PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
B44C 1/10, 5/04, B05D 5/06
B29C 45/14, 45/00, C08L 27/16
C08L 33/10, C09D 5/00

A2

(11) International Publication Number: WO 94/03337

(43) International Publication Date: 17 February 1994 (17.02.94)

(21) International Application Number: PCT/US93/07097

(22) International Filing Date: 28 July 1993 (28.07.93)

(30) Priority data:
07/919,663 31 July 1992 (31.07.92) US

(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

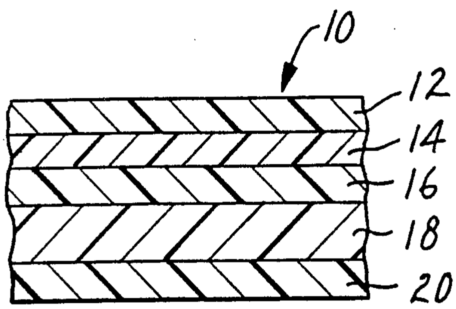
(72) Inventors: DUHME, Frederick, E. ; FLATT, Donald, V. ; JANSSEN, Jeffrey, R. ; MCMULLEN, Carl, W. ; NIEDERMAIR, Siegfried, A. ; PETERSON, Robert, W. ; PRIOLEAU, Lori-Ann, S. ; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: SKOLNICK, Steven, E. et al.; Office of Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: PAINT FILM AND METHODS FOR ITS MANUFACTURE



(57) Abstract

A paint film includes an extruded clear coat layer (14), a liner layer (12) releasably attached to the outer surface of the clear coat layer to assist in injection molding of the paint film to a substrate, a color layer (16) on the other side of the clear coat layer from the liner layer, a reinforcing layer (18) on the other side of the color layer from the clear coat layer, and an optional bonding layer (20) on the other side of the reinforcing layer from the color layer. The paint film may be applied by injection molding methods including applying a paint film to a deeply-drawn injection molded part during molding without the use of preformed inserts. Slides may be used to provide undercut surfaces on the part that are covered by paint film. Contiguous pieces of different paint films may be applied to a substrate during molding and paint film may be applied to opposite surfaces of a substrate during molding.

PAINT FILM AND METHODS FOR ITS MANUFACTURE

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to paint films used in surfacing objects such as exterior automobile parts. The invention also relates to methods of manufacturing and applying such paint films to a substrate.

Description of the Related Art

Exterior automobile body panels, trim components, and similar parts have traditionally been spray painted to provide the desired appearance and surface protection. The resulting paint coatings typically provide chemical resistance to automobile fluids, abrasion resistance and weatherability (i.e., they do not undergo ultraviolet degradation).

In recent years, it has been proposed to provide exterior surface paint coatings by prefabricating free-standing multi-layer films that are adhered to the surfaces of the parts, and there has been some commercial use of these films on certain exterior automobile parts. Such free-standing films avoid the environmental problems associated with evaporating paint solvents and eliminate the need for additional paint facilities and the equipment, ovens, sludge disposal, and emission control systems associated therewith. The use of such free-standing films also permits integration of part manufacture and surface finishing, improvements in appearance (e.g., avoiding coating problems, crazing, and adhesion problems that can exist with paint), and the use of substrate materials that are difficult to paint.

Examples of such paint films are described in Johnson et al. U.S. Pat. No. 4,818,589 and in Ellison et al. U.S. Pat. Nos. 4,931,324; 4,943,680; and 4,810,540. The paint films of these patents each include an outer clear coat layer and a pigmented layer formed by casting on a carrier layer and a bonding layer thereunder to attach to a substrate. The Johnson et al. paint film also had a reinforcing layer between the pigmented layer and the bonding layer. Johnson et al. mention applying the paint film to a substrate by vacuum application, thermo-pressure forming and injection molding. The Ellison et al. patents describe adhering the paint film to a supporting substrate by known laminating or bonding techniques such as thermoforming.

The application of a paint film to a part or object while the part is being injection molded is advantageous because a separate laminating step or other application method is not required. The film can be placed between the mold sections in its natural flat (planar) shape and formed and bonded to the contour of the part during molding. Alternatively, the film, when properly reinforced with a substrate compatible material, can be thermoformed into a preformed insert that has the shape of the mold cavity and inserted into the mold before molding.

Ellison, T. M., "Film Finishing Plastics in Practice", presented at Finishing Automotive Plastics Clinic, April 28-29, 1992, Dearborn, Michigan, describes an in-mold surfacing process involving advancing a paint film unwound from a supply roll into an open injection mold, closing the mold, and injecting plastic. It is mentioned that this in-mold surfacing process is suitable for parts that are relatively shallow, and that preformed inserts are used for more severe contours.

Ellison, T. M., and Shimanski, M. A., "Plastic Film Finishing of Exterior Automotive Components", Automotive News, March 20, 1989, p. E8, describes injection molding with an unsupported paint film for shallow profiles only and using a preformed insert for more complex parts.

The use of preformed paint film inserts during molding is also described in Williams, L. A., "In-Mold Painting of Thermoplastic Parts Using Paint Film Laminate Technology", presented at Finishing Automotive Plastics Clinic, April 28-29, 1992, Dearborn, Michigan and Fridley, C. H., "In-Mold Painting of Thermoplastic Parts Using Paint Film Laminate Technology", SAE Technical Paper FC91-374, September 23-25, 1991, Cincinnati, Ohio.

The following definitions apply herein.

"Paint film" means a multilayer, thermoplastic film that provides surface protection and decoration for an underlying object, is sufficiently flexible to conform to the contours of the underlying object at processing temperatures, and has a color layer that has color agent(s) throughout and one or more of the following layers adhered thereto: a clear coat layer (on the surface for appearance and protection), a reinforcing layer (below the color layer for strength), a bonding layer (at the bottom when needed to securely bond to the underlying object), and a liner layer (on the outer surface layer and removable therefrom).

"Chemical resistance" means that a surface layer of a film has characteristics such that the film will not appreciably change in appearance or adhesion when exposed to automobile fluids.

"Automobile fluids" means the following fluids: gasoline and/or other motor vehicle fuels, motor oil, engine coolant, windshield washer solution, lubricants, engine cleaner, brake fluid, waxes, window cleaner, chrome cleaner, tar and bug cleaner and vinyl cleaners.

"Weatherability" means having no appreciable change in appearance or adhesion after 2,000 hours of exposure to ultraviolet radiation according to the Society for Automotive Engineer's (SAE's) J1960 June 1989 test for accelerated exposure of automotive exterior materials.

"Optical clarity" means that a layer has a transmission haze of 3% or less for a 2 mil (51 μm) film according to the ASTM test D1003 (Third Edition 1988).

"Interior surface protection properties" means mar resistance and that the film will not appreciably change in appearance or adhesion when subjected to interior cleaning solutions, food, cosmetics, grease, oils and plasticizers.

"Thermoplastic" means a material that can be repeatedly heated and reformed.

SUMMARY OF THE INVENTION

In one aspect, the invention features, in general, a paint film that is suitable for use in surfacing an automobile body part or the like and includes a clear coat layer made of an extruded sheet of polymer and a color layer applied directly thereto. The clear coat layer has chemical resistance, weatherability and optical clarity. The use of an extruded clear coat layer, as opposed to a clear coat layer made by solvent casting or spraying, has advantages during manufacture in reducing exposure to particulate contamination and removing the need for handling evaporating solvents or other carrier liquids. The direct attachment of the clear coat layer to the color layer provides a reliable bond that is not subject to delamination when exposed to environmental conditions.

In preferred embodiments, the clear coat layer has a transmission haze of less than 1% and is made of a blend of at least two polymers, one having chemical resistance and one having bonding properties. Both polymers typically have weatherability. There is a higher proportion of the first polymer near the outer surface and a higher proportion of the second polymer near the surface bonded to the color layer, facilitating reliable, direct bonding thereto.

The first polymer is a fluorinated polymer (most preferably poly(vinylidene fluoride)), and the second polymer is made from an acrylic resin (most preferably blends or copolymers having at least two materials selected from the group consisting of methacrylate copolymers, methyl methacrylate, ethyl methacrylate, and butyl methacrylate). As used herein, acrylic resins and acrylates include methacrylic resins and methacrylates. The clear coat layer is made from a sheet (most preferably a coextruded sheet) having two layers with different proportions of the first and second polymers in the two layers. The clear coat layer could have another polymer, e.g., an aliphatic thermoplastic urethane, in addition to the other two polymers or in place of the acrylate.

The color layer typically includes a pigment in a suitable binder of, e.g., acrylate, vinyl or urethane.

A reinforcing layer is adhered to the other side of the color layer from the clear coat layer. The reinforcing layer may comprise polybutylene terephthalate, polyethylene terephthalate/polybutylene terephthalate copolyester, acrylonitrile-butadiene-styrene, polyester/polycarbonate, thermoplastic olefins, ethylene-propylene-diene monomer, thermoplastic urethane, polyvinyl chloride, polyamides, acrylates or blends thereof. A bonding layer can be attached to the other side of the reinforcing layer from the color layer.

Paint films made according to the invention can also be used to surface automobile parts and other exterior products that do not require optical clarity in clear coat layers. Paint films made according to the invention can also be used to surface interior products that do not require weatherability and do not require chemical resistance (to automobile fluids).

In another aspect, the invention features, in general, the use of a particular liner layer during injection molding of a paint film. The liner layer is releasably attached to, and in direct, intimate contact with, the outer surface of the paint film. The liner layer comprises a thermoplastic polymer having a break stress from about 2,000 psi (141 kg/cm^2) to 10,000 psi (704 kg/cm^2) at the injection mold temperature (in order to permit deformation and avoid wrinkling of the liner layer). The liner layer avoids tearing, melt-through and rupture of the paint film during injection molding and contributes with the other layers to maintaining the integrity of the color layer during molding (avoiding wash-out of the color layer). Thus, the paint film may be deeply drawn, thereby avoiding the need to use preformed inserts for parts having complex contours. The liner layer can also be used to control the appearance (e.g., gloss) of the outer surface of the paint film. Furthermore, a liner layer permits the use of less precisely finished molds. The liner layer also avoids damage to the paint film during shipping, handling and processing of finished parts.

Preferably the liner layer has a break stress from about 4,000 psi (282 kg/cm²) to 8,000 psi (563 kg/cm²) and a break elongation greater than 200% at the injection mold temperature (generally between 50°F (10°C) and 220°F (104°C)) to promote covering of the part. The liner layer also has thermal stability at the injection mold temperature. Examples of suitable liner layer materials include polyethylene terephthalate/polybutylene terephthalate copolyester (most preferably a 50%/50% by weight blend), nylon 6, and a tetrafluoroethylene/ethylene copolymer.

In another aspect, the invention features, in general, a method of applying a section of a planar paint film on an injection molded object. The paint film is deeply drawn without using preformed inserts. Thus, the need for thermoforming molds and thermoforming equipment as well as thermoforming and die cutting process steps prior to injection molding are avoided. The planar paint film section is supported between a cavity mold section and a core mold section. The film is subjected to three-dimensional drawing and can successfully achieve a draw down ratio of at least 1.2.

An initial contour is provided to the film by applying heat to the film (from the core mold section) and moving the mold sections toward each other so that a projecting member of the core mold section contacts and deflects the film, the moving being sufficiently slow to avoid tearing of the paint film and to permit the paint film to be softened and plastically deformed. After the two mold sections have closed, a flowable resin is injected into the space between the core mold section and the film to move the film into contact with the surface of the cavity, completing the forming process of the film. The method promotes uniform drawing of the paint film, avoiding wash-out of the color layer and tearing, melt-through and rupture of the paint film.

Movable members in the mold are extended to partially define the shape of the mold cavity during molding and are retracted after molding. Preferably, the movable members are near the opening to the cavity and provide an undercut surface on the injection molded object that is covered by the film. This feature can be desirably used to provide trim lines (i.e., edges of the film) on side or inwardly facing surfaces that are not visible. Such surfaces are also not subject to harsh treatment by car wash brushes and the like and are less exposed to salt and automobile fluids, which might weaken the bonding forces between the substrate and the paint film.

In another aspect, the invention features, in general, a paint film application method in which two contiguous paint films are placed in a mold and are applied during injection molding to cover adjacent areas of the product. The films can have overlapping edge portions or they can have edges that are butted up against each other with a tape that overlaps portions of both films to hold them together. The films could have a different color.

Other features and advantages of the

invention will be apparent from the following description of the drawings, the preferred embodiments and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more fully appreciated with reference to the following drawings in which similar reference numerals designate like or analogous components throughout.

FIG. 1 is a diagrammatic vertical sectional view of a paint film according to the invention.

FIG. 2 is a diagrammatic perspective view of a test panel to which a deeply-drawn film according to FIG. 1 has been applied during injection molding of the test panel.

FIG. 3 is a diagrammatic elevational view showing a paint film in position between cavity and core mold sections of an injection molding apparatus.

FIG. 4 is a diagrammatic partially vertically sectioned view of the FIG. 3 mold after injection molding.

FIG. 5 is a perspective view showing a paint film covered injection molded part with an undercut portion.

FIG. 6 is a partial sectional view, taken at 5-5 of FIG. 5, of the FIG. 5 part before trimming.

FIG. 7 is a perspective view of a cavity mold section of a mold used to make the FIG. 5 part.

FIG. 8 is a sectional view, taken at 8-8 of FIG. 7, of the FIG. 7 mold section and mating core mold section during closing of the mold sections.

FIG. 9 is a sectional view, taken at 9-9 of FIG. 7, showing the FIG. 8 mold sections after injection of a flowable resin.

FIG. 10 is a perspective view of an injection molded part that is covered with a paint film and has a reinforcing member on one side thereof.

FIGS. 11 and 12 are diagrammatic, partially sectioned, perspective views of parts covered with contiguous pieces of two different paint films.

FIG. 13 is a partial sectional view of an injection molded part having paint film attached to opposite sides thereof.

FIG. 14 is a diagrammatic sectional view of a molding apparatus for making the FIG. 13 part.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Structure of Paint Film and Test Panel

Referring to FIG. 1, paint film 10 includes a liner layer 12, a clear coat layer 14, a color layer 16, a reinforcing layer 18, and a bonding layer 20. Paint film 10 comprises thermoplastic materials; i.e., materials that can be repeatedly heated and reformed. Preferably, paint film 10 is from about 2 mils (51 μm) to 20 mils (508 μm) thick, more preferably from about 4 mils (107 μm) to 10 mils (254 μm) thick and does not include materials (e.g., fabric) that would undesirably distort surface appearance.

Liner layer 12 is a removable protective film that protects clear coat layer 14 during molding and provides strength (along with reinforcing layer 18) to paint film 10 during molding to avoid tears, melt-through and rupture thereof. Liner layer 12 may be left in place to protect the remaining layers of the paint film during shipping, handling and processing of finished, injection molded parts. Liner layer 12 can control the appearance (e.g., gloss) of clear coat layer 14. Consequently, the liner layer may be smooth or embossed to provide a desired texture. Liner layer 12 also permits one to use a less precisely finished mold surface than is needed in the absence of a liner layer. Liner layer 12 further permits one to avoid the use of release agents in removing parts from a mold. Liner layer 12 is in direct, intimate contact with clear coat layer 14; e.g., there is no visible entrapped air between the two layers.

Liner layer 12 is preferably from about 0.5 mil (13 μm) to 5.0 mils (127 μm) thick (more preferably 1.0 mil (25 μm) to 2.0 mils (51 μm) thick). It must have a minimum thickness to protect clear coat layer 14; the amount of additional thickness, used to provide strength to the film, depends upon the thickness of the other layers in film 10, primarily reinforcing layer 18, as well as the injected resin. Liner layer 12 has a break stress below about 10,000 psi (704 kg/cm^2), to permit deformation and avoid wrinkling during molding, but above about 2,000 psi (141 kg/cm^2), to provide a desired amount of strength to the film. Preferably the break stress is from about 4,000 psi (282 kg/cm^2) to 8,000 psi (563 kg/cm^2). The liner layer also needs to have sufficient break elongation, preferably greater than 200%, to conform to the contour of the mold, promote covering of the part, and avoid wrinkling, particularly for deeply drawn parts and parts with steep contours. Break stress and break elongation can be measured according to ASTM test D882 for tensile strength at break and percentage elongation at break, respectively, and should be measured at temperatures at or close to the injection mold temperature, as discussed in more detail below. The materials of liner layer 12 also need to have thermal stability, i.e., not melt, burn, or degrade at the injection mold temperature.

Suitable materials for liner layer 12 include polyethylene terephthalate/polybutylene terephthalate copolyester (from 40% to 60% by weight of each, most preferably a 50%/50% by weight blend such as VANDAR 2100 from Hoechst-Celanese), nylon 6 (CAPRAN ER-15 from Allied-Signal, Inc., a heat-stabilized nylon 6), and tetrafluoroethylene/ethylene copolymers (e.g., AFLEX from Asahi) having a break stress from about 2,000 psi (141 kg/cm²) to 10,000 psi (704 kg/cm²). Other materials useful for liner layer 12 include polyproplyene, polyethylene, glycol modified polyethylene terephthalate, linear low density polyethylene, poly(tetrafluoroethylene), ethylene tetrafluoroethylene, polyvinyl fluoride, fluorinated ethylene propylene, perfluoroalkoxy/tetrafluoroethylene blends, polyamides, and linear low density polypropylene materials having a break stress from about 2,000 psi (141 kg/cm²) to 10,000 psi (704 kg/cm²). Blends or composites of the foregoing materials may also be used. While actual testing of some of these materials (e.g., ethylene tetrafluoroethylene, fluorinated ethylene propylene, linear low density polyethylene/nylon-6/linear low density polyethylene multilayer composites, certain propylenes, certain polyethylenes, and glycol modified polyethylene terephthalate) has shown some wrinkling or melt through, it is believed that their performance can be improved by, for example, using thicker layers of these materials or stronger reinforcing layers. The liner layer may be supplemented with various fillers such as TiO_2, silica, aluminum flakes and the like to impart a desired surface appearance to the liner layer.

Clear coat layer 14 is formed from an

extruded polymer sheet. It has optical clarity, chemical resistance and weatherability and can provide controlled surface conditions, e.g., a glossy clear coat, for film 10. The use of an extruded clear coat layer permits direct bonding to color layer 16 by heat lamination to provide a consistent, reliable bond. Layer 14 may range in thickness from about 0.5 mil (13 μm) to 3.0 mils (76 μm), with thicknesses from about 1.0 mil (25 μm) to 2.0 mils (51 μm) being preferred.

Suitable materials for clear coat layer 14 include blends of at least two different polymers, one that has high chemical resistance properties (preferably a fluorinated polymer), and another that has good bonding properties (preferably made from acrylic, including methacrylic, resins). The preferred construction for clear coat layer 14 is a two-layer, coextruded (i.e., extruded together at the same time) sheet including poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA), as described in Published European Application No. 0 459 720 A1, which is hereby incorporated by reference. (Alternatively, the layers could be extruded separately and thereafter joined together, for example by lamination.) The top (i.e., outer) layer of the two-layer sheet comprises 80% PVDF and 20% PMMA, and the bottom (i.e., inner) layer comprises 80% PMMA and 20% PVDF. Layer 14 thus has a higher percentage of fluorinated polymer near the upper surface, where its chemical resistance property is needed, and a higher percentage of acrylate near the lower, bonding surface, where good bonding properties are needed. By having blends of the same polymers in the two coextruded layers, adhesion between the two is promoted.

Other acrylates could be used, e.g., medium to low molecular weight acrylic resins having a weight average molecular weight below 750,000, preferably blends or copolymers comprising at least two materials selected from the group consisting of methyl methacrylate, ethyl methacrylate, butyl methacrylate, and methacrylate copolymers. Clear coat layer 14 could have other ratios of components and could also include other components. For example it could comprise an outer layer with 70% to 100% poly(vinylidene fluoride), 0% to 30% acrylic resin, and 0% to 30% aliphatic thermoplastic urethane, and an inner layer with 0% to 30% poly(vinylidene fluoride), 0% to 90% acrylic resin, and 0% to 90% aliphatic thermoplastic urethane. (All percentages are percentages by weight, i.e., % by weight.) The inner and outer layers may include all three or only two of the three mentioned materials. Clear coat layer 14 also has ultraviolet (UV) stabilizers (e.g., the TINUVIN family of stabilizers available from Ciba-Geigy Corp.) to absorb ultraviolet radiation and to protect layers below from ultraviolet radiation. Clear coat layer 14 could also include a tint, i.e., a light shade of color that does not substantially change opacity. The light shade of color could be provided by a variety of agents including mica and pearlescent materials.

Clear coat layer 14 provides surface protection sufficient for film 10 to meet industry standards set forth in automobile manufacturer specifications regarding chemical resistance to various automobile fluids and does not appreciably change in appearance when exposed to such fluids as required by those standards. Clear coat layer 14 also does not appreciably change in appearance when subjected to acid rain, bird dung, and other environmental agents to which the paint film may be exposed. Clear coat layer 14 also meets industry standards set forth in automobile manufacturer specifications regarding weatherability and does not appreciably change in appearance when subjected to conventional accelerated weathering tests well beyond 2,000 hours.

Color layer 16 is visible through transparent clear coat layer 14 and provides color to paint film 10 by the incorporation in layer 16 of one or more of the following color agents: pigments (organic or inorganic), dyes, inks, mica, glass particles, glass beads and metallic particles including those treated to improve dispersion or alter light reflection properties. A typical composition for layer 16 is an acrylic/vinyl resin binder containing a pigment and, optionally, reflective particles (e.g., metallic flakes) to impart a metallic paint appearance to paint film 10.

A suitable binder system is a 50%/50% by weight mixture of ELVACITE 2028 copolymer (a pigment dispersing agent) and ELVACITE 2046 butyl acrylate (to provide compliance), both from E.I. duPont de Nemours & Co. Another suitable binder system is a 50%/50% by weight mixture of ACRYLOID B66 copolymer (a pigment dispersing agent) and ACRYLOID B72 (ethyl methacrylate) or ACRYLOID B82 (methyl methacrylate), all from Rohm & Haas Corp. Another suitable binder system is a 50%/50% by weight mixture of ACRYLOID B44 acrylic (from Rohm & Haas Corp.) and VYNS-3 polyvinyl chloride/polyvinyl acetate copolymer (from Union Carbide Corp.). Other suitable binder systems include other acrylates, vinyls and polyurethanes. Color coat layer 16 is preferably from about 0.5 mil (13 μm) to 4.0 mils (102 μm) thick, depending on the color, the need to cover the surface below, and the extent of drawing (and thus film thinning) during application to the substrate. Color coat layer 16 can include UV stabilizers.

Reinforcing layer 18 reinforces the other layers of paint film 10, providing strength, elongation, and heat deflection for the color layer at molding temperatures to facilitate injection molding of the film. It protects color coat layer 16 from washout and whitening during closing of the mold sections and the subsequent molding process. It allows film 10 to be molded without melt-through, cracking, tearing or rupturing. The thickness of layer 18 can vary from about 1.0 mil (25 μm) to 10.0 mils (254 μm), depending upon the strength provided by liner layer 12, the type of substrate material, and the particular part design. Layer 18 preferably is from about 3.0 mils (76 μm) to 6.0 mils (152 μm) thick.

Suitable materials for reinforcing layer 18 include extruded films made of polybutylene terephthalate (e.g., CELANEX from Hoechst-Celanese), a 50%/50% by weight blend of two polyethylene terephthalate/polybutylene terephthalate copolyesters (e.g., VANDAR 2100 and RITEFLEX 8929, each from Hoechst Celanese) with acrylonitrile-butadiene-styrene (e.g., CYCOLAC from General Electric Co.), copolyesters (e.g., EKTAR from Eastman Chemical Products, Inc.), thermoplastic olefins (e.g., ETA 3131 from Himont), ethylene-propylene-diene monomer, thermoplastic urethanes, polyvinyl chloride, acrylates, polyamides, or blends thereof. The reinforcing layer can include fillers and pigments.

Bonding layer 20 bonds reinforcing layer 18 to a substrate, e.g., substrate 22 of injection molded test panel 24 shown in FIG. 2. Bonding layer 20 may comprise a thermoplastic film or resin which is selected to be compatible with the substrate. Alternatively, bonding layer 20 may be a heat-activated adhesive. It may be necessary to coat reinforcing layer 18 with an adhesion promoting primer to facilitate adhesion of bonding layer 20 thereto.

In some situations, e.g., when the material of reinforcing layer 18 and the substrate are bondable, a separate bonding layer is not needed and layer 18 can be directly bonded to the substrate. In these situations, reinforcing layer 18 acts as a dual-function reinforcement/bonding layer.

FIG. 2 shows test panel 24, which has injection molded substrate 22 and a 3 in. (7.62 cm) diameter hemispherical projection 26 thereon. Paint film 10 which surfaces substrate 22 is deeply drawn. "Deep draw" in the injection molded paint film context and as used herein means a paint film which has been drawn three-dimensionally without wrinkling and which has experienced a "draw down ratio" of at least 1.2. "Draw down ratio" refers to the ratio of the surface area of the finished film to the surface area of the film before injection molding. Hemispherical projection 26 has a draw down ratio of 2.0. Ratios greater than 1.2 are considered to involve deep draw, and ratios greater than 1.5 are considered to be a particularly deep draw. The techniques described herein permit the paint film to successfully experience particularly deep draw (and even draw down ratios of 2.0 to 4.0), without the need for first thermoforming an insert, a limitation that has hindered commercial acceptability of paint films in the past.

In an already molded part, draw down ratio may be calculated by, for example, comparing the thickness of the paint film in an area which has undergone substantial three-dimensional drawing (stretching) with the thickness of the paint film in an area which has experienced very little, if any, three-dimensional drawing. Since, as explained herein, the paint film stretches during molding it also becomes thinner. Thus, the ratio of the thickness of the paint film at two different locations is proportional to the draw down ratio. Film thickness can be measured by using, for example, optical and electron microscopy techniques.

The materials used in substrate 22 (and in automobile and other parts to which the paint films of the invention are applied) include injection moldable thermoplastic resins such as acrylonitrile-butadiene-styrene (e.g., available under the CYCOLAC trade designation from General Electric Co.), acetals (e.g., available under the CELCON trade designation from Hoechst Celanese Co.), acrylics (e.g., available under the PLEXIGLAS trade designation from Rohm & Haas Corp.), phenolics (e.g., available under the DUREZ trade designation from Occidental), polyamides (e.g., available under the CAPRON trade designation from Allied Signal, Inc.), polycarbonates (e.g., available under the LEXAN trade designation from General Electric Co.), copolyesters (e.g., available under the EKTAR trade designation from Eastman Chemical Products, Inc.), polyethylene (e.g., available under the FORTIFLEX trade designation from Solvay Plastics), polypropylene (e.g., available under the POLYFORT trade designation from Schulman), polystyrene (e.g., available under the POLYSAR trade designation from Polysar), polyurethane (e.g., available under the ESTANE trade designation from Goodrich), polyvinyl chloride (e.g., available under the GEON trade designation from Goodrich), styrene/acrylonitrile blends (e.g., available under the TYRIL trade designation from Dow or the LYSTRAN trade designation from Monsanto), acrylonitrile-butadiene styrene/polycarbonate blends (e.g., available under the PULSE trade designation from Dow), acrylonitrile-butadiene-styrene/thermoplastic polyurethane blends (e.g., available under the PREVAIL trade designation from Dow), polybutylene terephthalate/polycarbonate alloys (e.g., available under the XENOY trade designation from General Electric Co.), olefins, thermoplastic polyolefins, thermoplastic polyesters, vinyls, polybutylene terephthalates, glass filled polybutylene terephthalates, polyphenylene oxides, blends and alloys of polycarbonate and polybutylene terephthalate, polyphenylene esters, blends of polyamides and polyphenylene esters and oxides, and blends of polyolefins and rubber and/or ethylene-propylene-diene monomer.

Substrate materials useful in the practice of reaction injection molding (RIM) typically comprise a two-part composition that is mixed just prior to or upon injection into a mold cavity, so that all or substantially all of the reaction occurs within the mold cavity after injection. One component comprises an isocyanate, and the other component comprises a polyol, a chain extender, a curing agent, and any optional additives. Suitable isocyanates include, for example, methylene-di-p-phenylene isocyanate and toluene diisocyanate. The polyols are preferably either polyether polyols or polyester polyols. Generally the polyurethane precursor materials also include various chain extenders and curing agents such as for example diamine compounds either alone or in various blends.

Manufacture of Paint Film

The following describes one way for providing a paint film according to the invention. Color layer 16 may be provided by dip roll coating and subsequently heat drying an ink or other color agent carrying system on a suitable carrier. Alternatively, it may be provided by die coating or other techniques known in the industry to provide a consistent layer with uniform thickness and uniform color such as screen printing, gravuere printing, reverse gravuere printing, knife coating, Meyer bar, and the like. (Techniques in which the color layer is cast onto a carrier and subsequently applied to the clear coat layer are preferred.)

A surface of reinforcing layer 18 (an extruded sheet) is, if necessary, primed to facilitate heat lamination of dried color coat 16 thereto. After color layer 16 has been applied to layer 18, the color layer carrier is removed, and clear coat layer 14 (an extruded sheet) is laminated to the exposed surface of color layer 16. Liner layer 12 (an extruded sheet) is then heat laminated to the exposed surface of clear coat layer 14. The exposed surface of reinforcing layer 18 may then be primed by coating an adhesion promoting primer thereon. Bonding layer 20 (whether a heat activated adhesive or a substrate compatible material) is then coated on or laminated to the primed surface of reinforcing layer 18.

The various layers can be combined in a different order if desired. For example, the color layer may be directly applied to the clear coat layer by the various coating and printing techniques mentioned above. Similarly, the reinforcing layer may be cast rather than laminated.

Paint film 10 can be stored and shipped in sheet or roll form prior to use by automotive component injection molders or other end users.

Injection Molding with Paint Film

As used herein, "injection molding" includes thermoplastic injection molding, thermoset injection molding (e.g., RIM and reinforced reaction injection molding (RRIM), structural foam injection molding, and coinjection molding. FIGS. 3 and 4 illustrate the general procedure for applying paint film 10 to a part by injection molding. Paint film 10 is unwound from a roll 30 and fed between a cavity mold section 32 and a core mold section 34 of a two-part mold. (Cavity mold section 32 has a cavity 38 in the shape of the desired contour for the outer surface of the part. Core mold section 34 has a projecting member 35 of size and shape to fit within the cavity mold section. Mold sections 32 and 34 are then closed, providing an initial contour to the film, and a flowable (i.e., molten, liquid or semi-liquid) resin is injected from a gate 36 into the region behind film 10, thereby urging, stretching and expanding the film into a cavity 38 and, eventually, into intimate contact with the mold cavity wall, as shown in FIG. 4. After the resin has solidified and cooled, the fully formed part, including a substrate 37 and paint film 10, is removed from the mold.

The paint film provides the exterior surface of the substrate (i.e., the solidified and cooled resin) and has a contoured shape repeating the mold shape. If the paint film is to be deeply drawn during the injection molding process, it is important to tautly engage the paint film while the mold sections close, and to control the closing speed of the mold sections, to avoid wrinkling, tearing, and rupture of the paint film. The paint film should be clampingly engaged about a substantial (e.g., at least about 80%) portion of the periphery of the film which is received within the mold interior. If the paint film is to be less substantially drawn, then the portion of the film, which must be tautly engaged may be reduced. The paint film may be engaged or secured in place by spring clamps, tape, static electricity, a vacuum, pins that are received by holes formed in the paint film for this purpose, or a removable frame constructed much like an embroidery hoop.

The temperature at which the mold is maintained is referred to as the "injection mold temperature", which preferably is a temperature from about 50°F (10°C) to 220°F (104°C), depending upon the particular resin being injected. (For example, polybutylene terephthalate and acrylonitrile-butadiene-styrene would have injection mold temperatures around 150°F (66°C), and polyolefins would have injection mold temperatures around 120°F (48°C).) The injection mold temperature should be maintained sufficiently high to help soften the paint film during closing of the mold and resin injection. It should also be maintained sufficiently high to assist in plastically deforming the film while the mold sections close. The injection mold temperature should not be maintained too high, as increased temperatures tend to increase cycle time needed to quench the part before it can be ejected.

The heat and pressure provided by contact of projecting member 35 during closing of the mold sections causes paint film 10 to soften and plastically deform (i.e., the dimensional change which the paint film experiences during the initial closing of the mold would not be substantially recovered if the mold was opened) and to have an initial contour. Depending on the part configuration, the materials comprising the paint film, and the venting method, the advancement of cavity mold section 32 during the final stage of the closing of the mold (i.e., after the projecting member contacts the film) could be at a typical fast speed used when injection molding without film (e.g., taking much less than 0.5 second to close), or the advancement of mold section 50 could be at a reduced speed (e.g., taking two to three seconds for the mold to close), in order to avoid tearing or wrinkling of the film.

With parts having a particularly deep draw, a reduced closing speed (e.g., between 0.5 in. (1.27 cm) and 1.0 in. (2.54 cm) per second) would advantageously allow for more uniform drawing of the paint film because the film would be more able to absorb heat generated by the mold. The taut engagement of the paint film forces the film to stretch uniformly during molding to help avoid wrinkles. The use of a reinforcing layer and a liner layer in the paint film also helps to avoid tearing of the paint film and promotes more uniform drawing. Having liner layer 12 in direct, intimate contact with clear coat layer 14, also helps prevent tearing and rupturing of the paint film. If desired, the clamping force can be reduced in one area (by reduced spring force) in order to provide slippage for the paint film (with liner layer) to more easily cover a particular contour on an injection molded part.

After cavity mold section 32 has closed against core mold section 34, a flowable resin is injected through gate 36 at a temperature between 80°F

(27°C) and 650°F (343°C), depending on the resin being injected and the type of injection molding. As the resin is injected, paint film 10 stretches and moves into contact with the surface of deep cavity 38. The injection of resin is at a sufficiently low flow rate and pressure so as to avoid melting through or rupturing the paint film. The use of a reinforcing layer and a liner layer helps to avoid melt-through, tearing and rupture of the paint film during resin injection.

If necessary, thermoplastic injection molding could be at low pressures of 2,000 psi (141 kg/cm^2) to 12,000 psi ((845 kg/cm^2) hydraulic pressure) in order to avoid melt-through, tearing and rupture of the paint film. For RIM and RRIM, pressures as low as about 100 psi (7 kg/cm^2) may be used. Other pressure ranges may be appropriate depending on the resin system being injected and the type of injection molding. Pressures can be increased above these levels if doing so does not result in melt-through, tearing or rupture. After injection, the injected resin is allowed to solidify before backing off cavity mold section 32. The injection molded part is then removed from the mold. Excess paint film may then be trimmed.

Referring to FIGS. 5 to 9, an injection molded part 130 includes an undercut portion 132. Part 130 is covered by a paint film 134 on a top surface 136, side surfaces 138, and surfaces 140 and 142 which define undercut portion 132. Line 144 (FIG. 6) defines the parting line of the mold. Paint films will often be trimmed at parting lines to provide a clean transition between the paint film and an otherwise uncovered surface. However, when a parting line is at a corner edge of a part, there is an increased risk that the paint film will delaminate from the substrate when trimmed at the corner edge. Delamination could result from harsh treatment by car wash brushes, fingers and similar forces attacking the paint film edge or from chemical attack at the film/substrate interface by such agents as road salt, gasoline and other automobile fluids. For this reason, it is desirable to continue the paint film coverage beyond parting line 144, as shown in FIG. 6. The coverage of paint film 134 beyond the parting line is achieved on part 130 by the use of movable slides in the mold.

Referring to FIG. 7, cavity mold section 148 includes two slide pairs 150 and 152, which are shown in a closed or extended position on FIG. 7. Slides 150 and 152 protrude by an amount that is less than the wall thickness. Hydraulic cylinders 160 move slides 150 and 152 into and out of position and lock them in place during molding. (Pneumatic cylinders and other mechanical actuators such as cams may also be used.) Passages 178 allow for heating and cooling of the mold. A mounting groove 180 is used for secure mounting of mold 148 in the injection molding machine.

Paint film 134 is secured to the front of a cavity 164 on an embroidery hoop-like frame 154 (FIGS. 8 and 9), which is aligned with the mold by pins 156 passing through slots 158 formed in slide pair 150 (FIG. 7). The mold is then closed and paint film 134 is provided with an initial contour by the closing forces of the molding machine and the elevated temperature of the core and cavity as described previously.

FIG. 8 shows a projecting member 153 of a core mold section 151 making initial contact with and deforming paint film 134. After the mold sections have closed, a flowable resin is injected into the mold and pushes film 134 initially against cavity surface 174 and then against back surfaces 168 and inner surfaces 170 (FIG. 9) of slides 150 and 152 (which correspond to surfaces 140 and 142 of part 130). Flowable resin 157 fills all voids between projecting member 153 and surfaces 168, 170, and 174, which are covered by paint film 134. Vents are provided under all slides in order to vent air and/or gases contained in cavity space 164 during the injection cycle. Vents 162 (FIG. 9) vent air and/or gases between paint film 134 and the cavity wall, and similar vents (not shown) in the core section vent the space above film 134. Slides 150 and 152 are locked by hydraulic cylinders 160 during the injection process to avoid movement due to the high pressures used in injection molding.

After the injected resin has solidified, the pressure applied by hydraulic cylinders 160 is released, and the cylinders are activated in the opposite direction so that slides 150 and 152 are retracted. The mold sections are then opened and molded part 130 is removed.

In the resulting molded part 130, paint film 134 continues beyond parting line 144. Excess paint film 176 (FIG. 6) is removed by knife trimming, water jet, die cutting or laser trimming.

Referring to FIG. 10, an injection molded part 400 has a paint film 402 on one surface of a substrate 404 and a reinforcing member (illustrated as a structural rib 406) secured to the opposite surface via an adhesive (e.g., available under the SCOTCHWELD 2216 trade designation from Minnesota Mining and Manufacturing Co.). (Other attachment methods for the reinforcing member could also be used such as friction welding and sonic welding.) Paint film 402 is applied during injection molding of substrate 404 while rib 406 is attached later. Traditionally, the reinforcing member is secured to the substrate and the part is then painted and oven cured. In such parts, a change in the appearance of the painted surface can occur over the area where the reinforcing member is attached. Such a change in appearance can be avoided when the reinforcing member is added to a paint film covered part. Rib 406 could be replaced by other reinforcing members such as a boss.

Referring to FIGS. 11 and 12, a part 410 (FIG. 11) is covered by two different paint films 412 and 414. Part 410 is provided by placing paint films 412 and 414 in contiguous relationship, adhering the films together at overlapping portion 416 (e.g., with adhesive or heat and pressure), placing the joined pieces in an injection mold, and injecting a flowable resin to provide a substrate 418. An adhesive for bonding paint films 412 and 414 at overlap 416 may have to be different than the bonding layer(s) (if any) that are associated with the paint films for bonding them to substrate 418. Paint films 412 and 414 may be the same or a different color.

FIG. 12 shows an alternate method for joining two films. Part 420 comprises a substrate 428 that is covered by two paint films 422 and 424 that have edges that are butted up against each other. A tape 426 overlaps portions of both films to secure them together. The two paint films may be the same or a different color. If tape 426 is on the underside of the paint films and will be exposed to the incoming resin, the tape should be bondable to the resin. Alternatively (but not shown separately in the drawings), tape 426 could be on the opposite (i.e., top) side of the paint films. If the seam between the two paint films (for either part 410 or part 420) is considered unaesthetic, the seam can be covered with a trim strip, a graphic carrying adhesive film or the like.

Referring to FIGS. 13 and 14, an injection molded part 430 has paint films 432 and 434 attached to opposite surfaces of a substrate 436. Part 430 is made in molding apparatus 438. Film 432 is supported on a mold section 440 which has a cavity 442. Film 434 is supported on a mold section 444 which has a gate 446. A hole 448 in paint film 434 is sealed around gate 446 to prevent injected resin from escaping through the hole and around the gate. After placing films 432 and 434 in position, mold sections 440 and 444 are closed. Resin is then injected through gate 446, causing film 432 to conform to the shape of cavity 442, and causing films 432 and 434 to be adhered to opposite surfaces of substrate 436, which is formed by the injected resin.

The invention will be more fully appreciated with reference to the following nonlimiting examples. Various abbreviations and tradenames employed in the examples are defined according to the table below.

Abbreviations and Tradenames

ABS	acrylonitrile-butadiene-styrene
ACRYLOID B-44	an acrylic resin commercially available from Rohm & Haas Corp.
AFLEX	a poly(tetrafluoroethylene)/ ethylene copolymer film commercially available from Asahi
CAPRAN ER-15	a nylon-6 film commercially

	available from Allied Signal, Inc.
cm	centimeter
CYCOLAC GDT-6300	an acrylonitrile-butadiene-styrene resin commercially available from General Electric Co.
CYCOLAC LS-1000	an acrylonitrile-butadiene-styrene resin commercially available from General Electric Co.
DBTL	dibutyl tin dilaurate
DESMODUR N-100	a polyisocyanate commercially available from Mobay Chemical Corp.
EKTAR GN001	a copolyester commercially available from Eastman Chemical Products, Inc.
FC-430	a fluorochemical surfactant commercially available from Minnesota Mining and Manufacturing Co.
5000 AR SPARKLE SILVER	an aluminum paste commercially available from Silberline Manufacturing Co., Inc.
fpm	feet per minute
g	grams
in	inch
kg/cm^2	kilograms per square centimeter
MEK	methyl ethyl ketone
min	minute
mpm	meters per minute

NUOSTAB 1923	a heat stabilizer commercially available from Witco Chemical Corp.
PARAPLEX G-62	an epoxidized soybean oil commercially available from C.P. Hall Co.
PET	polyethylene terephthalate
PMMA	poly(methyl methacrylate)
psi	pounds per square inch
PVC	poly(vinyl chloride)
PVDF	poly(vinylidene fluoride)
RAVEN 1200	a black pigment commercially available from Columbian Chemical
RT-759-D	a red pigment commercially available from Ciba-Geigy Corp.
TONE 201	a poly ϵ-caprolactone commercially available from Union Carbide Corp.
248-0061	a blue pigment commercially available from Sun Chemical Co.
μm	micron
VAGH	a poly(vinyl chloride)/poly(vinyl acetate) resin commercially available from Union Carbide Corp.
VANDAR 2100	a polyethylene terephthalate/polybutylene terephthalate copolyester resin commercially available from Hoecsht Celanese Co.
VYNS	a poly(vinyl chloride)/poly(vinyl acetate) resin commercially available

	from Union Carbide Corp.
XENOY 1102	a polyester/polycarbonate alloy resin commercially available from General Electric Co.

Example 1

Example 1 describes the preparation of a carrier film and an extruded clear coat used in several of the subsequent examples. A 3 mil (76 μm) thick, oriented, heat set PET film was dip roll coated with a urethane adhesive to provide a 0.5 mil (13 μm) thick layer thereof after drying in a three zone convection oven. The temperature of the first zone was 150°F (65°C), the temperature of the second zone was 250°F (121°C), and the temperature of the third zone was 320°F (160°C). The residence time in each zone was approximately equal and the total drying time was about 5 minutes.

The urethane adhesive comprised the following ingredients:

100 g	TONE 201;
0.5 g	1% DBTL in xylol;
60 g	propylene glycol methylether acetate;
0.6 g	10% FC-430; and
74 g	DESMODUR N-100.

The urethane adhesive coated carrier was used to support an extruded clear coat layer (sometimes referred to herein as a clear coat) as well as other layers of a paint film as described more fully below in other examples.

A clear coat was provided by a two layer coextruded film comprising an outer layer which included 80% PVDF and 20% PMMA and an inner layer which included 20% PVDF and 80% PMMA, such as described in previously incorporated published European Patent Application No. 0,459,720 A1. The urethane coated surface of the PET carrier was laminated to the outer layer of the clear coat using a steel nip roller/rubber nip roller laminator at 72°F (20°C) that provided a compression force of about 25 psi (1.8 kg/cm^2) on the films. The urethane adhesive-coated PET carrier was slightly wider than the clear coat thereby entirely supporting the clear coat. The laminated construction comprising the PET carrier and the clear coat was rolled up on a core for storage and further processing.

Example 2

Example 2 describes the preparation of a paint film comprising the extruded clear coat of example 1, a black color coat layer, and a dual function PVC reinforcement/bonding layer.

The color coat layer (sometimes referred to herein as a color coat or a color layer) was provided by a black ink comprising the following ingredients:

108.6 g	ACRYLOID B-44;
97.2 g	xylol;
54.3 g	diisobutyl ketone;
97.2 g	cyclohexanone;
49.8 g	VYNS;
10.24 g	RAVEN 1200;
3.28 g	PARAPLEX G-62;
1.64 g	NUOSTAB 1923; and
2.36 g	2-ethyl hexyl-2-cyano 3,3 diphenyl acrylate.

The black ink was reverse gravure printed using a 75 line ruling mill roll onto a 4 mil (102 μm) thick calendared PVC film having a 3 mil (76 μm) thick PET supporting film similar to the PET film described in example 1. The PVC film provided a dual purpose reinforcement/bonding layer.

The black ink was then dried in a three zone convection until all solvent was removed. The temperature of the first zone was 140°F (60°C), the temperature of the second zone was 260°F (127°C), and the temperature of the third zone was 340°F (171°C). The residence time in each zone was approximately the same and the total drying time was about 5 minutes. A 0.5 mil (13 μm) thick black color coat bonded to the PVC film resulted. The black color coat, PVC reinforcement/bonding layer, and PET supporting film were rolled up on a core for storage and further processing.

The color coat was laminated to the inner layer of the extruded clear coat of example 1 by wrapping the PET carrier film for the clear coat in a 180° arc on a 240°F (116°C) steel hot can laminator operating at a rate of 6 fpm (1.82 mpm). The PVC reinforcement/bonding layer was positioned against the rubber nip roller during lamination and its PET supporting film was simultaneously removed during the unwinding of the roll.

The paint film comprising the extruded clear coat, the black color coat, and the PVC reinforcement/bonding layer was ultimately provided by peeling off the urethane-coated PET carrier film at room temperature.

Example 3

Example 3 describes the preparation of a paint film comprising the extruded clear coat of example 1, a metallic blue color coat, and a copolyester dual function reinforcement/bonding layer.

The color coat was provided by a metallic blue ink comprising the following ingredients:

1209 g	MEK;
754 g	xylol;
476.9 g	248-0061 blue pigment;
250 g	5000 AR SPARKLE SILVER;
546.9 g	ACRYLOID B-44;
141.8 g	VYNS;
9.52 g	PARAPLEX G-62;
4.76 g	NUOSTAB 1923; and
10.95 g	2 ethylhexyl-2-cyano 3,3 diphenyl acrylate.

The metallic blue ink was dip roll coated onto a 3 mil (76 μm) silicone treated PET liner having a release value of about 28 grams/inch (11 grams/cm) as measured by a tape peel adhesion test using 3M brand #234 masking tape (commercially available from Minnesota Mining and Manufacturing Company). The coating gap was 4 mils (102 μm). The ink was dried in a three zone convection oven using the temperatures profile described in example 2 until the solvents had evaporated (approximately 5 minutes) thereby producing a 1.1 mil (28 μm) thick metallic blue color coat. The metallic blue color coated silicone treated PET liner was rolled up on a core for storage and further processing.

The dual function reinforcement/bonding layer was providing by extruding pellets of VANDAR 2100 resin into a 3 mil (76 μm) thick film. Pellets of VANDAR 2100 resin were dried at 220°F (104°C) for 4 hours and extruded with a PRODEX 7JX extruder fitted with a 1.75 inch (4.45 cm) diameter single screw. The barrel pressure was 2500 psi (176 kg/cm^2) and a temperature gradient through the barrel was provided according to the following schedule:

Barrel zone:	1	2	3	4	die
Temp. °F(°C):	410(212)	510(268)	540(284)	550(290)	550(290)

The extruded film was then primed with a solution comprising 15 g VAGH, 57 g MEK, and 28 g xylol using a 120 line ruling mill. The primed film was then dried in a 150°F (65°C) convection oven for about 1 minute to provide a 0.12 mil (3 μm) nominal thickness primer layer and rolled up on a core for storage and further processing.

The unprimed surface of the dual function reinforcement/bonding layer was wrapped in a 270° arc on a 280°F (137°C) steel hot can laminator and the primed surface was heat laminated to the metallic blue color coat at a processing speed of 8 fpm (2.4 mpm) and with a compression force of about 25 psi (1.8 kg/cm^2) on the films. The silicone treated liner for the color coat was removed upon exiting from the nip rollers and the laminate comprising the reinforcement/bonding layer and the color coat was rolled up on a core. An extruded clear coat prepared as described in example 1 was heat laminated to this composite according to the procedure of example 2 except using a 270° arc and a steel hot can laminator temperature of 280°F (137°C). The urethane-coated PET carrier for the clear coat was subsequently removed as described in example 2.

Example 4

Example 4 describes the preparation of a paint film comprising the extruded clear coat of example 1, the dual function reinforcement/bonding layer of example 3, and a blue color coat.

The blue color coat was provided by a blue ink comprising the following ingredients:

1110 g	cyclohexanone;
830 g	xylol;
551.5 g	ACRYLOID B-44;
240 g	248-0061 blue pigment;
143 g	VYNS;
9.6 g	PARAPLEX G-62;
4.8 g	NUOSTAB 1923; and
11.04 g	2 ethylhexyl-2-cyano 3,3 diphenyl acrylate.

The paint film of example 4 was prepared according to the procedure for example 3 with the exception that the dried color coat was about 1 mil (25 μm) thick.

Example 5

Example 5 describes the preparation of a paint film comprising the extruded clear coat of example 1, the blue color coat of example 4, and an ABS dual function reinforcement/bonding layer. Example 5 was prepared according to the procedure for example 4 except that the primed VANDAR 2100 reinforcement/bonding layer was replaced by an unprimed, 4 mil (102 μm) thick ABS film. The ABS film was provided by extruding naturally colored

CYCOLAC LS-1000 pellets that had been previously dried at 180°F (82°C) for 4 hours. The pellets were extruded following the procedure described in example 3 except that the temperature gradient through the barrel was as follows:

Barrel zone:	1	2	3	4	die
Temp. °F (°C):	350(178)	450(234)	480(251)	490(256)	490(256)

Example 6

A paint film comprising a copolyester dual function reinforcement/bonding layer and the blue color coat of example 5 was prepared. The reinforcement/bonding layer was prepared by extruding pellets of EKTAR GN001 resin that had been previously dried at 180°F (82°C) for 4 hours. The pellets were extruded following the procedure described in example 3 except the temperature gradient through the barrel was as follows:

Barrel zone:	1	2	3	4	die
Temp. °F (°C):	380(195)	480(251)	510(268)	520(273)	520(273)

The reinforcement/bonding layer was 4 mils (102 μm) thick. This film was then heat laminated to a hand prepared version of the color coat of example 5 using a 2 roll bench top laminator set to 300°F (149°C), a 180° wrap on the top roller for the dual function layer, and a feed rate of 3 fpm (0.9 mpm). The color coat supporting film was then removed. Example 6 did not include a clear coat.

Example 7

Example 7 describes the preparation of a paint film comprising the extruded clear coat of example 1, the dual function reinforcement/bonding layer of example 3, and a red color coat.

The red color coat was provided by a red ink comprising the following ingredients:

80 g	MEK;
80 g	xylol;
47.68 g	ACRYLOID B-44;
20.75 g	RT-759-D red pigment;
12.37 g	VYNS;
0.83 g	PARAPLEX G-62;
0.41 g	NUOSTAB 1923; and
0.95 g	2 ethyl hexyl-2-cyano 3,3 diphenyl acrylate.

The red ink was coated onto a 3 mil (76 μm) thick PET supporting film using a knife blade handspreader and a 6 mil (152 μm) air gap. The red ink-coated PET film was dried according to the procedure of example 3 to provide an approximately 0.8 mil (20 μm) thick color coat.

A dual function reinforcement/bonding layer prepared according to example 3 was heat laminated to the red ink-coated PET supporting film following the procedure of example 6 (with the exception of using the reinforcement/bonding layer of example 3), the primed surface of the dual function layer being in contact with the color coat. Upon exiting from the bench top laminator, the composite was cooled to about 72°F (22°C) and the PET supporting film was removed.

A clear coat similar to that described in example 1 was laminated to the composite comprising the color coat and the dual function reinforcement/bonding layer using a 2 roll bench top laminator heated to 300°F (149°C), a 90° wrap on the top roller for the clear coat, and a feed rate of 3 fpm (0.9 mpm). The inner layer of the extruded clear coat was bonded to the color coat. The urethane primed PET carrier for the clear coat was then removed.

Example 8

Example 8 describes the preparation of a liner layer useful in the practice of the invention. The liner layer comprised a polyethylene terephthalate/polybutylene terephthalate copoylester (VANDAR 2100). Pellets of the copolyester resin were dried and then extruded according to the procedure described in example 3 for the reinforcement/bonding layer onto a 2 mil (51 μm) thick PET carrier moving at a speed of 34 fpm (10.2 mpm) to provide a 1.5 mil (38 μm) thick liner layer. The liner layer demonstrated a break stress of 5700 psi (401 kg/cm²) and a break elongation of 500%.

Break stress and break elongation were measured according to ASTM test D882 for tensile strength at break and percent elongation at break, respectively. An INSTRON 1122 equipped with a SINTECH software package and an Applied Test Systems oven chamber were employed. The oven temperature was 150°F (66°C), the test speed was 12 in. (30 cm)/min, the jaw gap was 2 in. (5 cm), the load range was 50 pounds (22.7 kg), the oven dwell time was 5 minutes after the oven door was shut, and the specimen size was 4 in. (10.16 cm.) by 1 in. (2.54 cm). 1 to 2 mils (25 to 51 μm) thick samples were cut; 5 specimens were used for each sample and the results were averaged.

The liner layer was heat laminated to the outer layer of the extruded clear coat of the paint film of example 5 using a two roll bench top laminator heated to 270°F (132°C). The liner layer was wrapped about the top roll. The PET carrier for the liner layer was then removed. The liner layer was in direct intimate contact with the clear coat and no air pockets were visible.

Examples 9 to 11

A series of liner layers similar to that of example 8 was prepared in the same manner, the thickness of the liner layer being varied as shown below in Table 1.

Table 1

Example	Liner Layer Thickness mils (μm)
9	0.5 (13)
10	1.0 (25)
11	2.0 (51)

Each of the liner layers of examples 9 to 11 was heat laminated to the paint film of example 4 using the procedure described in example 8. In each case the liner layer was in direct intimate contact with the clear coat without visible air pockets therebetween.

Example 12

A liner layer provided by a 1 mil (25 μm) thick film of CAPRAN ER-15 was heat laminated to the outer layer of the extruded clear coat of the paint film of example 4 using a hot can laminator operating at 315°F (157°C) with a feed rate of 6 fpm (1.8 mpm) and a (270°) wrap on the hot can for the paint film. The liner layer was in direct intimate contact with the extruded clear coat and no air pockets between the two were visible. The liner layer of example 12 had a break stress of 8,000 psi (563 kg/cm^2) and a break elongation of 465%, when measured according to the procedures described in example 8.

Example 13

A liner layer provided by a 1 mil (25 μm) thick film of AFLEX was heat laminated to the outer layer of the extruded clear coat of the paint film of example 4 using a LEDCO Industrial Laminator operating at a feed rate of 4 fpm (1.2 mpm) with top and bottom shoe temperatures of 360°F (182°C) each. The liner layer was in direct intimate contact with the extruded clear coat and no air pockets between the two were visible. The liner layer of example 13 had a break stress of 4,400 psi (310 kg/cm^2) and a break elongation of 821%, when measured according to the procedures described in example 8.

Example 14

Example 14 describes the preparation of an injection molded part according to the invention comprising an injection molded polymer substrate having a deeply drawn paint film bonded thereto. The injection molded part of this example had the shape illustrated in FIG. 2

More specifically, the paint film of example 8, including the liner layer, was placed in an injection mold having the basic construction shown in FIG. 5 (with the exception that the projecting member and the complementary cavity were shaped to provide hemisphere 26). The paint film was secured to clamping bars 76 using SCOTCH 410 brand double sided tape (commercially available from Minnesota Mining and Manufacturing Co.) with the liner layer facing mold cavity source 60. Using a VAN DORN 300 injection molding machine, XENOY 1102 resin was injected at 500°F (260°C) into the injection mold maintained at 150°F (66°C). The cavity and core sections of the mold were closed at a speed of about 0.5 inches/second (12.7 mm/second) using a cycle time of 60 seconds. After the injected resin had solidified, the injection molded part comprising a polycarbonate/polybutylene terephthalate alloy substrate and the deeply drawn paint film of example 8 was removed. Excess paint film was trimmed by hand with a knife.

Examples 15 to 17

A series of injection molded parts similar to that described in conjunction with example 14 was prepared following the procedure of example 14 except using the paint films of examples 9 to 11, respectively.

Example 18

Example 18 describes the preparation of an injection molded part similar to examples 14 to 17 except that the injection molded resin for the substrate was CYCOLAC GDT-6300 and the paint film for surfacing the substrate was that of example 12 (including the liner layer). The extruder temperature was 390°F (190°C), the mold temperature was 145°F (63°C), and the cycle time was 55 seconds.

Example 19

Example 19 describes the preparation of an injection molded part similar to example 18 except that the paint film for surfacing the substrate was that of example 13 (including the liner layer).

Although the invention has been described as having particular utility in the provision of paint film-covered motor vehicle components, the invention in its broader aspects is not so limited. For example, paint films according to the invention may also be used to surface other outdoor products requiring ultraviolet protection (i.e., weatherability) and chemical resistance similar to that for automobile exteriors. Examples of such other products include outdoor telecommunication equipment, outdoor table tops, architectural siding, recreational equipment, snowmobiles, motorcycles, tractors or other yard and farm implements, boats and bicycles.

Paint films could also be used to provide a surface finish for indoor products (particularly injection molded products) that would not need ultraviolet protection, e.g., household appliances, computer housings (in which event it may be desirable to incorporate a conductive filler to provide electromagnetic interference shielding), industrial components and clock faces. Paint film used to surface interior products would not need to resist automobile fluids but would need to provide interior surface protection, namely mar resistance and resistance to appreciable changes in appearance when subjected to interior cleaning solutions, food, cosmetics, grease, mineral oils and plasticizers. Clear coat layers that provide chemical resistance for automobile fluids would also provide interior surface protection.

In general, paint films according to the invention would be useful in any application where conventional paint may be employed.

Paint film constructions beyond those specifically described above may also be provided within the scope of the invention. For example, paint films according to the invention could carry graphics in addition to the use of a continuous color agent throughout the color layer. The clear coat layer could be embossed to provide a desired surface finish (e.g., enhanced gloss, reduced gloss or texture). Alternatively, the clear coat layer could be extruded onto a liner layer that would give the outer surface of the clear coat layer the desired surface texture, avoiding the need for post embossing.

As well, paint films according to the invention may be applied to substrates other than polymeric materials such as metal sheets.

The molding apparatus may also be varied beyond that which is described hereinabove. For example, the mold sections may move horizontally (as illustrated in the drawings) or vertically. Clamping bars and frames could be used on molds of either type.

Other variations and modifications are possible within the scope of the foregoing specification and drawings without departing from the invention which is defined in the accompanying claims.

WHAT IS CLAIMED IS:

1. A paint film for use in surfacing an automobile body part or the like comprising

a clear coat layer of an extruded sheet of polymer, said sheet having chemical resistance, weatherability, and optical clarity, said clear coat layer having an outer surface and a bonding surface, and

a color layer directly applied to said bonding surface.

2. The paint film of claim 1 wherein said clear coat layer has a transmission haze of less than 1%.

3. The paint film of claim 1 wherein said sheet includes a blend of at least two different polymers, a first polymer of said blend having chemical resistance and a second polymer of said blend having bonding properties.

4. The paint film of claim 3 wherein said sheet has a higher proportion of said first polymer and a lower proportion of said second polymer in a region adjacent to said outer surface than said sheet has in a region adjacent to said bonding surface.

5. The paint film of claim 4 wherein said first polymer is a fluorinated polymer.

6. The paint film of claim 5 wherein said

first polymer is poly(vinylidene fluoride).

7. The paint film of claim 4 wherein said second polymer is made from an acrylic resin.

8. The paint film of claim 7 wherein said second polymer is a blend or a copolymer comprising at least two materials each selected from the group consisting of methacrylate copolymers, methyl methacrylate, ethyl methacrylate, and butyl methacrylate.

9. The paint film of claim 1 wherein said sheet has an outer layer comprising 70% to 100% by weight poly(vinylidene fluoride), 0% to 30% by weight acrylic resin, and 0% to 30% by weight aliphatic thermoplastic urethane and an inner layer comprising 0% to 30% by weight poly(vinylidene fluoride), 0% to 90% by weight acrylic resin, and 0% to 90% by weight aliphatic thermoplastic urethane.

10. The paint film of claim 9 wherein said at least two layers are extruded layers.

11. The paint film of claim 10 wherein said at least two layers are coextruded layers.

12. The paint film of any preceding claim to wherein said color layer includes a pigment dispersed in a polymeric binder, said binder being selected from the group consisting of acrylates, vinyls and polyurethanes.

13. The paint film of claim 12 wherein

said color layer includes a pigment dispersed in a vinyl/ acrylic resin.

14. The paint film of any one of claims 1 to 11 further comprising a reinforcing layer on the other side of said color layer from said clear coat layer.

15. The paint film of claim 14 wherein said reinforcing layer is from about 3.0 mils (76 Am) to 6.0 mils (152 gm) thick.

16. The paint film of claim 14 wherein said reinforcing layer comprises a material selected from the group consisting of polybutylene terephthalate, polyethylene terephthalate/polybutylene terephthalate copolyester, acrylonitrile-butadiene-styrene, polyester/polycarbonate alloy, thermoplastic olefins, ethylene-propylene-diene monomer, thermoplastic urethane, polyvinyl chloride, polyamides, acrylates, and blends thereof.

17. The paint film of claim 14 further comprising a bonding layer attached to the other side of said reinforcing layer from said color layer.

18. The paint film of any one of claims 1 to 11 further comprising a bonding layer attached to the other side of said color layer from said clear coat layer.

19. The paint film of any one of claims 1 to 11 further comprising a layer carrying graphics.

20. A paint film for applying to a part during injection molding of said part at an injection mold temperature comprising

a surface layer having an outer surface and a bonding surface, and

a liner layer releasably attached to said outer surface and in direct, intimate contact therewith, said liner layer having a break stress of from about 2,000 psi (141 kg/cm^2) to 10,000 psi (704 kg/cm^2) at said injection mold temperature.

21. The paint film of claim 20 wherein said liner layer has a break elongation greater than 200% at said injection mold temperature.

22. The paint film of claims 20 or 21 wherein said liner layer has a break stress of from about 4,000 psi (282 kg/cm^2) to 8,000 psi (563 kg/cm^2) at said injection mold temperature.

23. The paint film of claims 20 or 21 wherein said liner layer includes polyethylene terephthalate/polybutylene terephthalate copolyester.

24. The paint film of claim 23 wherein said copolyester has between 40% and 60% by weight polyethylene terephthalate and between 40% and 60% by weight polybutylene terephthalate.

25. The paint film of claims 20 or 21 wherein said liner layer includes nylon 6 or a copolymer of tetrafluoroethylene and ethylene.

26. The paint film of claims 20 or 21 wherein said liner layer includes one or more polymers selected from the group consisting of polyproplyene, polyethylene, glycol modified polyethylene terephthalate, linear low density

polyethylene, polytetrafluoroethylene, ethylene tetrafluoroethylene, polyvinylfluoride, fluorinated ethylene propylene, polyfluoroalkoxy/tetrafluoroethylene blends, polyamides, linear low density polypropylene, and blends and composites thereof.

27. The paint film of claims 20 or 21 wherein said liner layer is from about 0.5 mil (13 μm) to 5.0 (127 gm) mils thick.

28. A method of applying a paint film according to claims 20 or 21 on an injection molded object made at an injection mold temperature comprising

placing said paint film in an injection mold maintained at said injection mold temperature with said liner layer facing a cavity of said mold, and

injecting a flowable resin into a space on the other side of said film from said cavity, said film being urged into contact with the surface of said cavity and being adhered to said injected resin to result in a paint film covered injection molded object wherein said paint film experiences a draw down ratio of at least 1.2 during the formation of the paint film covered injection molded object.

29. A method of providing a paint film on

an injection molded object comprising

supporting a planar paint film between a first mold section that has a cavity in the shape of the desired contour for an outer surface of said part and a second mold section that has a projecting member of shape and size to fit in said cavity,

providing an initial contour to said film by applying heat to said film and moving said mold sections toward each other so that said projecting member contacts said film, said moving being sufficiently slow to avoid tearing, wrinkling and rupture of said film and to cause said film to be softened and plastically deformed, and

injecting a flowable resin into a space between said second mold section and said film to move said film into contact with the surface of said first mold section defining said cavity, said film being subjected to three-dimensional drawing during said moving of said mold sections and said injecting and experiencing a draw down ratio of at least 1.2 during formation of the injection molded object;

said cavity is partially defined by movable members in said cavity and near an opening to said cavity when said members are in an extended position during said injecting, and further comprising retracting said movable members after said injecting;

wherein said movable members provide an undercut surface in said part that is covered by said film.

30. The method of claim 29 wherein said object has a surface that is not covered by said film, and further comprising adding a reinforcing member to said object on said surface that is not

covered by said film.

31. An injection molded object comprising an injection molded substrate having a major surface, a side surface at one side of said major surface, and an undercut defined by undercut surfaces at the other side of said side surface from said major surface, and

a paint film applied to said substrate during injection molding and covering said major surface, said side surface, and said undercut surfaces.

32. A method of providing a paint film on an injection molded object comprising

supporting first and second overlapping paint films between first and second mold sections, and

injecting a flowable resin into a space between said first and second paint films.

33. An injection molded object comprising an injection molded substrate, two contiguous paint films applied to said substrate during injection molding and covering said substrate, one said film being attached to the other said film at edge regions of respective said films, one said film covering one region of a surface of an injection molded object and the other said film covering an adjacent region of said surface.

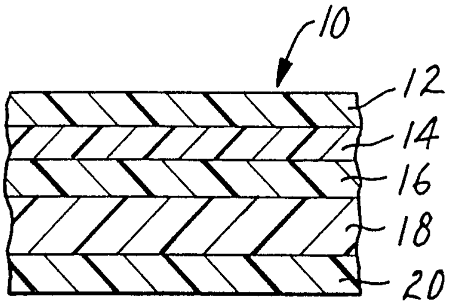


FIG. 1

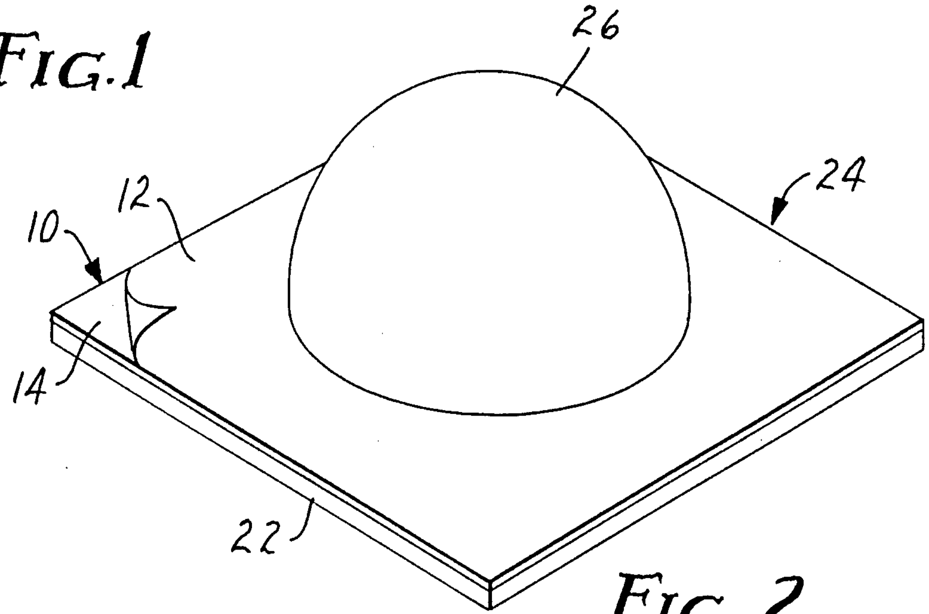


FIG. 2

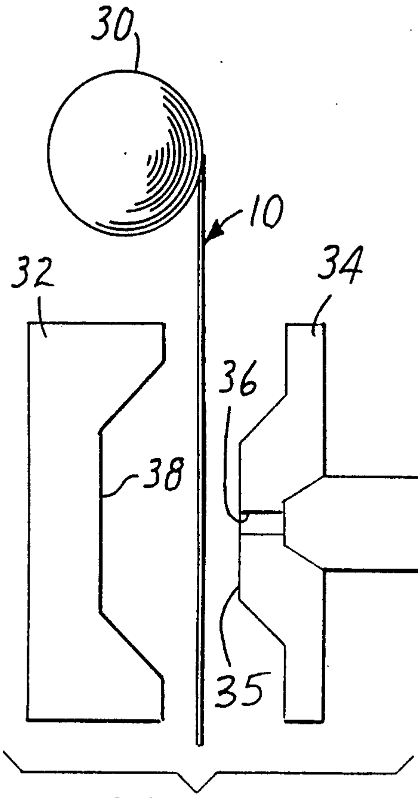


FIG. 3

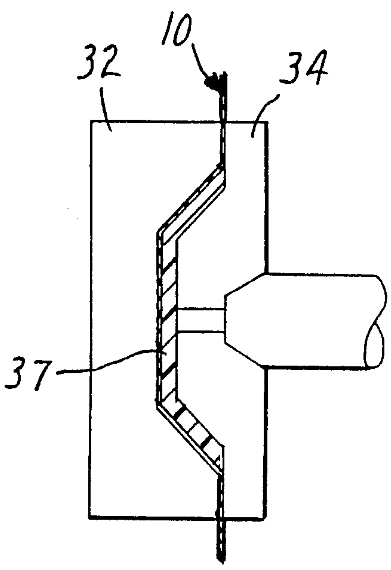


FIG. 4

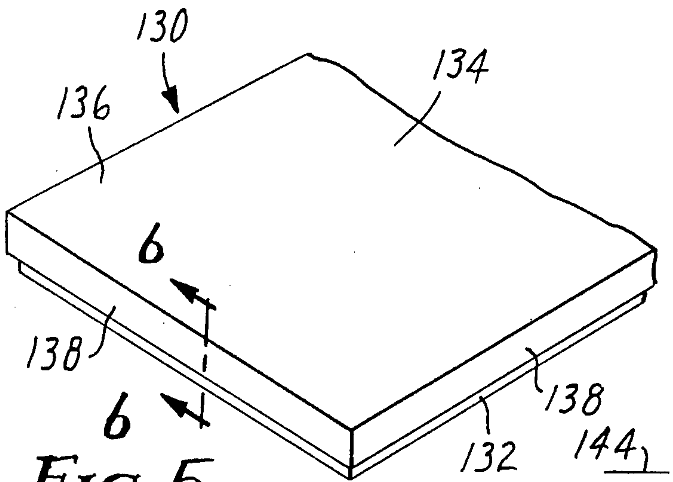


FIG. 5

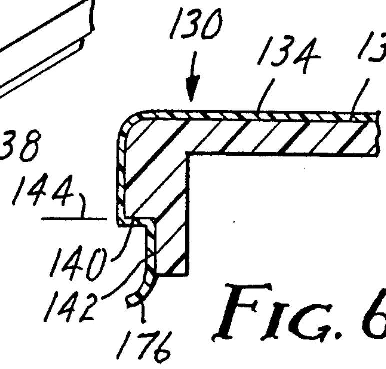


FIG. 6

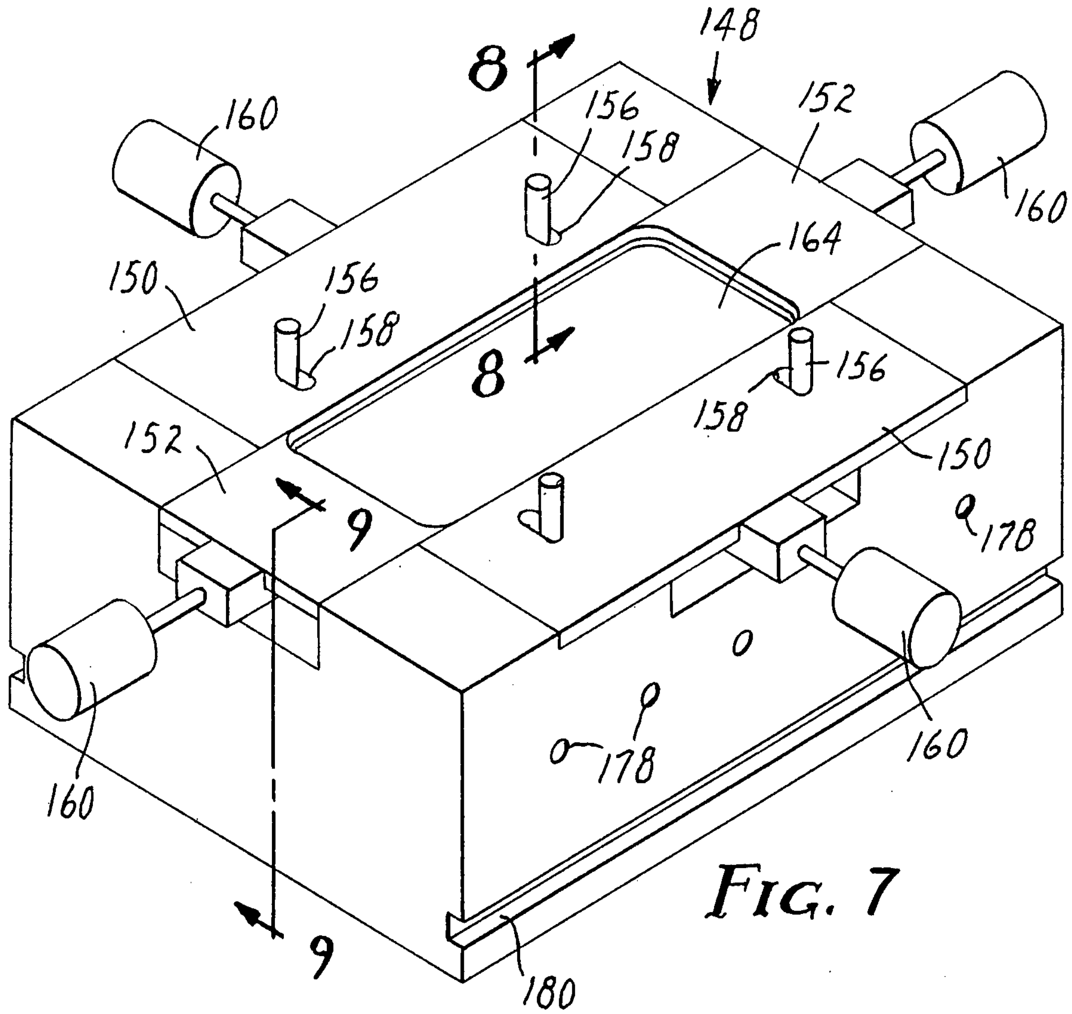


FIG. 7

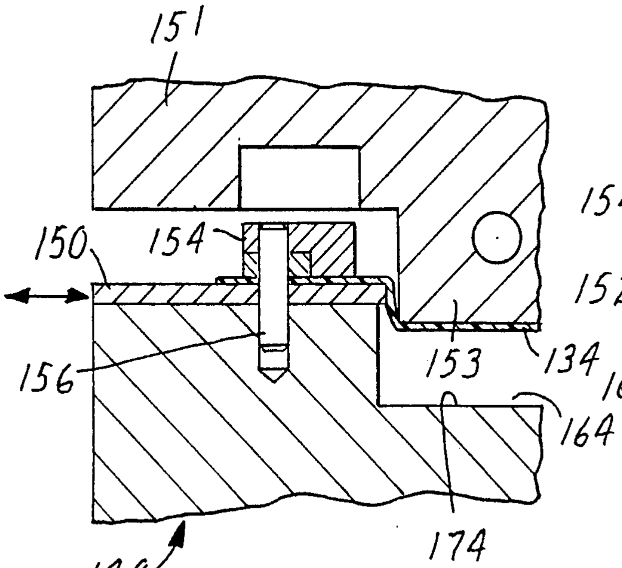


FIG. 8

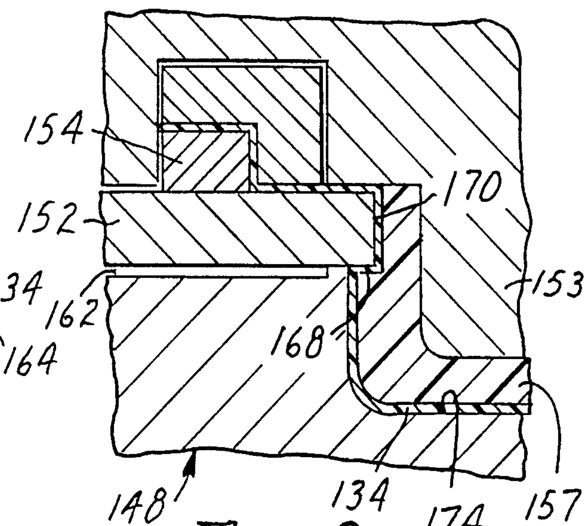


FIG. 9

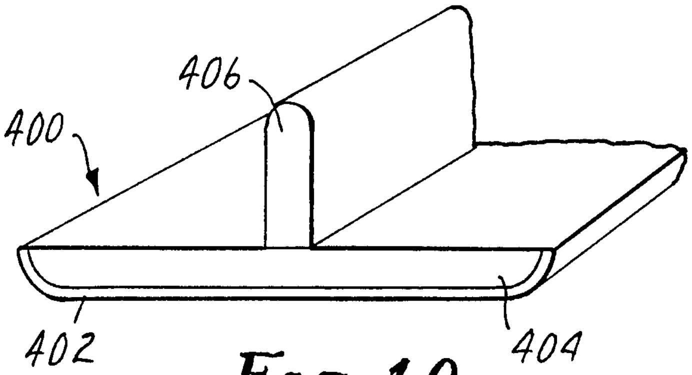


FIG. 10

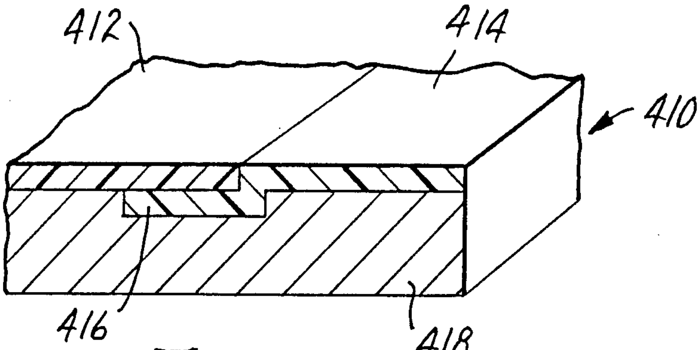


FIG. 11

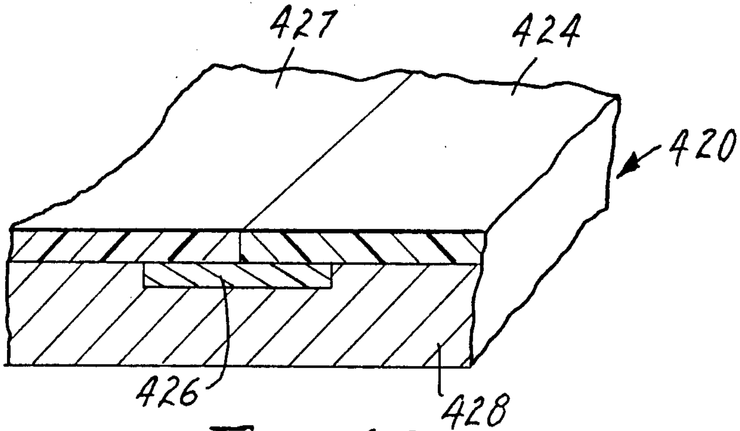


FIG. 12

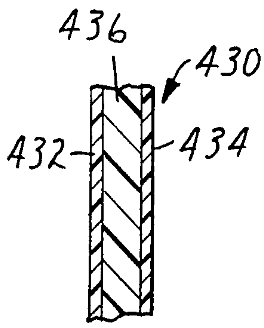


FIG. 13

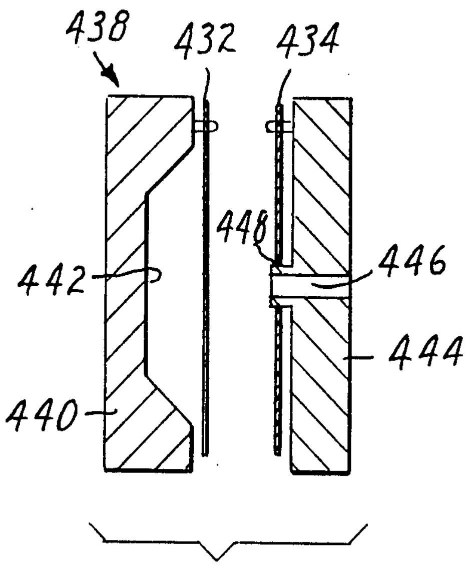


FIG. 14