (e.g., 1,4-diisocyanatobutane; 1,6-diisocyanatohexane; 1,12-diisocyanatododecane; and 2-methyl-1,5-diisocyanatopentane); cycloaliphatic diisocyanates (e.g., methylenedicyclohexylene-4,4'-diisocyanate; 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (isophorone diisocyanate); 2,2,4-trimethylhexyl diisocyanate; and cyclohexylene-1,4-diisocyanate), polymeric or oligomeric compounds (e.g., polyoxyalkylene, polyester, polybutadienyl, and the like) terminated by two isocyanate functional groups (e.g., the diurethane of toluene-2,4-

diisocyanate-terminated polypropylene oxide glycol); polyisocyanates commercially available under the trade designation MONDUR or DESMODUR (e.g., DESMODUR XP7100 and DESMODUR 3300) from Bayer Corporation (Pittsburgh, PA); and combinations thereof.

5           In general, the amounts of polyisocyanate to polyol, polyamine, and/or aminoalcohol are selected in approximately stoichiometrically equivalent amounts, although in some cases it may be desirable to adjust the relative amounts to other ratios. Typically, the equivalent ratio of polyisocyanate(s) to polyol(s), polyamine(s), and/or aminoalcohol(s) is in a ratio of from 1:3 to 3:1, although this is not a requirement. Those  
10 skilled in the art will recognize that any excess isocyanate present after cross-linking will typically react with materials having reactive hydrogens (e.g., adventitious moisture, alcohols, amines, etc.).

          In order to provide some degree of cross-linking in the polymeric protective layer, one or more of the above-described polymeric materials may be cross-linked using any  
15 known cross-linking technique including, but not limited to, (i) chemically cross-linking using reactive groups on the one or more polymeric materials, (ii) chemically cross-linking using a cross-linking additive used in combination with the one or more polymeric materials, (iii) physically cross-linking one or more polymeric materials using a cross-linking step, such as exposing the one or more polymeric materials to a cross-linking  
20 amount of radiation (e.g., electron beam radiation), or (iv) a combination of (i), (ii) and (iii).

          For example, the above-described waterborne polyurethane compositions can be cross-linked by the addition of a cross-linking agent (e.g., less than about 3 weight percent) such as diaziridine. A commercially available diaziridine is sold under the trade  
25 designation "NEOCRYL" (e.g., NEOCRYL CX-100) from DSM (Waalwijk, The Netherlands). Further, the above-described solvent-based polyurethane resin may be cross-linked, for example, by reaction with a cross-linking or curing agent such as a melamine resin. Other cross-linking agents suitable for use in the present invention include, but are not limited to, glycidyl esters, urea/formaldehyde resins, amines and  
30 amine-functional resins, and silanes.

          The above-described polymers or copolymers containing (i) at least one polar group along the polymer chain, (ii) at least one olefinic portion, or (iii) both (i) and (ii),

may be cross-linked, for example, using electron beam radiation. In some embodiments, the olefinic portion of the copolymer can be cross-linked, for example, using electron beam radiation. The copolymers can be cross-link by abstraction of a secondary hydrogen, resulting in the formation of a free radical intermediate. This free radical intermediate can then combine with other olefinic radicals or additional copolymers to form a higher molecular weight material. Depending on the structure of the olefinic portion of the copolymer, the free radical intermediate can undergo degradation reactions rather than reactions that increase the molecular weight by cross-linking reactions. If the olefinic portion includes polyethylene, the amount of degradation attributable to scission reactions is low. Polyethylene can cross-link when exposed to electron beam radiation whereas polypropylene has an increased tendency to undergo chain scission reactions compared to polyethylene.

Typically, the dosage is as high as possible without unduly causing the polymer to undergo chain scission reactions that are in excess of the cross-linking reactions. Loss of molecular weight can be an indicator that irradiation has unduly degraded the polymer. Accordingly, for polymers that tend to undergo chain scission reactions, the radiation dosage is typically limited such that the weight average molecular weight of the irradiated polymer is at least about 90%, at least about 95%, or at least about 99% of that of an otherwise identical copolymer that has not been irradiated. The weight average molecular weight of the cross-linked copolymer is preferably greater than the weight average molecular weight of an otherwise identical copolymer that has not been cross-linked.

In some embodiments, the electron beam radiation dosage is less than about 10 Mrads. For example, the dosage can be in the range of about 0.1 to about 10 Mrads or in the range of about 3 to about 7 Mrads. The radiation voltage can typically be up to about 600 kVolts. For example, the voltage can be in the range of about 25 to about 600 kVolts, about 50 to about 300 kVolts, or about 100 to about at about 200 kVolts. Higher voltages can be used to penetrate a greater thickness of the copolymer.

Other physical cross-linking steps suitable for use in the present invention include, for example, exposure to ionizing forms of radiation such as gamma radiation, x-rays and ultraviolet light.

Another alternative cross-linking method that is a combined chemical/physical method of cross-linking involves incorporating a sensitizing agent, such as a ultraviolet



light initiator, into the polymeric layer. Exposing the film to ultraviolet light initiates a cross-linking reaction within the polymeric protective layer. This method of post-cross-linking the film increases the utility of the film by affording the user more latitude for processing the metallized film. For instance, the user of the film may desire to have  
5 greater film elongation prior to and during adhesive application to a substrate, such as during a thermoforming step. Subsequently, however, the user may desire to increase the hardness and/or thermal resistance properties of the film, after it has been adhesively attached to a substrate, in an effort to achieve a closer match of properties between the film and the substrate. This can be especially true if addressing the specific needs and  
10 balances one desires when dealing with highly elastomeric substrates or complex three dimensional parts such as automotive weatherseals.

The polymeric protective layer may further comprise one or more additives incorporated into the one or more polymeric components of the polymeric protective layer. Suitable additives include, for example, dyes, pigments, wetting agents such as  
15 surfactants, plasticizers, inert filler materials (e.g., glass microspheres), waxes and slip agents, UV stabilizers such as benzotriazoles and benzophenones along with hindered amine stabilizers, and combinations thereof.

If present, the one or more additives may represent up to about 50 percent by weight (pbw) based on a total weight of the polymeric protective layer, with the balance  
20 being one or more polymeric materials. Typically, if present, each individual additive is present in an amount ranging from greater than about 0.05 pbw to about 20 pbw, preferably between about 0.1 and about 10 pbw, and most preferably between about 0.5 and about 5 pbw, based on a total weight of the polymeric protective layer, with the balance being one or more polymeric materials.

The polymeric protective layer may also have one or more surface treatments to alter outer surface properties of the polymeric protective layer, especially the second outer surface of the polymeric protective layer adjacent the metal layer (e.g., second outer surface 131 of polymeric protective layer 13 shown in Fig. 1). Suitable surface treatments include, for example, a corona discharge surface treatments, flame treatments, and glow  
25 discharge surface treatments. Any surface treatment capable of chemically grafting functional groups or oxidizing the surface of the film is acceptable so long as no  
30 macroscopic degradation occurs within or on the surface of the polymeric protective layer.

In one exemplary embodiment, the one or more surface treatments enhance the adhesion between the polymeric protective layer and the metal layer.

The polymeric protective layer can have a high or low gloss surface, as desired. Additionally, the polymeric protective layer can have high or low reflectivity, as desired.

5 The polymeric protective layer is desirably transparent to visible radiation so that the underlying metal layer is visible though the polymeric protective layer. As used herein, the term "transparent" refers to materials that allow at least about 50 percent of visible radiation to pass through the materials. For example, the transparent material can pass at least about 75 percent, at least about 80 percent, at least about 85 percent, at least about 90  
10 percent, or at least about 95 percent of visible radiation. In some applications, the polymeric protective layer is colored yet transparent. For example, the polymeric protective layer may contain dyes and/or pigments in order to provide a color to the polymeric protective layer.

In some embodiments, the polymeric protective layer may be provided as a  
15 preformed layer such as a self-supporting film or may be cast from a solution onto a release liner. For example, when the polymeric protective layer is an aliphatic waterborne polyurethane resin, the aqueous urethane dispersion can be cast onto a release liner such as a release coated polyester film. The cast urethane dispersion can then be dried to remove water. Typically, the polyurethane is also cross-linked in the drying step, although it may  
20 be cross-linked at a later time. In another example, a solvent-free or solvent-containing mixture of a polyisocyanate and a polyol can be cast onto a release liner. The cast mixture can then be dried to remove any solvent and cured to form a cross-linked film.

In some embodiments, the polymeric protecting layer is formed between two forming substrates (e.g., two release liners or two pieces of a mold). For continuous  
25 processes, the forming substrates typically comprise release liners. Suitable release liners for the polymeric protective layer include, for example, carrier substrates (e.g., polymer films or papers), optionally coated with a low surface energy coating, that releasably adheres to that material, typically without any adhesive transfer. Suitable carriers may include films such as biaxially oriented polyester and papers that may be coated or printed  
30 with a composition that will enable release from the polyurethane compositions. Suitable low surface energy coatings may include, for example, those formed from polyacrylics, silicone, and/or fluorochemicals.

The forming substrates impart predetermined topographical features to both the outer surface of the polymeric protective layer and the surface of the polymeric protective layer that is adjacent to the metallic layer (i.e., the second outer surface of the polymeric protective layer). While the forming substrates have a predetermined pattern, either or  
5 both of the forming substrates may appear to the unaided eye as being textured or smooth. The ability to control the topography of the second outer surface of the polymeric protective layer allows facile control of the final appearance of the metal layer, and hence the appearance of the metallized film. For example, forming substrates may be used to provide a uniform pattern of valleys and/or ridges along the first and/or second outer  
10 surfaces of the polymeric protective layer. In other embodiments, the forming substrates may be chosen to provide the first and/or second outer surfaces of the polymeric protective layer with a substantially smooth surface. Alternatively, the forming substrates can impart a randomly textured or matte surface to the first and/or second outer surfaces of the polymeric protective layer. Accordingly, release liners suitable for use in the present  
15 invention may include, for example, release liners disclosed in U.S. Pat. No. 6,984,427 (Galkiewicz et al.), the disclosure of which is incorporated herein by reference.

In some embodiments of the present invention, an outer surface of the polymeric protective layer may be separately embossed to provide a pattern in the outer surface prior to or after joining the polymeric protective layer with a metal layer. For example, in some  
20 embodiments, the outer surface of the polymeric protective layer opposite the metal layer may be embossed to provide a pattern on the metallized film. In other embodiments, the outer surface of the polymeric protective layer adjacent the metal layer may be embossed to provide a pattern on which a metal layer is deposited. Embossing methods suitable for use in the present invention include, for example, embossing methods disclosed in U.S.  
25 Pat. No. 5,897,930 (Calhoun et al.), the disclosure of which is incorporated herein.

In some embodiments of the present invention, the outer surface of the polymeric protective layer adjacent the metal layer may be a substantially flat, smooth, planar surface having very little, if any, topographical features thereon. As used herein, the term "planar" is used to describe a surface of a layer that is substantially within the same plane. In these  
30 embodiments, a subsequently applied metal layer may provide the metallized film with a mirror-like appearance. In other embodiments of the present invention, the outer surface of the polymeric protective layer adjacent the metal layer may have a non-planar surface,

such as a surface having topographical features thereon. As described above, an embossing technique may be used to provide the outer surface of the polymeric protective layer adjacent the metal layer with topographical features. Other techniques may include, for example, the use of another release liner having topographical features therein to form the outer surface of the polymeric protective layer adjacent the metal layer. In these 5 embodiments, a subsequently applied metal layer may provide the metallized film with an alternative appearance.

Advantageously, by applying low viscosity polymerizable materials onto the metal layer, it is typically possible to achieve good penetration of the polymerizable materials 10 into void areas of the metal layer resulting in good adhesion.

The polymeric protective layer typically has an average thickness of at least about 5 micrometers although the polymeric protective layer may have any desired thickness. In some applications, the polymeric protective layer has a thickness of at least about 10 micrometers, at least about 15 micrometers, at least about 20 micrometers, or at least about 15 25 micrometers. The thickness of the polymeric protective layer is usually less than about 250 micrometers, although there is no limitation on the thickness of the polymeric protective layer. In some applications, the polymeric protective layer has a thickness less than about 40 micrometers, less than about 35 micrometers, or less than about 30 micrometers. For example, the thickness can be in the range of about 5 to about 50 20 micrometers, or about 10 to about 40 micrometers, or about 20 to about 30 micrometers.

In some embodiments, the polymeric protective layer is formed by combining at least one crosslinkable material between two forming substrates. An exemplary process for forming the polymeric protective layer is shown for example in Fig. 7. Referring now to Fig. 7, reactive component(s) 703 is/are fed into static mixer 710. The mixed 25 component(s) are then fed to form rolling bank 715 which is disposed ahead of and between first and second forming substrates 721, 722 which are unwound from feed rolls 723, 724. As first and second forming substrates 721, 722 advance through nip 730 formed by first platen 740 and notch bar 735 entrapped air bubbles 717 are substantially or completely removed to give layer 750 which, after passing insulation barrier 760, contacts 30 heated platen 765 which facilitates cross-linking (e.g., curing) of the reactive component(s) to form an at least partially cross-linked polymeric protective layer 770 disposed between first and second forming substrates 721, 722. In some embodiments,

(e.g., those wherein the forming substrates are both release liners) first forming substrate 721 is then removed to expose a surface of the polymeric protective layer on which subsequently metallization occurs. In some embodiments, one of the release liners may be replaced in the coating process by a carrier having a metal layer releasably adhered thereto.

The first liner is typically may be removed after heating, but in some cases sufficient crosslinking may have occurred without heating to permit removal of the first liner while retaining a predetermined surface topography on the exposed surface of the polymeric protective layer.

Advantageously, by using the above described coating process it is generally possible to produce coated layers of material that are substantially void-free (i.e., free of bubbles or pinhole coating defects that are readily visible to an unaided human eye) over relatively large areas (e.g., greater than 1 square meter).

In general, the effectiveness of entrapped air removal will vary with the materials and conditions used, but typically a gap of 20 mils (0.51 mm) or less (e.g., less than or equal to 15 mils (0.38 mm), 10 mils (0.25 mm), 8 mils (0.20 mm), or even less than or equal to 5 mils (0.17)) may be effective. The gap may be created by any suitable means including, for example, nip roll(s), bars, platen(s), knife edge(s), or a combination thereof. Multiple nips (e.g., of decreasing gap) may also be used.

The reactive components should typically be fed at a sufficient rate such that the rolling bank is not depleted. Over time, heating of at least one of the elements (e.g., a notch bar) forming the gap due to reaction of the reactive components in the rolling bank may (especially near the rolling bank) result in a, typically non-uniform, decrease in the gap along the elements. This decrease in gap can be compensated for by heating the affected element(s) (e.g., using a flexible heating tape) to a temperature above that of the rolling bank.

In general, the first and second release liners should have the same rate of travel, however this is not a requirement. In some embodiments, the first liner may be a continuous belt. In some embodiments, the relative position of the first and second liner (e.g., as shown in Fig. 7) may be reversed.

Although a heated platen is shown in Fig. 7, any heating means may be used including, for example, infrared lamps, ovens, microwave radiation, and heated platens.

## 2. *Metal Layer*

The metallized films of the present invention further comprise a metal layer, such as exemplary metal layer 12 of exemplary metallized film 10. The metal layer may be opaque, reflective or non-reflective. In some embodiments, the metal layer provides a polished, mirror-like finish. Further, the metal layer may form a continuous or discontinuous pattern of metallic material between the polymeric protective layer and the polymeric primer layer.

The metal layer can be selected from a wide range of metal-containing materials such as, for example, metals, alloys, and intermetallic compositions. The metal layer can include tin, gold, silver, aluminum, indium, nickel, iron, manganese, vanadium, cobalt, zinc, chromium, copper, titanium, and combinations thereof. Examples of combinations include, for example, stainless steel and alloys having the trade designation INCONEL available from Special Metals Corporation (New Hartford, NY).

The metal layer is usually formed by deposition of metal onto the above-described polymeric protective layer. The metal can be deposited using any suitable technique. For example, suitable deposition methods include, for example, sputtering, electroplating, ion sputtering, or vacuum deposition. In some applications, the metal is deposited using vacuum deposition methods. Suitable metal deposition methods for use in the present invention include, for example, metal deposition methods disclosed in *Foundations of Vacuum Coating Technology* by D.M. Mattox, published by William Andrew/Noyes (2003), the disclosure of which is incorporated herein. In some embodiments, the metal layer is deposited on the carrier by a process that is terminated prior to or shortly after an onset of conductance within the metal layer.

The thickness of the metal layer can vary as needed to provide a desired surface appearance. In some embodiments, the metallized layer has an average thickness of at least 50 Angstroms. For example, the metal layer can have an average thickness of at least 100, at least 200, at least 400, at least 800, or at least 1000 Angstroms.

The metal layer may comprise a continuous pattern, for example, a metal layer comprising a single area of metallic material that substantially covers an outer surface of the polymeric protective layer. An example of this embodiment is shown in Fig. 2A, wherein exemplary metal area 30 completely covers exemplary polymeric protective layer 37 and comprises a single continuous pattern of metallic material that forms a single area

of metal. In another embodiment shown in Fig. 2B, a single continuous area of metallic material 40 may be used to form a pattern such as the letter "C" on outer surface 38 of the polymeric protective layer 37. In a further embodiment of the present invention, the metal layer may comprise a discontinuous pattern having two or more disconnected areas of metallic material on an outer surface of the polymeric protective layer such as in the exemplary embodiment shown in Fig. 2C. As shown in Fig. 2C, two disconnected areas of metallic material 50 may be used to form a discontinuous pattern comprising two separate letters "C C" on outer surface 38 of the polymeric protective layer 37.

Regardless of whether the metal layer comprises a continuous pattern or a discontinuous pattern, each area of metallic material (e.g., each of exemplary metal areas 30, 40 and 50) may comprise a plurality of individual metal areas positioned adjacent to one another to form a resulting metal area, such as exemplary metal area 120 as shown in Fig. 3A. It has been discovered that, in some embodiments, enhanced corrosion resistance of a metallized film may be obtained by incorporating a metal layer containing one or more metal areas, such as exemplary metal area 120, into the metallized film. As shown in Fig. 3A, exemplary metal area 120 comprises a plurality of discontinuous metal areas 62, which form a pattern of metallic material 64. In this embodiment, although metal area 120 appears to be visually continuous, metal area 120 is discontinuous in terms of surface conductivity or resistivity.

The discontinuity of exemplary metal area 120 results in a metal layer having a surface resistivity of at least about 2 ohms/cm<sup>2</sup>, desirably, at least about 10 ohms/cm<sup>2</sup>. In one exemplary embodiment, the metal area has a surface resistivity of at least about 3, at least about 5, at least about 10, or at least about 20 ohms/cm<sup>2</sup>. In some embodiments, it is desirable for performance reasons to have as high a surface resistivity as possible while maintaining as high an optical density that would satisfy the visual aesthetic requirements of the application.

One method of forming a metal area comprising a plurality of individual, adjacent metal area, such as exemplary metal area 120, comprises a metal deposition step, wherein the deposition step is terminated prior to or shortly after an onset of conductance within the metal area. Such a deposition step is illustrated in Fig. 3B, which depicts a cross-sectional view of exemplary metal area 120 shown in Fig. 3A. As shown in Fig. 3B, a plurality of discontinuous metal areas 62 extend upward from outer surface 38 of

polymeric polymer layer 37. It is believed that, during a metal deposition procedure, each individual metal area 62 is assembled in a step-wise process, wherein a base metal deposit, such as exemplary base metal deposit 62A, first attaches to outer surface 38 of polymeric polymer layer 37 at locations 39 along outer surface 38. Locations 39 may correspond to (i) a functional group on a polymeric material used in polymeric polymer layer 37, (ii) a functional group on an additive used in polymeric polymer layer 37, (iii) a surface treatment site resulting from one or more of the above-described surface treatments, or a combination of (i), (ii) and (iii). As shown in Fig. 3B, exemplary base metal deposit 62A are spaced apart from one another along outer surface 38 of polymeric polymer layer 37. As additional metal is deposited, one or more intermediate metal deposits, such as exemplary intermediate metal deposits 62B and 62C, result in individual metal areas 62 having an increased height (extending from outer surface 38) and a decrease in spacing between individual metal areas 62. At some point during the deposition step, if the metal deposition step is allowed to continue, individual metal areas 62 will merge with one another, forming a continuous metal area that is all electrically interconnected. Desirably, in some embodiments of the present invention, the metal deposition step is stopped such that outer peripheries of adjacent individual metal areas 62 have space therebetween such as shown in Fig. 3B. The primary driving force for the behavior of the metal during deposition is the high surface energy nature of the metal in relation to that of the organic-based polymeric layer. The relative surface energy difference does not enable a favorable interaction or wetting to occur between the metal and the polymeric layer thereby causing the metal initially be deposited into discrete microscopic domains.

As shown in Fig. 3B, outer peripheries 65 of uppermost metal deposits 62D of individual metal areas 62 are positioned close to one another, but desirably have spacing therebetween. In some embodiments, outer peripheries 65 of uppermost metal deposits 62D of individual metal areas 62 may come into contact with one another and still result in a metal area having a discontinuous conductivity. As used herein, the term "discontinuous conductivity" is used to describe a metal area or metal layer typically having a surface conductivity of less than about 0.1 mhos or a surface resistivity of at least about 10 ohms/cm<sup>2</sup> although this can vary depending on the metal used.

Typically, the amount of metal deposited on a given surface may be measured by the optical density of the metal layer, which is a measure of transmission and is obtained



by taking the negative log of transmission. Although the optical density will vary with the metal being deposited, typically, the metal layer has an optical density of less than about 2.0. For example, aluminum may have a desirable optical density lower than about 2.0, while tin may have a desirable optical density between about 2.0 and about 2.2.

5           It has also been discovered that maintaining a metal layer that is electrically discontinuous (i.e., has a discontinuous conductivity) provides additional benefit if formation of the metallized film involves using ionizing radiation to achieve cross-linking in the polymeric protective layer, the polymeric primer layer, or both. If the metal layer is conductive and electron beam radiation is used to cross-link one or more of the polymeric  
10           layers, the metal can act as a conductive shield, preventing electron radiation from penetrating through both layers. In acting like a shield, the conductivity of the metal layer actually creates a charge within the metal layer that exhibits massive and violent discharging, which results in considerable damage to the metal layer. This charging/discharging behavior prevents a usable film from being prepared if using electron  
15           beam to cross-link the polymeric layers. In contrast, by keeping the electrical resistance of the metal layer high, the dielectric properties of the film are maintained, which enables the use of electron beam radiation to cross-link either or both of the polymeric protective and primer layers.

### 3. *Polymeric Primer Layer*

The metallized films of the present invention also comprise at least one polymeric primer layer, such as exemplary polymeric primer layer 11 of exemplary metallized film 10. At least one polymeric primer layer covers an outer surface of the metal layer opposite the above-described polymeric protective layer as shown in exemplary metallized film 10 of Fig. 1. Like the polymeric protective layer, the polymeric primer layer provides the metal layer with one or more properties: scratch resistance, impact resistance, water resistance, weather resistance, solvent resistance, resistance to oxidation, and resistance to degradation by ultraviolet radiation. Additionally, the primer layer provides a surface that can be easily adhered to by other layers, e.g., adhesives. In most embodiments, the polymeric primer layer completely covers an outer surface of the metal layer opposite the above-described polymeric protective layer such that no portion of the metal layer is exposed.

The polymeric primer layer may comprise one or more of the above-described polymeric components and optional additives suitable for use in the polymeric protective layer. For example, the polymeric primer layer may be prepared using 90:10 weight:weight of K-FLEX 188 and FOMREZ 55-112 polyester polyols combined with DESMODUR N3300A (balanced equivalent weight based on -OH groups) polyisocyanate, catalyzed with dibutyltin dilaurate coated between two silicone coated polyester liners using a process as shown, for example, in Fig. 7. Further, the outer surfaces of the polymeric primer layer may have one or more of the above-described surface treatments in order to alter that surface. In one exemplary embodiment, the outer surface of the polymeric primer layer adjacent the metal layer (e.g., outer surface 111 of polymeric primer layer 11 shown in Fig. 1) is surface treated using one of the above-described surface treatments. In addition, the side of the polymeric primer layer opposite the metal surface may be treated to enhance adhesive to other layers using the methods described above, e.g., corona treatment, flame treatment or glow treatment.

In one exemplary embodiment of the present invention, the polymeric primer layer comprises one or more thermoplastic polymeric materials so as to provide the polymeric primer layer with an outer adhesive surface opposite the metal layer. The outer adhesive surface of the polymeric primer layer can be tacky at room temperature (e.g., pressure-sensitive) or after application of heat (e.g., heat-activatable). Thermoplastic polymers

suitable for use in the polymeric primer layer, optionally in combination with a tackifier, for providing an outer adhesive surface include, for example, polyolefins, polyurethanes, nylon, acrylics, and combinations thereof. For example, a polyamide/polyester based laminating adhesive available under the trade designation 3M THERMO-BOND 668 may  
5 be used as the polymeric primer layer.

Suitable pressure-sensitive adhesives and heat-activatable adhesives for use in the polymeric primer layer include, for example, adhesives disclosed in U.S. Pat. No. Re 24,906 (Ulrich) and Eur. Appl. Publ. EP 0 384 598 A1 (Johnson et al.), the disclosures of which are incorporated herein by reference. In addition, the outer adhesive surface of the  
10 polymeric primer layer opposite the metal layer may include a surface topography to provide air-bleed capabilities to the polymeric primer layer, provide repositionability, or both.

At least one of the one or more polymeric materials used to form the polymeric primer layer are cross-linked. As with the polymeric protective layer, the polymeric  
15 primer layer may have various degrees of cross-linking. In some embodiments of the present invention, only an outer surface of the polymeric primer layer adjacent the metal layer is cross-linked. In other embodiments of the present invention, cross-linked polymeric material is essentially distributed throughout an entire thickness of the polymeric primer layer (i.e., the entire polymeric primer layer is subjected to a cross-  
20 linking step as opposed to just an outer surface of the polymeric primer layer). In other embodiments, the degree of cross-linking within the polymeric primer layer varies to form a cross-linking gradient along a thickness of the polymeric primer layer, wherein an outer surface of the polymeric primer layer adjacent the metal layer has a relatively high degree of cross-linking, and the degree of cross-linking within the polymeric primer layer  
25 decreases as the distance from the outer surface of the polymeric primer layer adjacent the metal layer increases. In this embodiment, an outer surface of the polymeric primer layer opposite the metal layer has the smallest degree of cross-linking, if any, relative to the degree of cross-linking of the outer surface of the polymeric primer layer adjacent the metal layer.

Suitable cross-linking methods include any of the cross-linking methods described above with regard to the polymeric protective layer. If a cross-linking gradient is desired in a portion of the metallized film, electron beam cross-linking provides the opportunity to  
30

achieve a cross-linking gradient within the polymeric protective layer, the primer layer, or the overall metallized film construction.

The polymeric primer layer may be transparent to visible radiation so that the metal layer is visible through the polymeric primer layer, i.e., the polymeric primer layer allows at least about 50 percent of visible radiation to pass through the polymeric primer layer. For example, in some embodiments, the polymeric primer layer allows at least about 75 percent, at least about 80 percent, at least about 85 percent, at least about 90 percent, or at least about 95 percent of visible radiation therethrough. In some applications, the polymeric primer layer is colored yet transparent. For example, the polymeric primer layer may contain dyes and/or pigments in order to provide a color to the polymeric primer layer.

The polymeric primer layer may be provided as a preformed layer such as a self-supporting film or may be cast from a solution onto a substrate, such as a release liner or directly on the metal layer. In one exemplary embodiment, the polymeric primer layer is a self-supporting film, such as an ethylene acrylic acid (EAA) copolymer film.

If present as multiple layers, each polymeric primer layer may contribute to the overall metallized film construction. As noted above, at least a portion of the polymeric primer layer adjacent the metal layer is cross-linked. Any additional polymeric primer layers positioned away from the metal layer (i.e., adjacent another polymeric primer layer), may or may not be cross-linked. The additional polymeric primer layer(s) positioned away from the metal layer may serve as a tie layer between the polymeric primer layer adjacent the metal layer and an additional layer (e.g. a polyolefin layer) that has less than desirable adherence to the polymeric primer layer adjacent the metal layer.

Regardless of whether the polymeric primer layer comprises a single layer or multiple layers, the polymeric primer layer adjacent the above-described metal layer has an outer surface that is adjacent to the metal layer and that conforms to the metal layer surface. For example, as discussed above, in some embodiments of the present invention, the outer surface of the polymeric protective layer adjacent the metal layer is a substantially flat, smooth, planar surface having very little, if any, topographical features thereon. In these embodiments, the subsequently applied metal layer has a substantially planar outer surface on which a polymeric primer layer is applied. In these embodiments, the outer surface of the polymeric primer layer adjacent the metal layer also has a

substantially planar outer surface (e.g., a complementary outer surface to the corresponding outer surface of the polymeric protective layer). In other embodiments of the present invention, the outer surface of the polymeric protective layer adjacent the metal layer may have a non-planar surface, such as a surface having topographical features thereon. In these embodiments, the subsequently applied metal layer is a non-planar layer. In these embodiments, the outer surface of the polymeric primer layer adjacent the metal layer has complementary non-planar outer surface that matched the topographical features of the corresponding outer surface of the polymeric protective layer.

Each polymeric primer layer typically has an average thickness of at least about 5 micrometers. Depending on the given application for the metallized film, a polymeric primer layer may have an average thickness of greater than 1.0 millimeter (mm) or more. Typically, a polymeric primer layer has a thickness of at least about 10 micrometers, at least about 15 micrometers, at least about 20 micrometers, or at least about 25 micrometers. The thickness of a polymeric primer layer is usually less than about 50 micrometers although there is no limitation on the thickness of the polymeric primer layer. In some applications, a polymeric primer layer has a thickness less than about 40 micrometers, less than about 35 micrometers, or less than about 30 micrometers. For example, the thickness can be in the range of about 5 to about 50 micrometers, or about 10 to about 40 micrometers, or about 20 to about 30 micrometers.

In some embodiments of the present invention, each of the polymeric protective layer and the polymeric primer layer independently comprise one or more cross-linked polymeric components, and at least one polymeric component in each layer has functional groups thereon resulting in a similar overall surface charge or surface polarity for (i) the outer surface of the polymeric protective layer adjacent the metal layer (e.g., second outer surface 131 of polymeric protective layer 13 shown in Fig. 1), and (ii) the outer surface of the polymeric primer layer adjacent the metal layer (e.g., outer surface 111 of polymeric primer layer 11 shown in Fig. 1). An example of such an embodiment is shown in Fig. 4.

As shown in Fig. 4, each of second outer surface 131 of polymeric protective layer 13 and outer surface 111 of polymeric primer layer 11 has a positive surface charge or surface polarity on either side of metal layer 12. Although not shown, it should be understood that second outer surface 131 of polymeric protective layer 13 and outer surface 111 of polymeric primer layer 11 could have a negative surface charge or surface

polarity on either side of metal layer 12. As explained above, polymeric component may be used to provide a particular surface charge or surface polarity to a given surface. In other embodiments, additives may be used in each layer to provide a particular surface charge or surface polarity to a given surface. For example, one or more additives selected  
5 from the following additives may be used to provide a surface charge or surface polarity to a given surface: (i) additives having thereon an acidic functional group such as sulfonic acids, phosphoric acids, phosphonic acids, boric acids, carboxylic acids, salts of these acids, esters of these acids, or combinations thereof, and (ii) additives having thereon a  
10 basic functional group such as mercapto groups, amine groups, alkoxy groups, nitrile groups, heterocyclic moieties such as those described in U.S. Pat. No. 5,081,213 (Carlson), and the like. Exemplary additives include, for example, benzotriazoles, oxygen or sulfur containing compounds such as mercaptosilane.

In one exemplary embodiment, the polymeric component having functional groups thereon may comprise, for example, a waterborne polyurethane, a solvent-based  
15 polyurethane, a polymer or copolymer having acidic monomers therein (e.g., an ethylene acrylic acid (EAA) copolymer), or a polymer or copolymer having basic monomers therein (e.g., polyamides, or polyacrylamide copolymers).

In some embodiments of the present invention, each of the polymeric protective and polymeric primer layers independently comprises one or more cross-linked polymeric  
20 materials alone or in combination with one or more additives, wherein at least one of the polymeric materials or additives in each layer has acidic or basic functional groups thereon. In a further exemplary embodiment, each of the polymeric protective and polymeric primer layers independently comprises one or more cross-linked polymeric materials alone or in combination with one or more additives, wherein (i) at least one of  
25 the polymeric materials or additives in each layer has acidic functional groups, (ii) at least one of the polymeric materials or additives in each layer has basic functional groups, (iii) the outer surface of either layer adjacent the metal layer has a corona discharge or glow discharge surface treatment, (iv) both (i) and (iii), or (v) both (ii) and (iii).

#### 4. *Adhesive Layer*

30 The metallized films of the present invention may further comprise at least one adhesive layer, such as exemplary adhesive layer 14 of exemplary metallized film 10, for example, if an outer surface of the above-described corrosion-resistant metallized film

does not possess a desired degree of adhesive properties (e.g., if an second outer surface of the polymeric primer layer does not possess adhesive properties). In this embodiment, the adhesive layer covers an outer surface of the polymeric primer layer as shown in exemplary metallized film 10 of Fig. 1. Suitable adhesive layers include, for example, pressure-sensitive adhesive layers, heat-activatable adhesive layers, or a combination thereof. The pressure-sensitive adhesive layer may be a thermoplastic adhesive layer, a thermosetting adhesive layer, and/or a microstructured pressure-sensitive adhesive layer.

Any suitable adhesive polymer can be included in the adhesive layer. The adhesive polymer can be thermoplastic, thermosetting, or a combination thereof. The adhesive surface can be tacky at room temperature (e.g., pressure-sensitive) or after application of heat (e.g., heat-activatable). Suitable thermoplastic adhesives include, for example, polyolefins, polyurethanes, epoxies, nylon, acrylics, and combinations thereof. Suitable thermosetting adhesives include, for example, one or two part epoxies, one or two part polyurethanes, one or two part acrylics, or combinations thereof.

Suitable pressure-sensitive adhesives and heat-activatable adhesives for use in the present invention include, for example, adhesives disclosed in U.S. Pat. No. Re 24,906 (Ulrich) and Eur. Appl. Publ. EP 0 384 598 A1 (Johnson et al.), the disclosures of which are incorporated herein by reference.

In some embodiments, the adhesive layer on the outer surface of the polymeric primer layer comprises a pressure-sensitive adhesive, a hot melt adhesive, or a combination thereof. In one desired embodiment, the adhesive layer comprises a pressure-sensitive adhesive. If the adhesive layer has a pressure-sensitive adhesive outer surface, a release liner may be used to provide temporary protection to the pressure-sensitive adhesive outer surface.

In a further desired embodiment, the adhesive layer comprises a heat-activatable adhesive, such as a hot melt adhesive. In yet a further desired embodiment, the adhesive layer comprises a pressure-sensitive adhesive layer next to the polymeric primer layer, and a heat-activatable adhesive, such as a hot melt adhesive, on an outer surface of the pressure-sensitive adhesive layer.

Polar functional groups within the adhesive polymer (or the other above-described polymeric layers) may be used to promote adhesion between the polymeric primer layer (or the polymeric protective layer) and the metal layer, as well as adhesion between the

polymeric primer layer (or the polymeric protective layer) and the adhesive layer. Representative polar groups include, for example, acids (e.g., sulfonic acids, phosphoric acids, phosphonic acids, boric acids, and carboxylic acids), salts of these acids, esters of these acids, or combinations thereof. Other representative polar groups include amine groups, alkoxy groups, nitrile groups, heterocyclic moieties such as those described in U.S. Pat. No. 5,081,213 (Carlson), and the like.

In some embodiments, the polar groups are acids groups, esters thereof, or salts thereof. For example, the polar groups are carboxylic acids, carboxylate esters, or carboxylate salts. Suitable carboxylic acids, carboxylate esters, and carboxylate salts include, for example, acrylic acid, C<sub>1</sub> to C<sub>20</sub> acrylate esters, acrylate salts, (meth)acrylic acid, C<sub>1</sub> to C<sub>20</sub> (meth)acrylate esters, (meth)acrylate salts, or combinations thereof. Such groups typically can provide suitable adhesion to other surfaces such as polymeric layers, metal layers, and combinations thereof.

#### *B. Metallized Film Properties*

The metallized films of the present invention may possess one or more of the following properties. Isolating and constraining the metal layer between a cross-linked polymeric protective layer and a cross-linked polymeric primer layer enables the metal layer to maintain an overall planar orientation, which is a critically important for maintaining a desirable aesthetic mirror-like appearance. It also serves to achieve a level of performance if the film is exposed to elevated temperature environments during application processing steps such as heat-activated adhesive bonding, thermoforming or in actual use in the field. In prior art cases, direct contact is made between a metal layer and at least one thermoplastic layer. In this case, as the temperature is increased and approaches the softening point of the film, the metal layer becomes susceptible to movement itself that is a direct result of movement within the thermoplastic polymer layer. Simply going through a softening transition is capable of disrupting the metal layer and destroying the optical quality of the film.

It is also surprising that by isolating the metal layer between a cross-linked polymeric protective layer and the polymeric primer layer, the optical qualities of the metal layer are extremely stable to film deformation. In fact, it is very surprising that the shear magnitude of film deformation (in some cases greater than 100% or even greater than 150% film elongation) produces only a slight and acceptable loss of film opacity. In



contrast, this magnitude of film deformation of a similar film construction that does not comprise cross-linked polymeric protective and primer layers produces much greater, and typically, unacceptable loss in film opacity. This loss of opacity if using a thermoplastic layer in direct contact with the metal layer is proposed to result from irreversible stretch  
5 that is not recoverable due to the plastic-like flow that occurs in the thermoplastic layer. The effect of cross-linking the film limits plastic-like flow within the material and thus significantly reduces irreversible stretch in the film.

The metallized film comprising the polymeric protective layer, the metal layer, and polymeric prime layer serve as a standardized platform that can accommodate a variety of  
10 finished product constructions utilizing different adhesive layers. This affords the base metallized film the opportunity to be integrated into a variety of applications for the purpose of providing a stable and consistent look to various articles. For instance, the polymeric prime layer can be corona treated and an acrylic PSA laminated to the surface, which then allows the resulting metallized film to be simply laminated to a substrate such  
15 as a 'B' pillar post on an automobile. This provides the 'B' pillar a metallic chrome-like appearance. The same film construction can further be laminated with a heat-activatable adhesive, which can then be heat laminated to a weatherseal and installed on a automobile door surround, achieving the same look on the two disparate surfaces. Furthermore, the base metallized film can be thermoformed, and reinforced with a resin to provide metallic,  
20 chrome-like raised letters such as with an automotive identification badge. This can then be installed on the vehicle. In all three cases, the same base metallized film is capable of being modified to accommodate different processing conditions and adhesive requirements to provide a consistent appearance on a variety of surfaces on the automobile. This flexibility in use and application is a significant improvement over film  
25 constructions prior to the present invention.

## II. *Articles of Manufacture Including a Metallized Film*

The present invention is further directed to articles of manufacture, which include one or more of the above-described metallized films. The articles of manufacture of the present invention may comprise one or more of the following components in addition to  
5 the polymeric primer layer, the metal layer, the polymeric protective layer, and the optional adhesive layer described above.

### A. *Release Liner(s)*

Articles of the present invention may further include at least one release liner in addition to the above-described layers of the metallized films. As described above, a first  
10 release liner may be used to provide support for the polymeric protective layer, as well as temporary protection of the polymeric protective layer prior to removal of the first release liner. If a tacky adhesive layer (e.g., a pressure-sensitive adhesive layer) is present in an article of the present invention, such as the polymeric primer layer or an outer surface of the polymeric protective layer, a second release liner may be used to provide temporary  
15 protection of the adhesive layer prior to removal of the second release liner. Such an exemplary article is shown in Fig. 5.

As shown in Fig. 5, exemplary article 20 comprises a metallized film 25 comprising polymeric primer layer 11, metal layer 12, polymeric protective layer 13, and adhesive layer 14. In addition, article 20 comprises a first release liner 15 on first outer  
20 surface 133 of polymeric protective layer 13 and a second release liner 16 on outer surface 151 of adhesive layer 14. The presence of the first and second release liners allows a metallized film having a pressure sensitive adhesive outermost surface to be supplied in roll form. The release liner (i.e., exemplary second release liner 16 on outer surface 151 of adhesive layer 14 as shown in Fig. 5) can be removed for attachment of the metallized  
25 film to a surface of a substrate. The presence of the first and second release liners 15, 16 can also help minimize contamination of the adhesive layer on the metallized film, prevent damage to the polymeric protective layer, and facilitate handling of the metallized film.

The first and second release liners typically include one or more layers of materials. In some embodiments, the release liner contains a layer of paper, polyester,  
30 polyolefin (e.g., polyethylene or polypropylene), or other polymeric film material. The release liner can be coated with a material to decrease the amount of adhesion between the release liner and the adhesive layer. Such coatings can include, for example, a silicone or

fluorochemical material. Any commercially available release liner may be used in the present invention.

As discussed above, first release liner 15 may be used to provide topographical features to first outer surface 133 of polymeric protective layer 13. In addition, if desired, second release liner 16 may be used to provide topographical features to outer surface 151 of adhesive layer 14. For example, either release liner may provide a uniform (or non-uniform) pattern of valleys and/or ridges along an outer surface of polymeric protective layer 13 and/or adhesive layer 14. In some embodiments, either release liner may be used to provide an outer surface of polymeric protective layer 13 and/or adhesive layer 14 with a substantially smooth surface. As discussed above, release liners suitable for use in the present invention include, for example, release liners disclosed in U.S. Pat. No. 6,984,427 (Galkiewicz et al.).

Fig. 6 provides a view of article 20 of Fig. 5 attached to a given substrate after first release liner 15 and second release liner 16 have been removed. Once second release liner 16 has been removed, article 20 may be attached to substrate 18 using pressure with or without heat. Substrate 18 may be any substrate including, but not limited to, a polymeric substrate (e.g., a film, a foam, or a molded article), a glass substrate, a ceramic substrate, a metal substrate, and/or a fabric. Articles of the present invention may be useful in the preparation of various decorative items including, but not limited to, badging for automobiles and appliances, emblems, mirror films, solar reflecting films, decorative film laminates, and/or graphics. For some uses, one of the layers of article 20 may be colored.

#### *B. Thermoformable Layer(s)*

Articles of the present invention may include at least one of the above-described metallized films in combination with at least one thermoformable layer. One or more thermoformable layers may be positioned on the outer surface of the polymeric protective layer, the polymeric primer layer, or both. Thermoformable layers may be adhesively attached to the metallized film via the polymeric primer layer or an additional adhesive layer, or may be a component (e.g., a layer) used during the formation of the polymeric protective layer, the polymeric primer layer, or both. The resulting thermoformable article comprising at least one of the above-described corrosion-resistant metallized films in combination with at least one thermoformable layer may be thermoformed to form a

thermoformed article comprising a corrosion-resistant metallized film. Any conventional thermoforming technique (e.g., molding) may be used to form the thermoformed article. Thermoformable materials suitable for use in the present invention include, for example, any thermoplastic material, a thermosetting material, or a combination thereof.

5 Thermoplastic materials such as ABS (acrylonitrile/butadiene/styrene), polycarbonate, polyester, polyurethane, polypropylene, polyethylene, acrylics, vinyls, and polyolefin blends are examples of useful thermoformable materials. In one desired embodiment, the thermoformable layer comprises an engineering thermoplastic material. Suitable  
10 engineering thermoplastic materials include, for example, polycarbonates, polyesters (e.g., polybutylene terephthalate), some polyethylenes, polyamides, polysulfones, polyetheretherketones (PEEK), ABS (acrylonitrile/butadiene/styrene), SAN (styrene/acrylonitrile), polyurethanes, polyacrylics, and blends thereof.

In a further desired embodiment, the thermoformable article comprises at least one of the above-described metallized films in combination with a polycarbonate or polyester  
15 thermoformable layer. The polycarbonate or polyester thermoformable layer may be bonded directly to the outer adhesive surface of the polymeric primer layer (e.g., if the polymeric primer layer comprises a cross-linked PSA) or to an additional adhesive layer (e.g., a PSA layer) on the outer surface of the polymeric primer layer.

The resulting thermoformable or thermoformed articles may be used in a variety of  
20 applications. In one exemplary embodiment, the thermoformable or thermoformed articles are used in signage, such as outdoor signage and backlit displays. Such displays typically comprise a box, which houses a light fixture, wherein the front face of the box housing is covered with a film. One such device in which the front face is covered with a transparent film is described in U.S. Pat. No. 5,224,770 (Simmons et al.), the disclosure of  
25 which is incorporated herein by reference. Another such device in which the front face is covered with a perforated film is described in U.S. Pat. No. 6,767,609 (Aeling et al.), the disclosure of which is incorporated herein by reference, wherein a perforated film is placed over a housing so that the film reflects light during the day to display an image, but can be backlit at night to illuminate an image or indicia from behind the film.

30 The metallized films may be used similar to the transparent film in the '770 and '609 patents. The metallized films of the present invention and thermoformable or thermoformed articles made therefrom have sufficient light transmission, typically about

15-25% light transmission, so as to illuminate the sign from the backside at night or in the dark. The metallized films desirably comprise enough metal coated on the film so as to reflect light during the daytime or in a lit room to display an image (e.g., a three-dimensional image that was thermoformed in the film). In one specific embodiment of the present invention, the film is imaged (e.g., graphics are applied to the metallized film) on the polymeric protective layer side and is then coated with a pressure sensitive or heat activated adhesive on the polymeric primer side. The film can then be laminated to a suitable polymeric material, such as an engineering thermoplastic, and then thermoformed to a desired shape to form a cover for a housing containing a light. Alternatively, the film can be laminated to the thermoplastic and thermoformed to provide a three dimensional image. Such constructions are suitable for daylight/nighttime signage.

*C. Additional Top Coat Layer(s)*

Articles of the present invention may include at least one of the above-described metallized films in combination with one or more additional top coat layers provided on the outer surface of the polymeric protective layer. Suitable top coat layer materials include, for example, polymeric materials used to form the above-described polymeric protective layer. If present, the one or more additional top coat layers (i) provide some form of protection to the polymeric protective layer (e.g., UV protection, scratch resistance, and/or weather resistance), (ii) acts as a tie layer between the polymeric protective layer and an additional layer that has less than desirable adherence to the polymeric protective layer (e.g., a polyolefin layer), or (iii) both (i) and (ii).

*D. Permanently Attached Substrate(s)*

Articles of the present invention may include at least one of the above-described metallized films in combination with one or more permanently attached substrate layers provided on the outer surface of the polymeric protective layer, the polymeric primer layer or both. As discussed above, suitable substrate layers (e.g., exemplary substrate 18 shown in Fig. 6) include, for example, a polymeric substrate (e.g., a film, a foam, or a molded article), a glass substrate, a ceramic substrate, a metal substrate, or a fabric. In one desired embodiment of the present invention, the substrate comprises an elastomeric substrate.

The elastomeric substrate can be a thermoset material formed, for example, by cross-linking an ethylene-propylene-diene monomer. Alternatively, the elastomeric substrate can be a thermoplastic material formed, for example, by blending a rubbery

material with a thermoplastic material. Suitable thermoplastic materials include, for example, polyethylene, polypropylene, and polyvinyl chloride. Suitable rubbery materials include, for example, ethylene-propylene rubbers, ethylene-propylene-diene rubbers, nitrile rubbers, polychloroprene, chlorosulfonated polyethylene, and styrene butadiene  
5 rubbers. The rubbers can be vulcanized, dynamically vulcanized or non-vulcanized. Commercially available elastomeric substrate materials include, for example, those having the trade designations SANTOPRENE, VYRAM, GEOLAST, TREFSIN, VISTAFLEX, or DYTRON. The thermoplastic or thermoset material is often compounded with a variety of additives and fillers such as carbon black, stabilizers, plasticizers, and the like.

10 The amount of thermoplastic or thermoset material can vary widely depending upon the physical properties sought for the application and is typically at least about 15 weight percent based on the weight of the elastomeric material. In some embodiments, the weight of thermoplastic material is no greater than about 85 weight percent, no greater than about 70 weight percent, or no greater than about 60 weight percent based on the  
15 weight of the elastomeric material. The amount of rubbery material is at least about 5 weight percent based on the weight of the elastomeric material. In some embodiments, the weight of the rubbery material is no greater than about 85 weight percent, no greater than about 70 weight percent, or no greater than about 60 weight percent based on the weight of the elastomeric material.

20 In some elastomeric materials, the weight ratio of rubbery material to thermoplastic or thermoset material is from about 5:95 to about 95:5. For example, the weight ratio of rubbery material to thermoplastic or thermoset material can be from about 20:80 to about 80:20, from about 30:70 to about 70:30, or from about 40:60 to about 60:40.

25 In one desired embodiment of the present invention, the article comprises at least one of the above-described metallized films permanently attached to a substrate layer in the form of an elastomeric weatherseal. In this embodiment, the metallized film may be permanently attached to the weatherseal via a heat-activatable adhesive layer alone or in combination with a separate pressure-sensitive adhesive layer positioned between the heat-  
30 activatable adhesive layer and the metallized film. For example, a heat bond laminator, such as Heat-Bond Laminator MODEL TE 2417 from EHVO GmbH (Kuehnheide, Germany), may be used to preheat a weatherseal (e.g., an EPDM rubber profile) directly

before contacting the weatherseal with the heat-activated adhesive surface of the metallized film. An exemplary temperature of the air stream used to pre-heat the weatherseal may be about 650°C at a flow rate of about 90 liters/min. The tape application speed can be about 12 m/min with an infrared radiation setting at 55 percent.

5 Further details concerning various polymeric primer layers, metal layers, and polymeric protective layers may be found, for example, in PCT Pat. Appln. No. US2006/010786 (Steelman et al.), filed March 24, 2006, the disclosure of which is incorporated herein by reference.

10 Objects and advantages of this invention are further illustrated by the following non-limiting examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and, details, should not be construed to unduly limit this invention.

## EXAMPLES

### Example 1

An 8.5 mil thick polycarbonate film (trade designation LEXAN from GE Plastics (Pittsfield, MA)) was loaded around the cooling drum of a metal vapor coating chamber. The cooling drum temperature was set at 15.6 °C (60 °F) and the chamber was pumped down to a vacuum of about  $3 \times 10^{-5}$  torr (4 mPa). Behind a shuttered aperture, an electron beam gun was used to heat two graphite crucibles holding tin by gradually increasing the power to a setting of 220 milliAmps. The film was pulled over the cooling drum at a speed of 3.05 mpm (10 feet/minute) past the partially opened aperture exposing the film to vaporous metal and allowing the metal to condense onto the film to form a metallized film. Conditions were adjusted to obtain a metallized film having an optical density of less than 2. The optical density was calculated by taking the negative logarithm of the light transmittance of the film and the transmittance was measured using a Macbeth model TD504 densitometer. The surface resistivity of the coated film was about 10 ohms/cm<sup>2</sup>. The surface resistivity was measured using a model 717 CONDUCTANCE MONITOR manufactured by Delcom Instruments, Inc. (Prescott, WI). The surface resistivity was recorded in ohms/cm<sup>2</sup>. Surface conductivity is the reciprocal of the resistance units and was recorded in mhos.

An EAA (ethylene acrylic acid available under the trade designation PRIMACOR 3330 from Dow Chemical Company (Midland, MI)) film was extruded to a thickness of 30.5 μm (1.2 mil) thick onto a silicone release coated polyester film. The EAA film was then cross-linked by exposure to 5 Mrads of electron beam radiation at 175 kV to form a primer layer.

The metal-coated polycarbonate film was then laminated to the EAA primer layer using a hot can set at 112.8 °C (235 °F). After cooling to room temperature the polycarbonate film was carefully peeled away from the metal layer, leaving it adhered to the EAA layer. The resulting metallized EAA layer exhibited no visible distortion of the metal layer. A 2-part polyurethane composition was prepared by mixing 6 parts of an aliphatic isocyanate (trade designation DESMODUR N3300 available from Bayer, Inc. Material Science (Toronto, Ontario, Canada)) with 6.6 parts of a polyester polyol (trade designation KFLEX 188 available from King Industries, Inc. (Norwalk, CT)), 0.55 parts of



a polycaprolactone polyol (trade designation TONE POLYOL 0305 available from Dow Chemical Co. (Midland, MI)), and 2 drops of dibutyltin dilaurate. All amounts were in parts by weight. The two substrates were positioned between a slotted knife and a platen with a gap of about 0.15 mm (6 mils) between the two substrates. The composition was  
5 fed between the two substrates to form a rolling bank just in front of the slotted knife. The top substrate was a silicone release coated polyester film, and the bottom substrate was the EAA layer on the polyester film with the metallized side of the EAA film receiving the coating. The substrates were allowed to polymerize at room temperature overnight. The next day the polyester release films were removed to provide a metallized composite film  
10 having superior corrosion resistance as measured by exposing the film to a copper chloride accelerated salt spray environment. The EAA side of the film was available for further bonding to other substrates.

#### Example 2

15 A 2-part polyurethane composition was prepared by mixing 6 parts of an aliphatic isocyanate (trade designation DESMODUR N3300 available from Bayer, Inc. Material Science) with 7.6 parts of a polyester polyol (trade designation KFLEX 188 available from King Industries, Inc., Norwalk, CT), and 2 drops of dibutyltin dilaurate. All amounts were in parts by weight. Two silicone-coated polyester release liners were positioned between a  
20 slotted knife and a platen with a gap of about 0.15 mm (6 mils) between the two substrates. The composition was fed between the two release liners to form a rolling bank just in front of the slotted knife. The coating was allowed to polymerize at room temperature on a flat surface over the course of several days to form a polyurethane protective layer. The top polyester release liner was then removed from the coated film  
25 laminate and the polyurethane film surface was oxygen glow discharge treated and then metallized according to the conditions outlined in Example 1.

The crosslinked EAA film on a polyester liner, described in Example 1, was then laminated to the metallized polyurethane surface using a hot can set a 112.8 °C (235 °F) to form a film composite. The polyester release liners were removed from both sides of the  
30 film composite and the film was tested for corrosion resistance. It exhibited superior corrosion resistance as measured by exposing the film to a copper chloride accelerated salt spray environment for 24 hours.

## Example 3

The liners were removed from the film composite of Example 2 and the film was thermoformed by positioning it with the polyurethane protective layer against a gas-porous mold so that it covered the entire surface of the mold. Vacuum was then applied to the mold which was held at a temperature of 150 °F (65.6 °C) and the film was then observed to elongate into the recessed areas of the mold. A two-part polyurethane backfill resin was then deposited into the recessed, thermoformed areas of the mold and an acrylic pressure-sensitive adhesive on a release coated paper liner was laminated against the backfill resin using a roller so that the excess backfill resin was removed. After the resin gelled, the vacuum was released and the thermoformed sheet was removed from the mold. The thermoformed metallized film surface was observed to be highly reflective and specular and exhibited a mirror-like appearance in all areas of the molded part.

## Example 4

The polyester release film was removed from the EAA side of the film laminate of Example 2, and the EAA surface was corona treated at atmospheric pressure at a speed of 3.05 m/minute (10 feet/minute) with a power setting of 26 Hz and 250 watts. The EAA surface was then laminated to a layer of acrylic pressure-sensitive adhesive on a release liner using a nip roll heated to about 65.6 °C (150 °F). The acrylic adhesive had a composition of 81 parts of isooctyl acrylate and 19 parts of acrylic acid. The acrylic adhesive was then bonded to the primed surface of a layer thermoplastic heat-activatable adhesive. The heat-activatable adhesive was a thermoplastic copolymer of ethylene and propylene (trade designation PP7035E5 IMPACT COPOLYMER available from ExxonMobil Chemical Co. (Houston, TX)). The heat-activatable adhesive was primed by grafting N,N-dimethylacrylamide onto the surface using electron beam radiation according to the procedure described in EP 0 384 598 A1 (Johnson et al.). The resulting laminate was then heat bonded to a wing-shaped weatherseal using a heat pressure laminator, trade designation MODEL WL-30 LAMINATOR, 3M Company (St. Paul, MN), by heating the weatherseal surface and the heat-activatable adhesive side of the metallized laminate with a stream of hot air just before the two surfaces are laminated together using the applicator wheel of the laminator. The weatherseal was formed from a dynamically vulcanized

elastomer that was a blend of propylene and EPDM rubber commercially available from Advanced Elastomer Systems, LLP (Akron, OH) under the trade designation SANTOPRENE.

5 The resulting weatherseal had a specular appearance that could be deformed by (i) pressing on it with hand pressure or (ii) by wrapping the composite article completely around a 6.35 mm (0.25 inch) mandrel without losing its metal-like appearance and exhibited good elastic recovery. The elastic recovery is the amount of recovery that the film underwent after stretching. The stretched film was allowed to come to a final film length by laying the sample on a flat surface for at least an hour at ambient temperature  
10 (about 22 °C) before measuring. Most of the recovery of the film occurred within the hour.

#### Example 5

A polyurethane film was prepared according to the procedure for Example 2  
15 except that the bottom substrate was a second silicone release coated polyester film. After curing, one of the polyester films was removed. The polyurethane film on the release film was corona treated and then metallized according to the procedure for Example 1 except that the exposed polyurethane film was on the outside of the drum and the polyester film was against the coating drum. The vacuum in the coating chamber dropped to about  $10^{-6}$   
20 torr (0.1 mPa) indicating that no volatiles were pulled out of the film in the coating chamber. The crosslinked EAA primer was laminated to the metal layer using a hot can set at 112.8 °C (235 °F).

## Example 6

The release liner was removed from the EAA side of the polyurethane film of Example 2, and the EAA surface was laminated to a layer of 1.5 mil (0.38 micron) thick cross-linked acrylic pressure-sensitive adhesive on a release liner. The hot melt acrylic adhesive had a composition of 95.42 parts 2-methyl butyl acrylate, 3.98 parts acrylamide and 0.60 parts benzophenone that had been cross-linked by exposure to 500 mJ/cm<sup>2</sup> of UV-A radiation from a medium pressure mercury lamp.

Sheets of 1.59 mm (0.0625 inch) thick polycarbonate (available from McMaster Carr (Elmhurst, IL)) measuring 30.5 cm (12 in) by 30.5 cm (12 in) were dried for 3 hours at 65.6 °C (150 °F).

The pressure-sensitive adhesive side of the metallized film was laminated to the polycarbonate sheet to form a laminated stack sample. The laminated stack samples were dried at 65.6 °C (150 °F) for 12 hours.

The samples were thermoformed on a LABFORM 2024 THERMOFORMER (available from Hydro-Trim Corporation (W. Nyack, NY)) with the polycarbonate side of the stack against the surface of a mold made of medium density fiberboard. The mold was rectangular having overall length and width dimensions of about 17.8 cm (7 in) by 17.8 cm (7 in) and a height of 3.8 cm (1.5 in). The opposing width edges each had an enclosed angle of 80 degrees. The length edges had an enclosed angle of 60 degrees on one edge and an enclosed angle of 75 degrees on the opposing edge. The mold had a V-shaped groove with a 90 degree enclosed angle, and positioned a distance of 8.9 cm (3.5 in) from the edge having an enclosed angle of 60 degrees. The groove divided the planar surface of the mold into a large planar surface and a small planar surface with the bottom of the groove positioned 9.6 mm (0.38 in) above the lower edge. The stack was heated on both sides for 90 seconds using an oven set at an oven temperature of 229.4 °C (445 °F), then vacuum formed over the mold for 9 seconds with the polycarbonate side of the stack against the mold. The resulting molded part had a mirror like finish and exhibited small amounts of extension.

## Example 7

A metallized polyurethane protective film was prepared according to the procedure outlined in Example 2, except that the EAA film was not laminated to it. The hot melt

adhesive of Example 6 was laminated directly onto the metal layer. The resulting adhesive coated film was laminated onto a polycarbonate sheet to form a laminated stack sample, dried, and thermoformed according to the procedure outlined in Example 6. The resulting molded part had a mirror like finish.

5

Various modifications and alterations of this invention may be made by those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

We claim:

1. A metallized film comprising:
  - 5 a polymeric primer layer comprising a first polymer at least a portion of which is cross-linked;
  - a polymeric protective layer comprising a second polymer at least a portion of which is cross-linked; and
  - 10 a metal layer between the polymeric primer layer and the polymeric protective layer;wherein the polymeric protective layer has a first outer surface opposite the metal layer and a second outer surface adjacent to the metal layer, wherein the first and second outer surfaces have a respective predetermined surface topography, and wherein (i) the polymeric primer layer has an outer adhesive surface opposite the metal layer or (ii) the  
15 metallized film further comprises an adhesive layer on the polymeric primer layer opposite the metal layer, the adhesive layer having an outer adhesive surface opposite the polymeric primer layer.
2. The metallized film of claim 1, wherein the first and second outer surfaces have  
20 respective predetermined surface topographies that correspond to surfaces of release liners used in their formation.
3. The metallized film of claim 1, wherein the respective predetermined surface  
25 topography of at least one of the first and second outer surfaces corresponds to a surface of a mold used in its formation.
4. The metallized film of any one of claims 1 to 3, wherein the metal layer is a  
visually continuous layer having a discontinuous conductivity.
- 30 5. The metallized film of any one of claims 1 to 4, wherein the metal layer has a conductivity of less than about 10 mhos.

6. The metallized film of any one of any one of claims 1 to 5, wherein the metal layer has a surface resistivity of at least about 3 ohms/cm<sup>2</sup>.
7. The metallized film of any one of claims 1 to 6, wherein the outer adhesive surface  
5 comprises a pressure sensitive adhesive or a hot melt adhesive.
8. The metallized film of any one of claims 1 to 7, wherein the outer adhesive surface comprises a pressure sensitive adhesive
9. The metallized film of any one of claims 1 to 8, wherein the metallized film  
10 comprises a pressure sensitive adhesive layer and a hot melt adhesive layer.
10. The metallized film of claim 9, wherein the outer adhesive surface comprises a pressure sensitive adhesive and a hot melt adhesive layer is attached to the outer adhesive  
15 surface.
11. The metallized film of any one of claims 1 to 10, further comprising a release liner covering at least one outermost surface of the metallized film.
12. The metallized film of any one of claims 1 to 11, wherein at least one outermost  
20 surface of the metallized film has topographical features thereon.
13. The metallized film of any one of claims 1 to 12, wherein both a first surface of the first polymer and a second surface of the second polymer face the metal layer and have: (i)  
25 acidic functional groups on the first and second surfaces, (ii) basic functional groups on the first and second surfaces, (iii) a corona discharge or glow discharge surface treatment, (iv) both (i) and (iii), or (v) both (ii) and (iii).
14. The metallized film of any one of claims 1 to 13, wherein the polymeric primer  
30 layer, the polymeric protective layer, or both comprise a waterborne polymeric material.

15. The metallized film of any one of claims 1 to 14, wherein the first and second polymers are substantially cross-linked throughout a thickness of the polymeric primer layer and the polymeric protective layer.
- 5 16. The metallized film of any one of claims 1 to 15, wherein the polymeric protective layer comprises a cross-linked polyurethane, a cross-linked polymer or copolymer containing carboxyl groups thereon, a cross-linked polyolefin, a cross-linked ethylene/vinyl acetate/acid terpolymer, or a combination thereof; and the polymeric primer layer comprises a cross-linked polyurethane, a cross-linked polymer or copolymer  
10 containing carboxyl groups thereon, a cross-linked polyolefin, a cross-linked ethylene/vinyl acetate/acid terpolymer, or a combination thereof.
17. The metallized film of any one of claims 1 to 16, wherein the polymeric protective layer comprises an optically clear cross-linked polyurethane; and the polymeric primer  
15 layer comprises a cross-linked ethylene acrylic acid copolymer.
18. The metallized film of any one of claims 1 to 17, wherein the metal layer comprises indium, aluminum, tin, stainless steel, copper, silver, gold, chromium, nickel, alloys thereof, or a combination thereof.  
20
19. The metallized film of any one of claims 1 to 18, further comprising an adherable substrate adhesively bonded to the outer adhesive surface.
20. The metallized film of claim 19, wherein the adherable substrate comprises an  
25 elastomeric substrate.
21. The metallized film of claim 20, wherein the elastomeric substrate comprises a weatherseal substrate.
- 30 22. The metallized film of claim 21, wherein the adherable substrate comprises a thermoformable layer.



23. The metallized film of claim 22, wherein the thermoformable layer comprises polycarbonate or polyester.

5 24. The metallized film of claim 23, wherein the thermoformable layer comprises polycarbonate.

25. A thermoformable article comprising the metallized film of any one of claims 1 to 19 and 22 to 24.

10 26. A molded part comprising the metallized film or thermoformable article of any one of claims 1 to 19 and 22 to 24.

27. Signage comprising the metallized film, thermoformable article or molded part of any one of claims 1 to 19 and 22 to 26.

15

28. Backlit signage comprising the metallized film, thermoformable article or molded part of any one of claims 1 to 19 and 22 to 26.

29. A method of forming a metallized film, the method comprising the steps of:

20 providing a polymeric protective layer having first and second outer surfaces by a method comprising: forming a rolling bank of a first cross-linkable composition, wherein the rolling bank contacts first and second forming substrates; passing the first and second release liners with the cross-linkable composition therebetween through a nip; at least partially cross-linking the cross-linkable composition to provide a polymeric protective layer; and removing the second liner from the at least partially crosslinked polymeric protective layer to expose the second outer surface;

25

depositing a metal layer over at least a portion of the second outer surface of the polymeric protective layer;

applying a second cross-linkable composition over the metal layer;

30

at least partially cross-linking the second cross-linkable composition to provide a polymeric primer layer; and

optionally applying an adhesive layer over the polymeric primer layer;

wherein either (i) the polymeric primer layer has an outer adhesive surface opposite the metal layer or (ii) the metallized film comprises the adhesive layer over the polymeric primer layer opposite the metal layer, the adhesive layer having an outer adhesive surface opposite the polymeric primer layer.

5

30. The method of claim 29, wherein the first and second forming substrates with the first cross-linkable composition therebetween are passed through the nip under conditions sufficient to provide a substantially void-free layer of the first cross-linkable composition.

10

31. The method of claim 29 or 30, wherein the first cross-linkable composition comprises a two-part urethane cross-linkable composition.

32. The method of any one of claims 29 or 31, wherein the first cross-linkable composition is solvent-free.

15

33. The method of any one of claims 29 or 32, further comprising applying an adhesive layer over the polymeric primer layer.

34. The method of any one of claims 29 to 33, further comprising surface treating the second outer surface of the polymeric protective layer, an outer surface of the polymeric primer layer, or both using a corona discharge surface treatment, a flame surface treatment, or a glow discharge surface treatment.

20

35. The method of any one of claims 29 to 34, further comprising attaching at least one additional layer to an outer surface of the polymeric primer layer opposite the first surface, an outer surface of the protective layer opposite the second surface, an outer surface of the adhesive layer if present, or a combination thereof.

25

36. The method of claim 35, wherein the at least one additional layer comprises a release liner.

30

37. The method of any one of claims 29 to 36, further comprising providing topographical features to one or both outermost surfaces of the metallized film.

5 38. The method of any one of claims 34 to 37, wherein the step of cross-linking the polymeric protective layer occurs after the attaching step.

39. The method of any one of claims 29 to 38, further comprising attaching a thermoformable layer to the outer adhesive surface to form a thermoformable article.

10 40. The method of claim 39, further comprising thermoforming the thermoformable article.

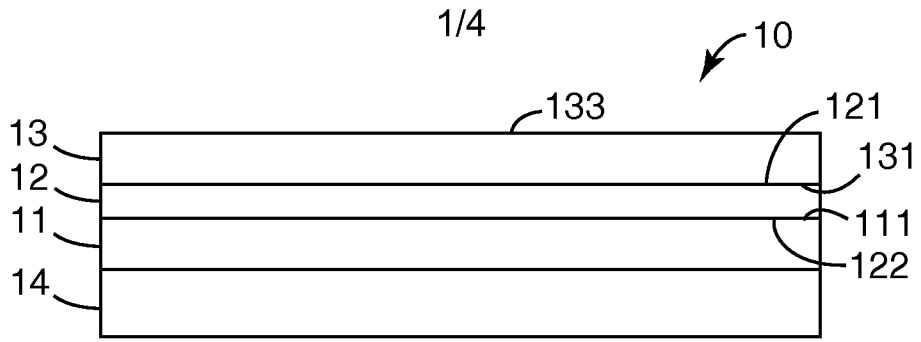
41. The method of any one of claims 29 to 40, further comprising applying graphics to the metallized film.

15

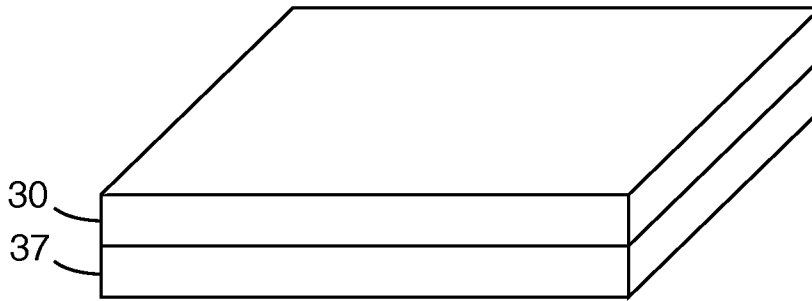
42. The method of any one of claims 29 to 41, further comprising incorporating the metallized film into signage or backlit signage.

43. A product made by the process of any one of claims 29 to 42.

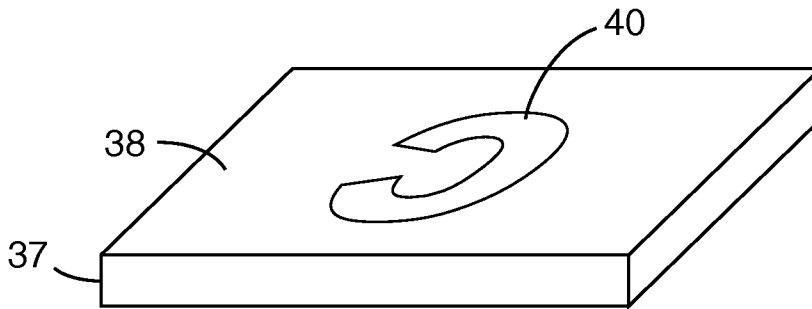
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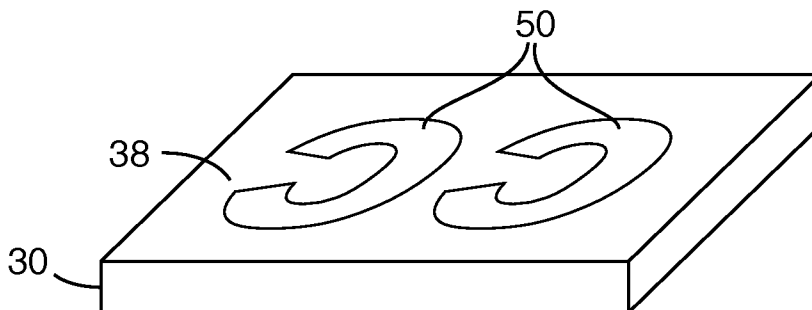
**Fig. 1**



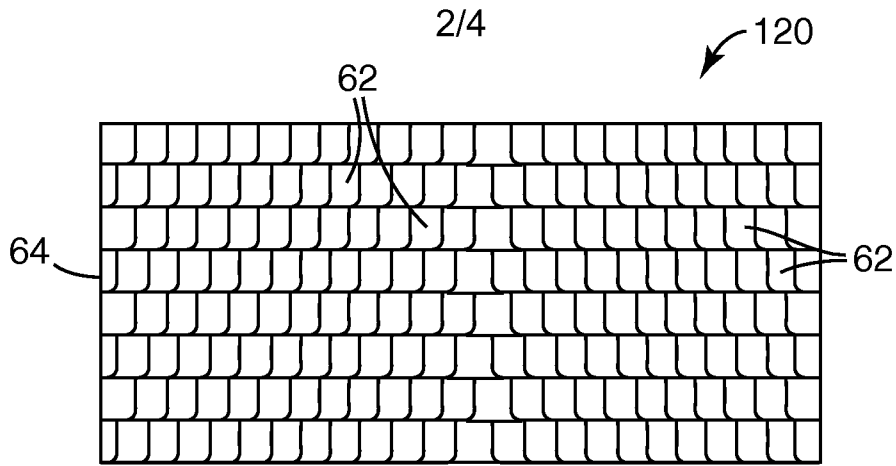
**Fig. 2A**



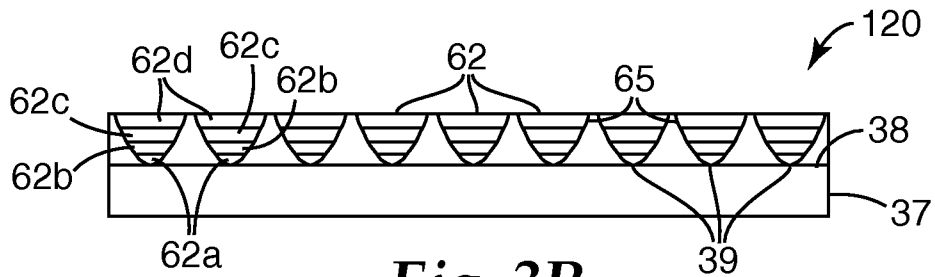
**Fig. 2B**



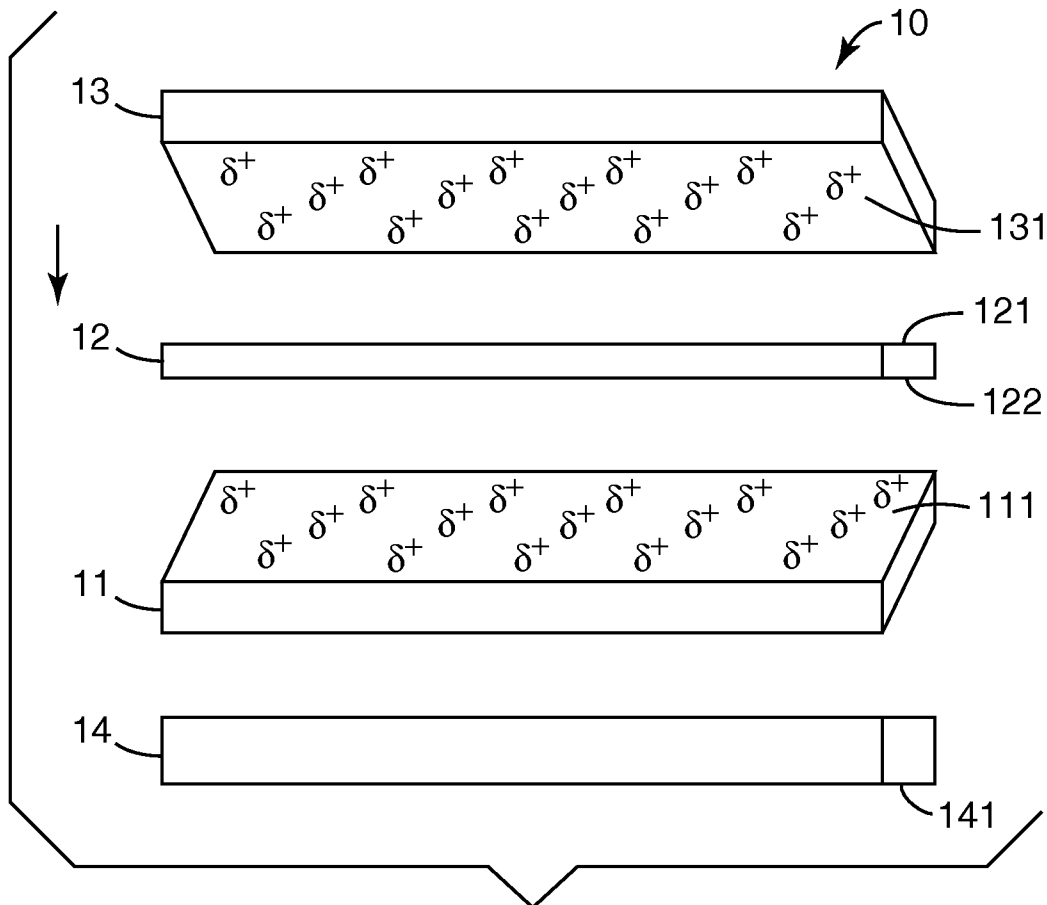
**Fig. 2C**



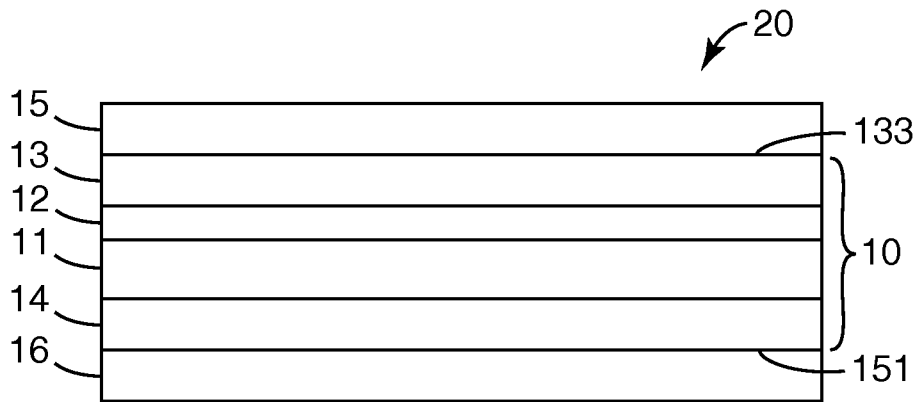
**Fig. 3A**



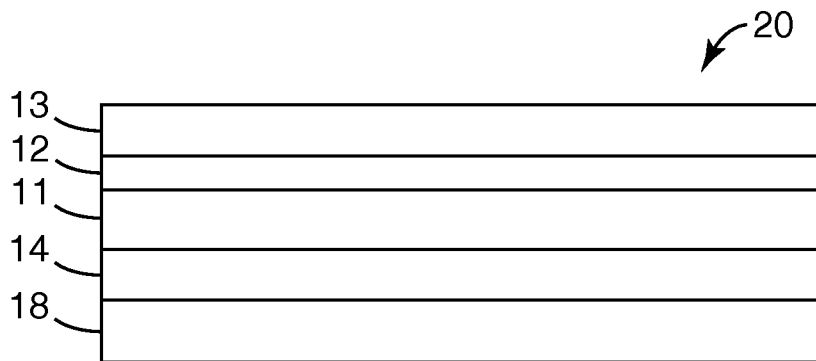
**Fig. 3B**



**Fig. 4**



*Fig. 5*



*Fig. 6*

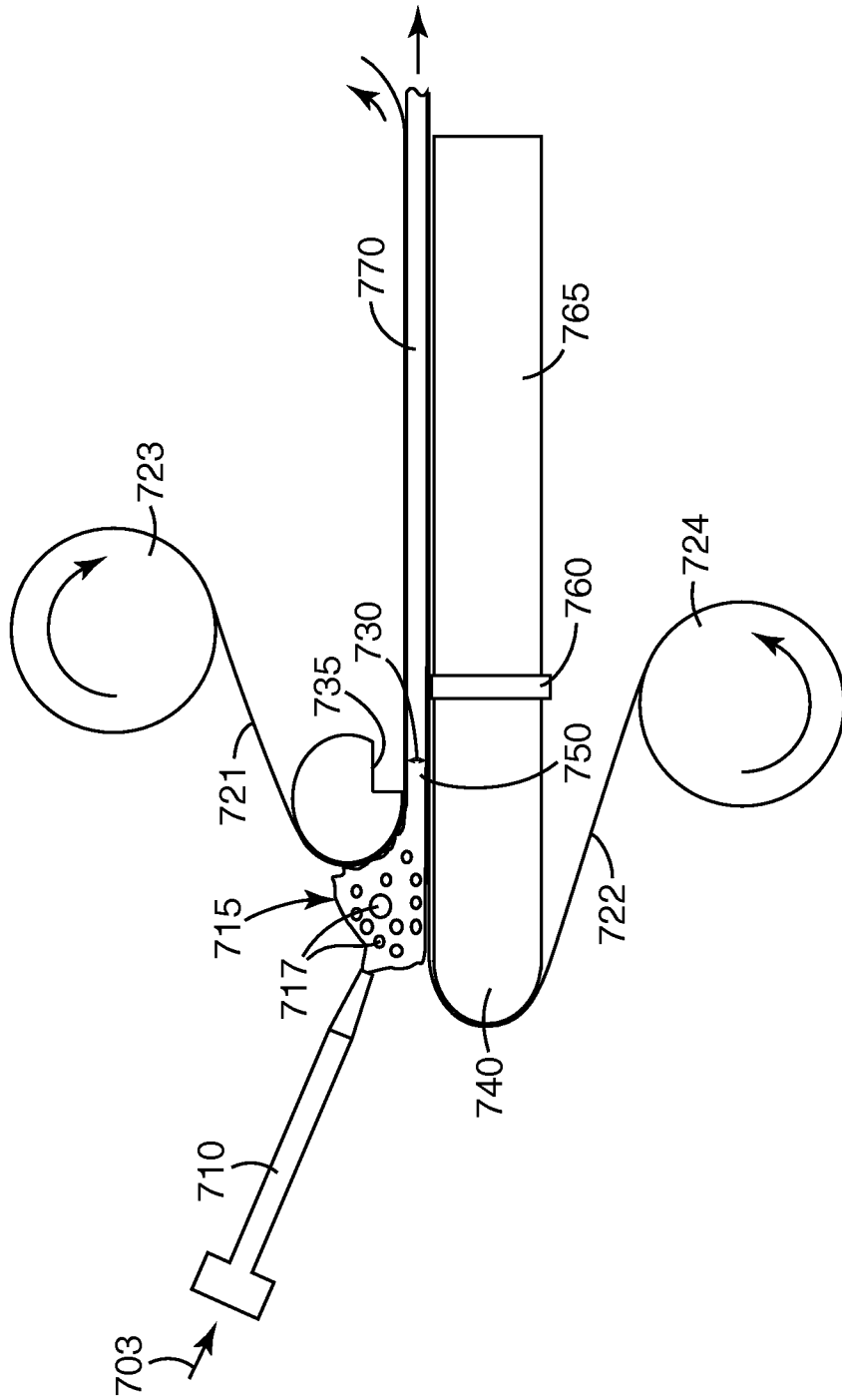


Fig. 7