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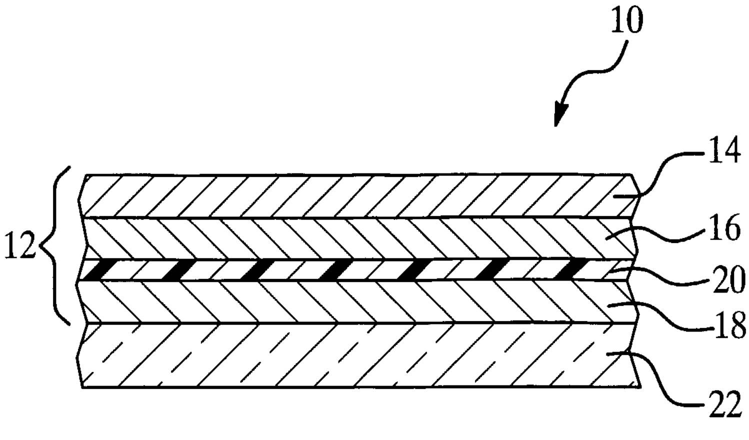
(54) Title: MULTILAYER FILM HAVING AT LEAST ONE IONOMERIC LAYER AND AN ADHESIVE TIE LAYER AND ARTICLE MADE THEREFROM



(57) Abstract: A multilayer film and article including the same in which the multilayer film includes an ionomeric layer, a thermoplastic layer, and an intermediate layer containing at least one material that exhibits adhesion with the thermoplastic layer and at least one ionomeric adhesion promoter. At least one solid visual enhancement material is dispersed in the ionomeric layer.

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MULTILAYER FILM HAVING AT LEAST ONE IONOMERIC LAYER AND AN ADHESIVE TIE LAYER AND ARTICLE MADE THEREFROM

BACKGROUND

[0001] The present invention claims priority to U.S. Serial No. 60/605,811 filed 31 August 2004, now pending.

[0002] The present invention pertains to multilayer polymeric films in which one layer contains an ionomeric polymeric material. More particularly, the present invention pertains to multilayer film constructs having an ionomeric layer and a tie or adhesive layer exhibiting enhanced performance characteristics. Finally, the present invention pertains to polymeric substrates having a multilayer film with the foregoing attributes on the outer surface thereof.

[0003] The aesthetic value and desirability of various items can be enhanced if the items can be formulated in a variety of colors or hues. Various native polymeric materials exist in shades of gray or natural tan. To render these more pleasing, it has been contemplated that the materials be pigmented with various shades. This has been accomplished with varying degrees of success. However, the finish of the polymeric articles so pigmented can lack the sheen, luster, or beauty desired for the end product.

[0004] It has been proposed that various polymeric substrates be painted or overlaid with a suitable pigmented lacquer material applied in a spray, dip, or brush application process. Such processes are labor-intensive and may not impart the desired surface finish. Additionally, such application processes can present surface adhesion difficulties. Accordingly, it has been proposed that a polymeric film be integrated into overlying relationship with the desired surface or surfaces of the polymeric substrate. The polymeric film can be composed of one or more layers with at least one layer colored to the desired shade or hue. Such films can be integrated with the substrate article by various methods. One such example of a suitable integration method includes an injection molding process whereby the film is intimately connected to the surface of the polymeric substrate during the article formation process.

[0005] Heretofore, colored polymeric films have been successfully manufactured by various casting processes. However, such processes are labor intensive and present difficulties when multilayer film constructs are desired. Extrusion methods have been proposed in the past. However, extrusion methods producing multilayer films suitable for use as a colored or pigmented outer layer have been problematic. Extruded films using materials such as ionomeric polymeric materials in one or more of the multiple layers of the film construct have been difficult to produce successfully. Additionally, single layer ionomeric materials have proven difficult to integrate with the surface of the substrate in a manner that will last the lifetime of the finished product. Such layers, when produced, lack the requisite adhesives for cohesive strength to accomplish uniform bonding for the lifetime of the part.

[0006] Thus, it would be desirable to provide a multilayer film having an intermediate or tie layer that can be uniformly and effectively employed with a layer containing an ionomeric polymeric material and with a layer composed of another suitable nonionomeric polymeric material. It is also desirable to provide an article having an outer surface layer that has an aesthetically pleasing, uniform color characteristic that is uniformly bonded to the article substrate. It would also be desirable to provide articles having the aforementioned outer surface that can be utilized in an automotive setting such as, for example, automotive facia, bumpers, trim, and the like.

SUMMARY

[0007] Disclosed herein is a multilayer film material having at least one layer composed of an ionomeric thermoplastic material. The film has at least one additional layer composed of a non-ionomeric thermoplastic material. Interposed between the two layers is a tie or intermediate layer composed of a polymeric alloy containing an ionomeric adhesive material and a material having adhesive qualities relative to the nonionomeric material layer. The respective materials are present in dispersed relationship relative to one another. Also disclosed is an article having a substrate and an outer surface composed of a pigmented polymeric film. The polymeric film includes at least one layer containing ionomeric material and a layer containing polymeric materials different from the ionomeric layer as well as a layer interposed therebetween, such as an intermediate or tie layer. The tie layer contains an ionomeric adhesive, an adhesive having an affinity to the material of the nonionomeric layer in dispersed relationship to one another.

DESCRIPTION OF THE DRAWINGS

[0008] The objects, features, and advantages of the disclosure herein will become more readily apparent from the following description, in which reference is made to the following drawings, and in which:

[0009] FIG. 1 is a sectional view through an article configured with an embodiment of polymeric film as disclosed herein;

[0010] FIG. 2 is a line drawing depiction of a photomicrograph depicting ionomeric layer /tie layer interface in an embodiment as disclosed herein;

[0011] FIG. 3 is a line drawing depiction of photomicrograph depicting the interface between backing layer and tie layer in an embodiment as disclosed herein;

[0012] FIG. 4 is a process flow diagram of a process for producing an article having the polymeric film disclosed herein;

[0013] FIG. 5 is a schematic cross section of an injection molding device such as can be used in producing articles as disclosed herein;

[0014] FIG. 6 is a graph of tie layer composition versus peel test values.

DETAILED DESCRIPTION

[0015] Disclosed herein is a polymeric film construction or laminate having a first layer that contains an ionomeric compound or compounds integrated therein. The polymeric film includes at least one additional layer composed of a thermoplastic material that differs from the composition of the first layer. Interposed between the two layers is a layer, such as an intermediate or tie layer, that contains at least one ionomeric adhesive and at least one nonionomeric adhesive in a dispersed mixture relative to one another. The additional thermoplastic layer may be composed of a material that provides suitable reinforcement and/or structure to the polymeric film construct. This material can be a material that is suitable for contact or integration with various injection molding materials. The polymeric film includes at least one additive in the layer containing the ionomeric compound that imparts appropriate aesthetic characteristics to the construct. These aesthetic characteristics can include color, hue, or other visual characteristics. The polymeric film disclosed herein is one suitable for incorporation into or onto the surface region of a suitable polymeric work piece or substrate.

[0016] Also disclosed herein is a method for preparing a polymeric film containing the tie layer disclosed herein as well as methods for preparing the tie layer itself.

[0017] The polymeric film disclosed herein can be described as a multilayer plastic film 12 that can be made using a suitable polymeric coextrusion process. The multilayer polymeric film 12 can be composed of coextruded layers of two or more materials. Typically, the multilayer plastic film 12 includes an optional clear layer 14 in overlying relationship to a pigmented polymeric layer 16. Layers 14 and 16 can be positioned in overlying relationship to a backing layer 18 and can be suitably adhered to the backing layer 18 by a suitable tie layer 20. The various layers 14, 16, 18, and 20 form a unitary coextruded film such as multilayer polymeric film 12.

[0018] As depicted in FIG. 1, the multilayer polymeric film 12 can be present in adhered overlying relationship to a suitable substrate 22. Substrate 22 is typically placed into essentially permanent contact with the multilayer polymeric film 12 through a suitable process such as injection molding and can be composed of any appropriate material that is amenable to injection molding and is compatible with the materials employed in the multilayer polymeric film 12. Compatibility between the substrate 22 and the multilayer polymeric film 12 is taken to include, for example, appropriately similar melt temperatures, composition temperatures, physical processing characteristics, and the like. The materials employed in the substrate 22 are typically thermoplastic compositions capable of appropriate contact and association with the material employed in the backing layer 18. "Contact" and "association" as used herein is taken to include processes whereby the backing layer 18 and all layers associated therewith are brought into essentially permanent overlying contact with the surface of the substrate 22. Such essentially permanent and complete contact can include, but need not be limited to, such processes as adhesion, cohesion, bonding, and processes such as molecular or physical welding whereby the region proximate to the outermost surface of the backing layer 18 fuses with polymeric material proximate to the surface of the substrate 22. In instances where such fusion is accomplished, it is contemplated that the contact or fusion can occur by any suitable process. Nonlimiting examples of suitable processes include heat fusion and the like as would occur during injection molding operations.

[0019] The multilayer polymeric film 12 can include appropriate pigmentation and color augmentation in at least one layer of the construct. As depicted herein, the pigmentation and/or color augmentation are present in layer 16. Such pigmentation or color augmentation can occur by any suitable process or methodology. As depicted, one such method and device for pigmentation and color augmentation includes the presence of particles dispersed throughout the thermoplastic material of the associated layer. Color augmentation elements include but are not limited to solid opalescence agents and the like. Nonlimiting examples of visual enhancement agents include reflective materials such as metallic flakes, mica, and the like, that can add attributes such as light reflectivity, perceived depth of field, and the like. Pigmentation and color augmentation can include the incorporation of appropriate particulate pigments, as well as other additives that enhance or augment the aesthetic characteristics of the film and resulting work piece. Nonlimiting examples of such other materials include metallic flakes as well as inorganic materials such as mica and the like. The metallic materials and/or inorganic materials can be present in the form of flakes or other geometric shapes and configurations to provide a desired visual effect. Nonlimiting examples of such shape include spheres, nodules, and combinations thereof. The size of solid material present in dispersed state in the ionomeric layer will generally be that size capable of effective integration into the ionomeric layer 16 with the upper size limit bounded by processing constraints and considerations of visual perception of hue, color, color continuity, and the like.

[0020] Choice of particulate pigment and color augmentation agents, as well as size, may also be governed by considerations such as color consistency over the surface, the multilayer film, and/or consistency over variations in the angle of visual incidence. Materials of choice will be of a size and shape to accomplish any or all of these objections as well as others as desired or required.

[0021] The ionomeric layer 16 can be composed of ionomeric materials capable of melt-processable extrusion. Suitable materials include, but need not be limited to, ionomers derived from sodium, lithium, or zinc. Suitable ionomeric resins include those available from DuPont under the trade name SURLYN®. These resins include sodium-containing ionomers under the SURLYN® designations 1601, 1605, 1707, 1802, 1901, and the like; zinc containing ionomers such as those designated as 1650, 1652, 1702, 1705-1, 1855, and 1857. Lithium-containing ionomers available under the SURLYN® designation include AD8546, 7930, 7940.

[0022] The multilayer polymeric film 12 can also include an over layer or clear layer 14 optionally present as part of the film construct. The overlayer 14 is positioned linearly outward of layer 16. Where desired or required, the overlayer 14 may be the outermost layer. The outermost or clear layer 14 can be composed of any suitable clear, polymeric material. Examples of suitable clear materials include thermoplastics capable of melt-processible extrusion. Suitable thermoplastic materials include, but need not be limited to, ionomers derived from sodium, lithium, or zinc, and ethylene/unsaturated carboxylic acid or anhydride copolymers. Suitable ionomer resins include those available from Dupont under the trade name SURLYN®. These resins are identified as being derived from sodium, lithium, or zinc, and copolymers of ethylene and methacrylic acid. Included in this group are sodium-containing ionomers available under the SURLYN® name and having the following designations: 1601, 1605, 1707, 1802, 1901, and the like. Also included are zinc-containing ionomers available under the SURLYN® name having the following designations: 1650, 1652, 1702, 1705-1, 1855, and 1857. Lithium-containing ionomers available under the SURLYN name include the following designations: AD8546, 7930, and 7940.

[0023] As defined herein, the term "clear" as used with the clear layer 14 is defined as a material that can be seen through. The clear layer 14 may have an optic transmissivity greater than that of the layer 16 such that the presence of clear layer 14 does not adversely affect perception of layer 16. The polymeric material of choice employed in the clear layer 14 can be one that imparts suitable scratch and abrasion resistance as desired or required. As such, it is contemplated that the clear layer can include suitable abrasion resistance enhancing additives as would be known to the skilled artisan. It is also contemplated that the clear layer can include additives which impart ultraviolet resistance and resistance to other undesirable environmental factors. Once again, such additives are typically known to the skilled artisan.

[0024] Where the clear layer contains additives as discussed previously, it is contemplated that concentrations of light stabilizers such as ultraviolet (UV) light absorbers and/or other light stabilizers can be employed. These additives are included to provide characteristics such as enhanced outdoor weatherability properties. The concentrations of light stabilizers in the clear layer can be in any suitable range. Exemplary ranges include about 1,000 to about 20,000 ppm based on the weight of the clear layer 14. Exemplary concentrations can, more specifically, include concentrations in the range of about 2,000 to about 20,000 ppm based on weight with more specific ranges varying from about 5,000 to about 20,000 ppm, or about 8,000 to about 18,000 ppm. Useful light stabilizers include the hindered amine light stabilizers. The hindered amine light stabilizers may, for example, be derivatives of 2,2,6,6-tetraalkyl piperidines or substituted piperizinediones. A number of hindered amine light stabilizers useful in the invention are available commercially such as from Ciba-Geigy Corporation under the general trade designations "Tinuvin" and "Chemissorb", and from Cytec under the general designation "Cyasorb-UV." Examples include Tinuvin 783 which is identified as a mixture of poly [[60[(1,1,3,3,-

tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidyl)imino]hexamethylene [(2,2,6,6-tetramethyl-4-piperidyl)imino]] and dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol; Tinuvin 770 which is identified as bis-(2,2,6,6-tetramethyl-4-piperidinyl)-sebacate; Tinuvin 765 which is identified as bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate; Tinuvin 622 which is a polyester of succinic acid and N-beta-hydroxy ethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidine; and Chemissorb 944 which is poly[6-(1,1,3,3-tetramethylbutyl)amino]-s-triazine-2,4-diy[(2,2,6,6-tetram ethyl-4-piperidyl)imino]hexamethylene (2,2,6,6-tetramethyl-4-piperidyl)imino]. A useful stabilizer is available under the trade name Ampacet 10561, a product of Ampacet, identified as a UV stabilizer concentrate containing 20% by weight of a UV stabilizer and 80% by weight of a low density polyethylene carrier resin; the UV stabilizer in this product is Chemissorb 944. Useful light stabilizers are also provided in Ampacet 150380 and Ampacet 190303, both of which are pigment concentrates discussed above. Ampacet 150380 has a UV stabilizer concentration of 7.5% by weight. Ampacet 190303 has a UV stabilizer concentration of 4% by weight. The UV stabilizer in each of these products is Chemissorb 944. Ampacet LR-89933 is a gray concentrate having a UV stabilizer concentration of 4.5% by weight, the UV stabilizer being Tinuvin 783.

[0025] Various materials and compounds can be added to enhance scuff and abrasion resistance. Non-limiting examples of these materials include primary amides such as stearamide, behenamide, oleamide, erucamide, and the like; secondary amides such as stearyl erucamide, erucyl erucamide, oleyl palimitamide, stearyl stearamide, erucyl stearamide, and the like; ethylene bisamides such as N,N-ethylenebisstearamide, N,N-ethylenebisolamide and the like; and combinations of any two or more of the foregoing amides. Examples of suitable additive packages include those utilized as antislip additives. Non-limiting examples of such materials include additive packages available from Dow Chemical such as Elvax CE9619-1. This resin concentrate contains 20% by weight silica, 7% by weight of an amide slip additive, and 73% by weight of Elvax 3170 (a product of DuPont identified as an ethylene/vinyl acetate copolymer having a vinyl acetate content of 18% by weight). The additive can be used at a concentration in the range of up to about 1% by weight, and in one embodiment about 0.01% to about 0.5% by weight. The slip additive can be used at a concentration in the range of up to about 1% by weight, and in one embodiment about 0.01% to about 0.5% by weight. The total amount of material employed will be an amount that is less than that which will adversely effect gloss characteristics for the clear layer. This will generally be amounts less that about 2000 ppm additive by weight of the clear layer, with levels below about 1500 being preferred.

[0026] The multilayer polymeric film 12 includes at least one pigmented polymeric layer 16. The pigmented polymeric layer 16 can be employed independently or can be positioned such that the outer clear layer 14 is in overlying relationship with the pigmented layer 16. As depicted in FIG. 1, the clear layer 14 can be in direct overlying relationship and contact with at least one pigmented layer 16. It is also contemplated that the multilayer polymeric film 12 can include multiple pigmented layers 16 as desired or required. The pigmented layer or layers 16 can include various pigmenting and opacifying agents that will provide the color, hue, and desired level of opacity for the multilayer polymeric film 12. The pigmented layer 16 is composed of a suitable melt processible and extrudable thermoplastic polymer or polymers. Examples of suitable polymeric materials are ionomers derived from sodium, lithium, or zinc, and ethylene-unsaturated carboxylic acid or anhydride such as ethylene-methacrylic acid copolymers. These ionomers can include, but are not limited to those discussed previously in conjunction with clear layer 14.

[0027] It is contemplated that the polymeric material used in pigmented layer(s) 16 may also include minor amounts of various other polymeric compounds or materials. It is also contemplated that the polymeric material employed in the pigmented polymeric layer(s) 16 can also include various additives such as UV stabilizers and the like, as desired or required. Nonlimiting examples of suitable additives are those listed previously in connection with clear layer 14.

[0028] The pigmented polymeric layer 16 can include various materials suitable for providing the appropriate color or hue characteristics as desired or required. Nonlimiting examples of suitable pigments include various metallic pigments, heavy metal-based pigments, heavy-metal free pigments, or various organic pigments. As used herein, a heavy metal pigment is defined as one including lead, cadmium, chromium, or antimony, or complexes derived therefrom. The pigments that can be successfully used include titanium dioxide, both rutile and anatase crystal structure. The titanium dioxide may be coated or uncoated. The pigment can be dispersed in the polymeric matrix in any suitable fashion which will provide the desired color or hue characteristics.

[0029] Examples of suitable materials include materials typically available as pigment concentrates that can be readily added to the ionomeric matrix during processing. The pigment concentrates are typically pigments present in resin carriers. Suitable resin carriers include various thermoplastic polymers having a melting point of in the range of about 100 °C to about 175°C. Examples of such materials include polyethylene, polypropylene, polybutylene, ionomeric materials and the like. The pigment material can be present in the concentrate such that the blend is between about 30 percent and about 70 percent by weight polymeric matrix, and about 70 percent to about 30 percent pigment material. An example of a commercially available pigment concentrate that can be suitably used is one available from A. Shulman, Inc. under the trade name Polybatch White P8555 SD. This material is identified as a white color concentrate having a coated rutile titanium dioxide concentration of 50 percent by weight in a polypropylene homopolymer carrier resin. Ampacet 150380 can also be used. This material is a product of Ampacet Corporation and is identified as a red pigment concentrate. Ampacet 190303 is also a product of Ampacet Corporation, and identified as a black pigment concentrate. Ampacet LR-87132 Orange PE MB is also a product of Ampacet Corporation, and is identified as a lead molybdate/lead chromate pigment concentrate. Examples of heavy-metal free pigment concentrates that can be used include Ampacet LR-86813 Yellow UV PE MB, Ampacet LR-86810 Red PE MB, Ampacet LR-86816 Orange PE MB, and Ampacet LR-86789 red UV PE MB. It is contemplated that the concentrations of pigment in the resulting pigmented layer 16 can be up to about 25 percent by weight. Various embodiments can include between about 5 percent and about 25 percent by weight. It is also contemplated that the pigment concentrate can be between about 10 percent and about 20 percent by weight.

[0030] In order to provide enhanced or alternate visual effects, the pigmented polymeric layer 16 can include particulate visual enhancers or visual augmentation agents dispersed therein. These can include metallic particulate material as well as various inorganic compounds that provide visual enhancement and interest. Nonlimiting examples of metallic visual enhancers include at least one of aluminum, silver, tin, graphite, or the like. Nonlimiting examples of inorganic particulate visual enhancers include mica, and the like. Particulate visual enhancers can have any suitable form desirable to achieve the appropriate sparkle or other visual effect. Thus, the particulate visual enhancement material can be present in the form of flakes, geometric shapes, spheres, or the like. It is also contemplated that the metallic material can be present in a plurality of shapes to provide the appropriate or desired visual effect. The particulate visual enhancement material 24 will be of a size that disperses readily in the polymeric matrix while providing the desired light diffraction, reflectivity, and the like.

[0031] The multilayer polymeric film 12 further includes a suitable backing layer 18. The backing layer 18 can be composed of at least one thermoplastic polymer. The backing layer 18 may be composed of a single thermoplastic polymer or a blend of thermoplastic polymers as desired or required. The backing layer 18 may also be composed of blends of various thermoplastic polymers and suitable materials that can promote contact and association with suitable substrate materials as desired or required. Additionally, the backing layer may include other processing components and stabilizing components as desired or required.

[0032] The backing layer 18 can be composed of various melt-processible polymeric materials. Nonlimiting examples of suitable melt processible polymeric materials include various melt processible polyolefins. Other thermoplastic polymers having similar processing characteristics can be effectively employed as desired or required. Nonlimiting examples of such materials include melt processible polyamides, thermoplastic elastomers, and the like. The material of choice will be one that can impart flexible strengthening characteristics to the multilayer polymeric film 12. Additionally, the material of choice in the backing layer 18 will be one that will exhibit appropriate bonding characteristics with the material or materials employed in the substrate 22.

[0033] Polyolefins that are useful in the backing layer 18 include, but are not limited to, polyethylene, polypropylene, polybutylene, as well as copolymers of ethylene, propylene or butylenes with various alphaolefins. The alphaolefins include those containing three to eighteen carbon atoms. Such materials include propylene, ethylene, butylenes, butene, hexane, 4-methyl pentene, octane, and the like.

[0034] It is also contemplated that the backing layer 18 may be made of a blend of polyolefins such as polyethylene and various materials such as ethylene propylene copolymers. Medium density polyethylenes and linear medium density polyethylenes can be useful in the construction disclosed herein.

[0035] In the embodiment as depicted in Fig. 1, the multilayer film 12 includes a tie or intermediate layer 20 interposed between the upper layer 16 and the backing layer 18. The tie layer contains a melt processible thermoplastic polymeric material that exhibits an affinity to the layer 16 and the backing layer 18 respectively. It is contemplated that the intermediate layer 20 contains a portion of a suitable polyolefin adhesion promoter and a portion of an ionomeric adhesion promoter in blended relationship to one another. As used herein, the term “ionomeric adhesion promoter” is defined as a material or composition that exhibits an affinity to the ionomeric material in layer 16. In a preferred embodiment of the invention as disclosed herein, the ionomeric adhesion promoter is a melt-processible thermoplastic material that includes at least one of an ethylene-unsaturated carboxylic acid or anhydride, such as ethylene/acrylic acid copolymers, or ethylene-methacrylic acid copolymers, ionomers derived from sodium, lithium, or zinc, and ethylene/unsaturated carboxylic acid or anhydride such as ethylene-methacrylic acid copolymer. It is also contemplated that combinations of two or more of the foregoing can also be successfully employed. One non-limiting example of a suitable adhesion promoter is material commercially available from A Schulman as FORMION 134.

[0036] The polyolefin adhesion promoter employed in the intermediate layer 20 can be any material that exhibits affinity with the polyolefin material employed in the backing layer 18. The promoter used in the tie or intermediate layer 20 can include materials such as polyethylene, polypropylene, or polybutylene, as well as copolymers of ethylene, propylene, or butylenes with an alphaolefin. The alphaolefin can be selected from those alphaolefins containing from 3 to about 18 carbon atoms, including propylene, ethylene, butylenes, butene, hexane, 4-methylpentene, and octane. The polyolefin backing layer may be made by a blend of polyolefins such as polyethylene and ethylene propylene copolymers. Medium density polyethylene and the linear medium density polyethylenes are useful. A nonlimiting example of a useful polyolefin is a product available from Exxon Chemical identified as XV404.

[0037] Where desired, the backing layer 18 may be formulated to contain amounts of the polyolefin adhesion promoter. In such instances, it is contemplated that the backing layer 18 may be a blend of one or more polyolefins such as polyethylene and ethylene propylene copolymers with materials such as medium density polyethylene and the linear medium density polyethylene being useful in some applications.

[0038] The ionomeric adhesion promoter material employed in the intermediate layer 20 can be a melt processible thermoplastic material such as those that include, but are not limited to, ethylene/unsaturated carboxylic acid or anhydride copolymers, ionomers derived from sodium, lithium, or zinc, and ethylene/unsaturated carboxylic acid or anhydride copolymers, as well as combinations of two or more thereof. Thermoplastic materials available from A. Schulman under the designation FI 134 are non-limiting examples of suitable ionomeric materials.

[0039] Additional polymers that can be utilized as an adhesive component in conjunction with the ionomeric adhesive include materials such as alkylene/acetate copolymers. Nonlimiting examples of suitable copolymeric resins can include materials such as ethylene/vinyl acetate copolymers. Suitable ethylene/vinyl acetate copolymers are available from Dupont under the trade designation "Elvax". Examples include Elvax 3170 and 3190 LG. Adhesive resins available from Dupont under the trade name "Bynel" can also be used. These include ethylene/vinyl acetate resins available under trade designation Series 1100, acid-modified ethylene acrylic polymers (Series 2000), anhydride modified ethylene acrylic copolymers (Series 2100), anhydride-modified ethylene/vinylacetate copolymers (Series 3,000), acid-and-acrylate-modified ethylene/vinyl acetate resins (Series 3100), anhydride-modified ethylene/vinyl-acetate copolymers (series 3800), anhydride-modified ethylene/vinyl acetate resins (Series 3900), anhydride-modified high density polyethylene resins (Series 4,000), anhydride-modified linear low density polyethylene resins (Series 4100), anhydride-modified low density polyethylene resins (Series 4200), and anhydride-modified polypropylene resins (Series 5000). BYNEL CXA 1123 and BYNEL CXA 3101 are specific nonlimiting examples. These can be used individually or in combination with the ionomeric adhesion promoter and polyalkylene adhesion promoter.

[0040] The intermediate layer 20 can be composed of a thermoplastic material containing the polyalkylene adhesion promoter and the ionomeric adhesion promoter in a ratio sufficient to provide laminar connection between the ionomeric layer 16 and the backing layer 18 sufficient to withstand peeling or separation during the useful life of the multilayer polymeric film 12 and any article or work piece to which it is associated. Such adhesion or bonding characteristics can be defined by various methods depending upon the industry and/or work piece. One such method is peel strength as defined in ASTM test method 1735. It is contemplated that ratios of polyolefin adhesion promoter to ionomeric adhesion promoter that evidence post processing peel strength at about 2 pounds per inch may be appropriate in various applications. It is also contemplated that various ratios of ionomeric adhesion promoter and polyalkylene adhesion promoter can be utilized to achieve post processing peel strengths at about 4 pounds per inch or greater as appropriate in various specific applications. It is to be understood that peel strength requirements may vary depending on the application and contemplated end use. Thus the values discussed are considered to be nonlimiting examples of suitable peel strengths. Ionomeric adhesion promoter materials include, but are not limited to, the Formion FI134 materials available form A Schulman discussed previously.

Non-limiting examples of suitable polyolefins include polyalkylene based polymers and alkylene-acrylic polymers. Suitable materials include materials commercially available from Exxon Mobile under the trade name ESCOR, such as ESCOR AT XV4.04, 310, 320 and 325.

[0041] It is believed that such ESCOR materials are acid terpolymers having a density between 0.940 and 0.955 glcm^3 and a melt index between 5 g/10 min and 20 g/min based on Exxon Mobil test methods. The material can have VICAT softening point as determined by ASTM D-125 between 40°C and 66°C.

[0042] The ionomeric adhesion promoter is formulated to provide adhesion between ionomeric materials to polar or nonpolar substances. Suitable materials can be alkylene-based thermoplastics. Nonlimiting examples of suitable materials include adhesion promoters available from A Schulman under the trade name FORMION. Examples of these include FORMION FI 131 and FORMION FI 134. Suitable materials can have a density between 0.89 and 0.93 (ISO 1183/1) and a melting point between 190 and 230°C.

[0043] "Post processing" as defined herein, is taken to mean peel test data derived subsequent to process simulation testing such as humidity and high temperature exposure as defined in test method ASTM 1735. Suitable ratios of the two adhesive components will typically be those that need or exceed the peel test value for the specific application for the specific film material. It is contemplated that the ratio of the ionomeric and polyolefin adhesion promoter material will provide a post processing peel strength of at least 2 pounds per inch. Depending on the specific application, it is contemplated that the tie layer will provide a peel strength of at least 4 pounds per inch for the multilayer polymeric film 12. Such values even more particularly will be those that meet or exceed a peel test value of 4 pound per inch when the multilayer polymeric film 12 is integrated with a suitable substrate or facia as at reference numeral 22.

[0044] It is contemplated that a blend containing a ratio of polyolefin adhesion promoter to ionomeric adhesion promoter in a range between about 65:35 and 30:70 polyolefin material to ionomeric material respectively can be utilized to achieve the peel strength values desired. Material ratios between 60:40 to 40:60 polyalkylene material to ionomeric resin material may be advantageously used in some applications with material ratios between 55:45 and 45:55 being advantageous in others. The respective adhesion promoter materials are blended such that discrete regions of one material exist within the matrix of the other material. It is contemplated that the respective regions will be dispersed throughout the matrix in an essentially random manner. By "random manner", it is contemplated that the material may be present in a manner that evidences minimal or no dispersion gradient between the respective materials through out the extruded layer. It is also contemplated that the material contained within the matrix will be present in discrete compact matrix formations with a minimum of fibrous bodies formed therein.

[0045] The intermediate layer 20 as discussed herein is employed in a multilayer polymeric film 10 that is integrated onto a suitable polymeric substrate 22. The resulting multilayer film structure includes overlying layers of ionomeric thermoplastic material joined to a suitable backing layer 18 in which the interface between the backing layer 180and the intermediate layer 20 is characterized by a transitional region in which ionomeric adhesive is dispersed in spherical bodies throughout a matrix composed of the polyolefin adhesion promoter region. Where desired or required, the backing layer 18 may contain up to 30 percent by weight ionomeric adhesion promoter material, with ionomeric adhesion promoter level between 0 and 15% being suitable in various applications. At the interface, it is contemplated that an intermediate region is present that contains ionomeric adhesion promoter material, polyolefin adhesion promoter material, and polyalkylene. The materials will exist with the three materials present in discrete regions identifiable locations or regions.

[0046] The interface between the ionomeric layer and the adhesion or intermediate layer 20 can be characterized by a compressed region of interpenetration between material layers. The compressed region contains identifiable regions of ionomeric adhesion promoter material, ionomer, and polyolefin adhesion promoter material. The respective interface layers are characterized in the photomicrographs set forth in Figs. 2 and 3.

[0047] The multilayer film 12 disclosed herein can be integrated into an article that includes a thermoplastic substrate 22. It is contemplated that colored finished articles 10 according to the embodiment(s) discussed herein can include a suitable substrate 22 integrally attached to the backing layer 18. The substrate layer can be of any suitable thickness and configuration as dictated by the specifications and requirements of the finished article 10.

[0048] The substrate 22 is composed of suitable injectable, melt-processible polymeric material(s). The material(s) of choice may exhibit thermoplastic or thermo setting characteristics. Nonlimiting examples of such materials are engineered polymers such as those characterized as thermoplastic elastomers (TPE). As used herein, the term "thermoplastic elastomer" refers to rubber-like materials that can be processed and recycled as thermoplastics. In particular, olefinic thermoplastic elastomers can be successfully employed. Such materials are commonly referred to as thermoplastic polyolefins (TPO).

Olefinic thermoplastic elastomers can be materials having characteristics that allow the various components to soften and permit the polymeric matrix to flow at processing temperatures. When the material of choice cools, the hard segments solidify and re-establish a desirable rubber-like structure. Olefinic TPEs are typically multiphase material that includes crystalline or amorphous polyolefins such as polyethylene, polypropylene, and ethylene/propylene rubbers such as EPDM. Also included are materials such as polybutylene, polyisobutylene, polymethylpentene and the like. Materials of choice can have tensile strengths and melt temperatures suitable for use with the multilayer film material. In certain applications, tensile strength in the range of 1,000 to 3,000 psi and melt temperatures in the range of 150° C to 230° C.

[0049] Nonlimiting examples of such articles 10 include automotive component parts, particularly exterior automotive component parts such as bumpers, facia, trim, and the like. It has been found, quite unexpectedly, that articles 10 having the multilayer film as disclosed herein present a durable weather resistant exterior surface that can maintain color quality and consistency when and where desired.

[0050] In order to produce an article 10 having a multilayer polymeric film 12, it is contemplated that the article 10 can be produced by the method disclosed herein as outlined in FIG. 3. The method 100 involves the step of producing a film having multiple layers as at reference numeral 110. The multilayer polymeric film 12 can be produced by any suitable method. As disclosed herein, it is contemplated that the film is produced by a suitable co-extrusion process utilizing processing temperatures, mixing speeds, and flow rates, that effectively produce a film having a suitable ionomeric layer(s), a backing layer and interposed tie layer.

[0051] The produced multilayer polymeric film 12 is introduced into a suitable mold cavity as at reference numeral 112. The mold cavity is formed in a suitable injection mold die. The polymeric film is introduced such that the film is positioned proximate to at least a portion of the mold cavity surface. Introduction of the film can be accomplished by any means. Thus, the film can be coextruded and directly introduced into the mold cavity. Alternately, the produced film material can be accumulated, cut to size, etc., prior to positioning relative to the mold cavity surface.

[0052] Once the multilayer polymeric film 12 is introduced into the mold cavity, a substrate material 22 can be introduced into the mold cavity as at reference numeral 114 such that the film 12 forms the outermost surface of the molded material upon completion of the mold cycle. It is contemplated that the injection molding process can be any suitable process for introducing a polymeric material such as a thermoplastic polyolefin (TPO) into the desired mold cavity to form the article of choice. The injection process occurs such that the introduced film forms an outermost surface of the resulting article formed of the molded material. Thus, location of injection port and selection of flow rates, injection pressures and the like will be adjusted to facilitate interposition of the film material between the cavity surface and the introduced injectable material.

[0053] It is contemplated that processing temperatures will be such that the film material is bonded to the substrate material in an essentially permanent fashion upon completion of the mold cycle. As used herein, the term “essentially permanent” is taken to mean that the substrate and overlying film material are integrally connected to one another throughout the life of the associated part.

[0054] Processing temperatures appropriate for the introduction of the substrate material can vary depending upon the composition of the material employed. Typically the substrate material will have a temperature between about 38° C and about 60° C as measured at the nozzle.

[0055] The resulting article 10 has a polymeric substrate with an overlying outer skin. The skin has a suitable color and clear coat as desired or required in which the color/clear coat layers are bonded to the substrate by means of a tie layer and adhesion layer.

[0056] Where desired or required, the produced polymeric film 12 can be formed into a suitable preform prior to introduction into the mold cavity. Preforming into a suitable three-dimensional shaped “preform” can be accomplished by various formation operations such as thermoforming, vacuum forming, or combinations thereof. Other acceptable thermoforming apparatus and operations may also be employed. The preform may be an approximate match to the contour of the finished article. However, it is also contemplated that the preform can be an intermediate shape of suitable contour and configuration to permit further formation upon insertion into the mold cavity as at reference numeral 112, and introduction of substrate material into the mold cavity as at reference numeral 114.

[0057] Suitable vacuum forming apparatus can include vacuum molding buck or dies as well as suction holes in the die and appropriate pumps and regulators. It is also contemplated that the vacuum-forming apparatus may include appropriate apparatus for heating the inserted sheet to a suitable preheating temperature to permit or facilitate vacuum formation. Once preheating has been achieved, the buck or die may be raised toward the sheet or vacuum to draw the sheet in contact with the working surface of the die as desired or required. After the sheet has cooled, the resulting preform will have a shape approximating that of the working surface of the die. As discussed previously, this shape may have a contour of the intended trim part or may be an intermediate shape.

[0058] It is contemplated that the process may be utilized to create appropriate locator elements, pinholes, tabs, and the like, as desired or required. The male or female vacuum forming device may be utilized in different embodiments to shape the appropriate preform. It is also contemplated that positive air pressure may be applied to the free face of the sheet opposite the side of the buck in order to increase pressure. Additionally, elements such as springs, air bladders, or other biasing means may be provided to apply force to the free face of the sheet on the opposite side of the buck during vacuum formation in order to increase the forming pressure and/or provide for an appropriately contoured surface. Once the preform has been produced, it may be trimmed as desired or required using any suitable trimming method. Such trimming can occur as an individual step either before, during, or after vacuum forming in the vacuum forming die.

[0059] The term "preform" as used herein describes a three-dimensionally shaped multilayer sheet that has been formed by a process such as thermoforming. The preform can be placed or inserted into a suitable cavity half of an injection molding apparatus by any suitable insertion method such as manual insertion, robotic insertion, or use of other automation. The preform can be held in place in the apparatus through use of any suitable devices, such as utilizing gravity, various pins, tape, static electricity, vacuum force, and the like.

[0060] The preform may be inserted into various different injection molding devices. It is contemplated that the injection molding device may function as both vacuum forming and injection molding device if desired or required. Alternately, separate vacuum forming and injection molding devices can be employed. Referring to FIG. 5, the injection molding apparatus has first and second mold halves. The preform is shaped so as to approximate the shape or contour of the inner surface of one of the mold halves or dies. The preform is preferably placed or located in the cavity so that the surface to be viewed by an observer of the finished article or part comes to rest against the working surface of the die. Thereafter, heated, semimolten polymeric material can be injected into the cavity through a suitable aperture or apertures in order to form the molded substrate. The term "semimolten" is taken to mean capable of flowing into the molding area.

[0061] It is contemplated that the pressure from the polymeric material injected into the cavity combined with the temperature within the cavity and in the die surfaces can cause the introduced semimolten resin to fuse with or bond to the interior surface of the backing layer. Once the operation is complete, the molded article can be removed from the cavity and the process repeated.

[0062] Having thus described the invention and various embodiments thereof disclosed herein, reference is made to the following nonlimiting examples. These examples are to be considered illustrative of the present invention and do not seek to limit the scope thereof.

EXAMPLE 1

[0063] A test article configured as an automotive facia is prepared. A multilayer film is prepared by coextrusion of a film structure having an ionomeric clear coat layer of .005". The film structure also has an ionomeric color layer of .009" directly underlying and contacting the clear coat layer. Both clear coat and color layer are formulated from SURLYN® 1601, with suitable pigmentation integrated into the color layer. The coextruded film also includes a backing layer of .0015" prepared from polymeric material obtained from ExxonMobile. A tie or intermediate layer of .003" is interposed between the back layer and the color layer and is coextruded with the associated layers. The tie or intermediate layer is composed of a blend of adhesion promoters suitable for the respective surrounding layers in the automotive fascia article. The tie layer is composed of 65 percent of a polyalkylene adhesion promoter available from Exxon Mobil Chemical Corporation under the trade name ESCORXV.04. The tie layer also contains 35 percent by weight of an ionomeric adhesion promoter commercially available from A. Schulman Corporation under the name FORMION FI134.

[0064] The multilayer film is subjected to preforming operations by placing the film in a vacuum forming thermoforming press for an interval of 30 seconds at a die temperature of 100 degrees. The preform produced is allowed to age for an interval of 36 hours after which it is inserted into an injection mold cavity where a thermoplastic substrate composed of an injection moldable TPO is injected into the cavity at a temperature of 232° C and allowed to bond to the backing layer.

[0065] The resulting test facia was subjected to environmental exposure pursuant to the process outlined in ASTM method D1735. After completing the environmental exposure phase, the facia was evaluated to determine peel test value pursuant to Daimler Chrysler Test Procedure LP463LB10-1. Peel test values were expressed in terms of pounds per minute. The values for both prehumidity testing and post humidity testing are set forth in Fig. 6.

EXAMPLES 2-6

[0066] Various test laminates and associated facia are prepared in which the composition of the tie layer varied in ratios of polyalkylene adhesion promoter to polyalkylene adhesion promoter. Material ratios 60:40; 55:45; 50:50; 45:55; and 30:70 are evaluated. The materials are extruded and processed in the manner outlined above.

[0067] Tests and evaluation of the peel strength is determined according to the method outlined in Example 1. The expected results are set forth in the graph in FIG. 6.

[0068] It can be seen from the associated data that film and associated facia parts produced therefrom will have a peel strength of at least 2 pounds/inch. With peel strengths at or greater than 4 pounds per inch obtainable with certain formulations.

[0069] While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiments but, on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims, which scope is to be accorded the broadest interpretation so as to encompass all such modifications and equivalent structures as is permitted under the law.

What is claimed is:

1. A multilayer film comprising:

at least one layer containing an ionomeric thermoplastic material;

at least one layer containing a thermoplastic material; and

at least one intermediate layer interposed between, the intermediate layer containing at least one ionomeric adhesive material and at least one polymeric material exhibiting adhesion with the thermoplastic material in dispersed relationship to one another.

2. The multilayer film of claim 1 wherein the ionomeric thermoplastic layer contains at least one aesthetic characteristic enhancement additive.

3. The multilayer film of claim 2 wherein the aesthetic characteristic enhancement additive is a solid material dispersed therein and alters at least one of color, hue, or visual perception.

4. The multilayer film of claim 1, 2, or 3 wherein the ionomeric thermoplastic layer, polyolefin thermoplastic layer, and intermediate layer are in co-extruded relationship with one another such that the intermediate layer is in direct contact with the ionomeric layer and polyolefin layer.

5. The multilayer film of claim 1, 2, 3, or 4 further comprising an overlayer composed of ionomeric thermoplastic material in overlying relationship with the ionomeric layer having an optic transmissivity greater than optic transmissivity of the ionomeric layer.

6. The multilayer film of claim 5 wherein the overlayer is in direct contact with the ionomeric layer.

7. The multilayer film of any preceding claim wherein the respective layers are in direct overlying contact.

8. The multilayer film of any of the preceding claims wherein the ionomeric layer contains particulate material dispersed therein, the particulate material being at least one of a pigment, color augmentation agent, or visual augmentation agent.

9. The multilayer film of claim 8 wherein the particulate material is a solid pigment including at least one of metallic pigments, heavy metal-based pigments, and organic pigments.

10. The multilayer film of claim 9 wherein the solid pigment is contained in a resin carrier including at least one of polyethylene, polypropylene, polybutylene, and ionomeric materials.

11. The multilayer film of any of the preceding claims wherein the intermediate layer comprises a polyolefin adhesion promoter and an ionomeric adhesion promoter present in a ratio in a range between about 65:35 and 30:70 polyolefin adhesion promoter to ionomeric adhesion promoter respectively.

12. The multilayer film of claim 11 wherein the polyolefin adhesion promoter is at least one of polyethylene, polypropylene, polybutylene, or alphaolefin copolymers of at least one of ethylene, propylene, or butylene in which the alphaolefin contains between 3 and 18 carbon atoms.

13. The multilayer film of claims 11 or 12 wherein the ionomeric adhesion promoter includes at least one of ethylene/unsaturated carboxylic acid copolymers, ethylene/unsaturated anhydride, ionomers derived from at least one of sodium, lithium, or zinc and ethylene/unsaturated carboxylic acid or anhydride, and copolymers of alkylene and acetate.

14. The multilayer film of any of the preceding claims wherein the polyolefin thermoplastic layer further comprises between 0 and 15 percent by weight ionomeric adhesion promoter.

15. The multilayer film of any of the preceding claims further comprising an interfacial region located between the intermediate layer and the polyolefin layer, the interfacial region characterized by interpenetration zones having discrete polymeric regions of polyalkylene matrix and at least one of polyolefin adhesion promoter and ionomeric adhesion promoter.

16. The multilayer film of any of the preceding claims further comprising an interfacial region located between the intermediate layer and the ionomeric layer characterized by interpenetration zones having discrete regions of ionomeric resin matrix and at least one of polyolefin adhesion promoter and polyolefin adhesion promoter.

17. A molded article comprising:

a polymer substrate; and

a multilayer film having at least one layer containing an ionomeric thermoplastic material and at least one layer containing a polyolefin thermoplastic material and at least one layer interposed between the ionomeric and non-ionomeric layers containing a polymeric alloy, the polymeric alloy containing thermoplastic ionomeric adhesive material and at least one polyolefin thermoplastic exhibiting adhesion to the polyolefin layer, wherein the ionomeric layer contains at least one visual enhancement particulate and the non-ionomeric layer is positioned proximate to the polymeric substrate.

18. The molded article of claim 17 wherein the polymeric substrate is a thermoplastic elastomer including at least one thermoplastic polyolefin.

19. A method for producing the molded article of claim 17 or 18 comprising the steps of:

co-extruding a multilayer film having at least one ionomeric layer, at least one polyolefin layer, and at least one intermediate layer comprising at least one ionomeric adhesion promoter and one polymeric material exhibiting adhesion with the polyolefin material in dispersed relationship to one another;

introducing the co-extruded multilayer film into a mold cavity proximate to at least a portion of the mold cavity surface; and

introducing a thermoplastic substrate material in a liquid state into the mold cavity.

20. The method of claim 19 wherein the liquid thermoplastic substrate material is introduced at a temperature between 38° C and 232° C.

21. The method of claims 19 or 20 further comprising the step of shaping the multilayer film into a three-dimensional preform prior to introduction into the mold cavity.

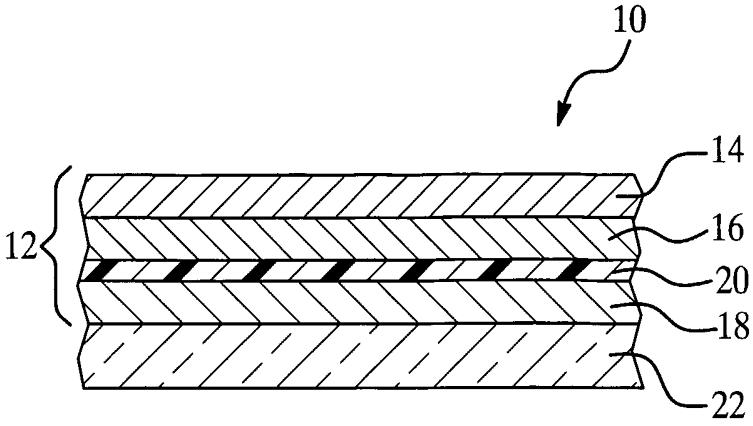

Figure 1

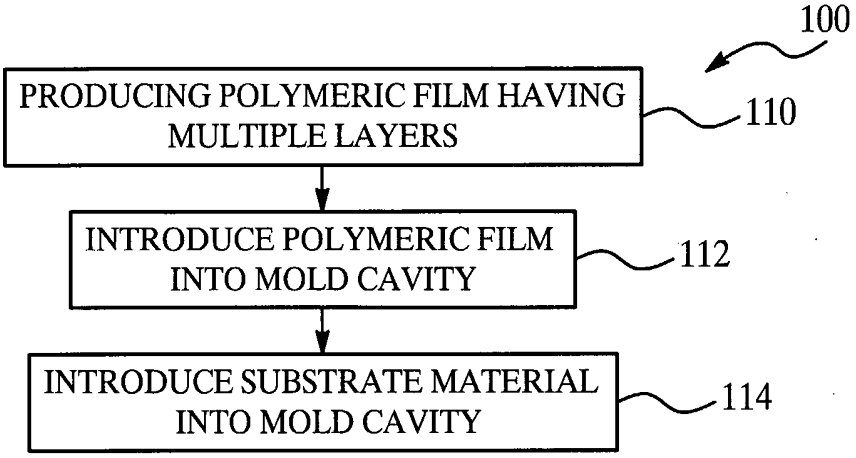

Figure 4

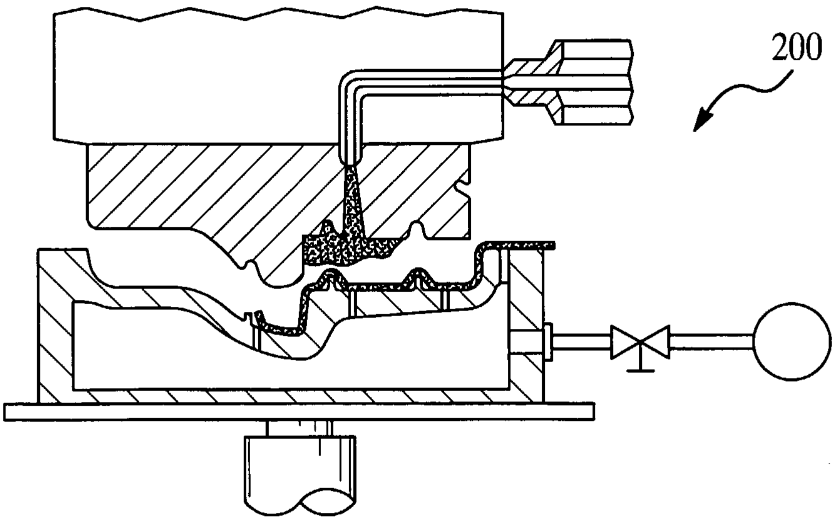

Figure 5

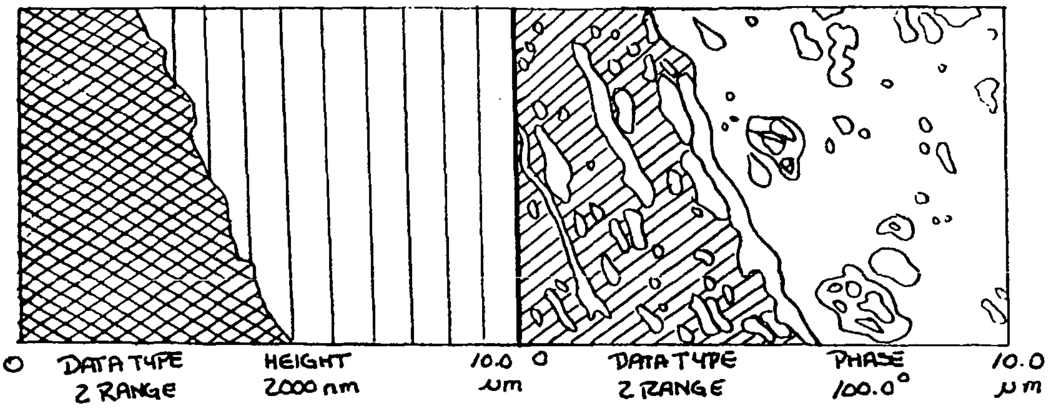
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FIG. 2

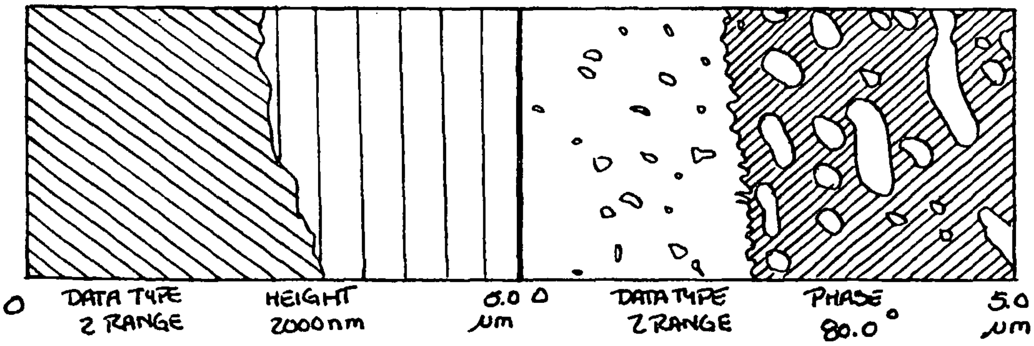
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FIG. 3

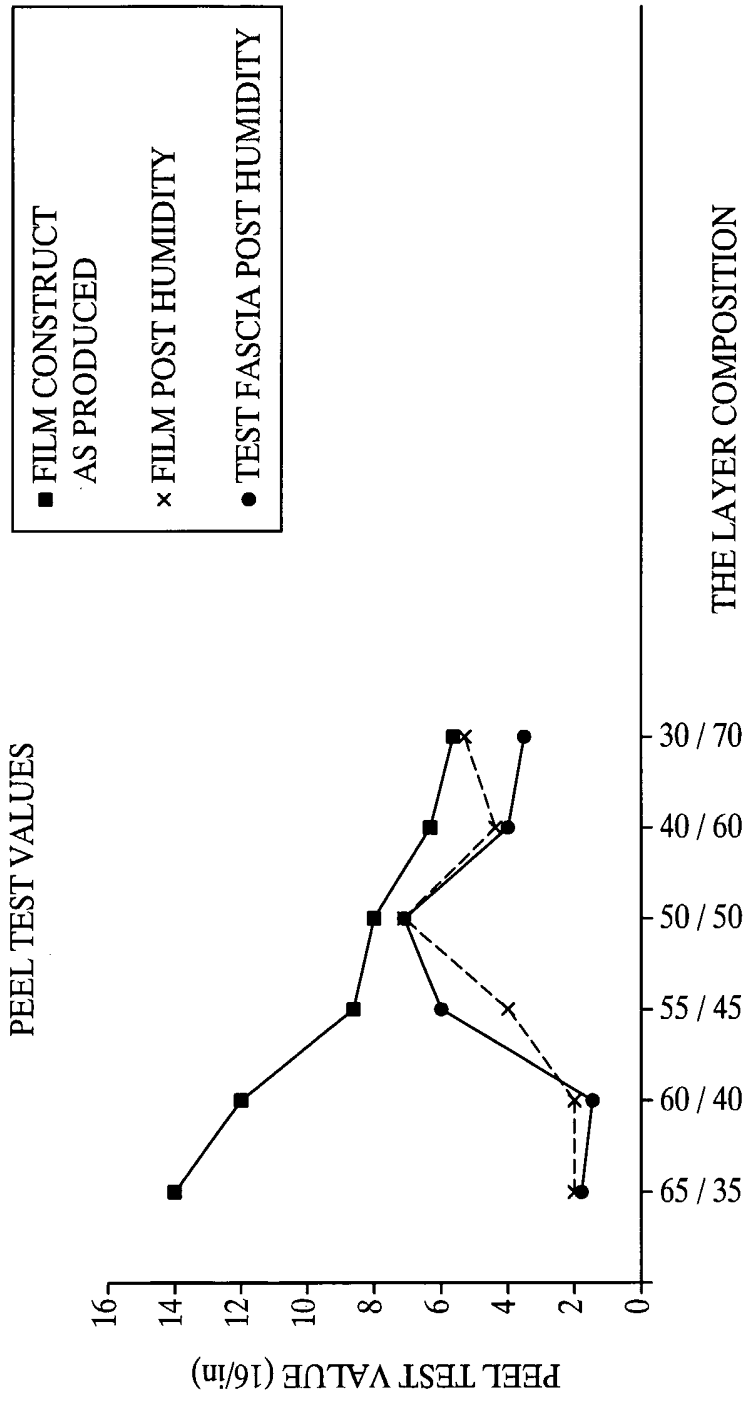
PEEL TEST VALUES
■ FILM CONSTRUCT AS PRODUCED
× FILM POST HUMIDITY
● TEST FASCIA POST HUMIDITY
PEEL TEST VALUE (16/in)
16
14
12
10
8
6
4
2
0
65 / 35
60 / 40
55 / 45
50 / 50
40 / 60
30 / 70
THE LAYER COMPOSITION

Figure 6