



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B44C 5/00	A2	(11) International Publication Number: WO 00/51829 (43) International Publication Date: 8 September 2000 (08.09.00)
(21) International Application Number: PCT/US00/03919 (22) International Filing Date: 16 February 2000 (16.02.00) (30) Priority Data: 09/259,975 1 March 1999 (01.03.99) US (71) Applicant (for all designated States except US): REXAM INDUSTRIES CORP. [US/US]; Suite 340, 4201 Congress Street, Charlotte, NC 28209 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): HUFFER, Scott [US/US]; 3060 Crestview lane, Lancaster, SC 29720 (US). SONG, Quan [US/US]; 732 Bradbury Lane, Matthews, NC 28104 (US). (74) Agents: HUMPHREY, Christopher, M. et al.; Alston & Bird LLP, P.O. Drawer 34009, Charlotte, NC 28234-4009 (US).		(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: DECORATIVE SHEET MATERIAL WITH CHLORINATED POLYOLEFIN ADHESIVE LAYER (57) Abstract <p>The flexible, weatherable decorative sheet material provided by the present invention comprises a thermoformable decorative paint film having an inner surface and a weatherable outer surface suitable for forming an exterior finish for a part, such as an automobile body part. The decorative sheet material includes an adhesive layer overlying the inner surface of the decorative paint film, wherein the adhesive layer comprises a chlorinated polypropylene component and a chlorinated polyolefin component. The chlorinated polypropylene component has a peel strength of at least about 0.8 lbs./in. at 100 °C and the chlorinated polyolefin component has a peel strength of at least about 5 lbs./in. at room temperature. The two chlorinated components have similar chlorine contents, such as between about 20 to about 40 weight percent chlorine. A method of constructing the decorative sheet material and a composite shaped part including the decorative sheet material are also provided.</p>		

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DECORATIVE SHEET MATERIAL
WITH CHLORINATED POLYOLEFIN ADHESIVE LAYER

FIELD OF THE INVENTION

The present invention relates to sheet materials generally and more particularly relates to a sheet material suitable for use as a flexible, weatherable paint film.

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BACKGROUND OF THE INVENTION

Manufacturers have shown increasing interest in using paint films in lieu of spray painting for providing a decorative surface finish for parts, such as automobile body parts. This manufacturing technique reduces the environmental concerns associated with painting and has the potential to reduce manufacturing costs. An automobile body part utilizing a plastic paint film to provide a high quality base coat/clear coat automotive finish is disclosed, for example, in U.S. Patent No. 4,810,540, which is incorporated by reference herein in its entirety. In producing the part, the paint film is typically formed into a contoured three-dimensional configuration corresponding to the shape of the outer surface of the part by suitable methods, such as by thermoforming.

Automotive manufacturers, for example, require that automotive parts have an exterior paint appearance which meets demanding performance and appearance specifications, such as weatherability, resistance to ultraviolet light degradation, high gloss, and high distinctness-of-image (DOI). In addition, the adhesive layer used to bond the paint film to a substrate must withstand the effects of changes in temperature over a wide range of temperatures without losing adhesion or cohesive strength. For instance, some industry tests involve subjecting the paint film to an abrupt change in temperature from approximately 0°C to approximately 100°C. The adhesive must be capable of withstanding such a temperature change without delamination of the paint

film from the substrate occurring. Further, since the paint film may be used to surface parts having complex three-dimensional configurations, the adhesive must exhibit good elongation properties at thermoforming temperatures. There remains a need for an adhesive material that possesses the characteristics listed above.

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SUMMARY OF THE INVENTION

The adhesive composition of the present invention comprises a mixture or blend of a chlorinated polypropylene and a higher molecular weight chlorinated polyolefin that provides both good adhesion to adjacent film layers and good
10 elongation and cohesive strength over a wide range of temperatures. The chlorinated polypropylene has a higher softening point than the chlorinated polyolefin, which enhances the cohesive strength of the adhesive composition, while the chlorinated polyolefin component provides good adhesion at room temperature. The two chlorinated components have comparable chlorine content in order to ensure chemical
15 compatibility.

The adhesive composition of the present invention includes a chlorinated polypropylene component having a peel strength of at least about 0.8 lbs./in. at 100°C and a chlorinated polyolefin component having a peel strength of at least about 5 lbs./in. at room temperature. Room temperature is defined as about 15°C to about
20 30°C. In one embodiment, the chlorinated polypropylene component has a peel strength of at least about 1.0 lbs./in. at 100°C, and the chlorinated polyolefin component has a peel strength of at least about 7 lbs./in. at room temperature. Preferably, the chlorinated polyolefin is present in the composition at a concentration of about 1 to about 10 weight percent and the chlorinated polypropylene is present in
25 an amount of about 5 to about 20 weight percent. The adhesive composition may further comprise any compatible solvent known in the art.

Preferably, the chlorinated polypropylene component has a peel strength of at least about 0.8 lbs./in. at room temperature, and the chlorinated polyolefin component has a peel strength of at least about 0.2 lbs./in. at 100°C. Most preferably, the
30 chlorinated polypropylene component has a peel strength of at least about 1.0 lbs./in.

at room temperature, and the chlorinated polyolefin has a peel strength of at least about 0.4 lbs./in. at 100°C.

The two chlorinated components have similar chlorine contents. Preferably, both components have a chlorine content of about 20 to about 40 weight percent.

- 5 Additionally, the chlorinated polypropylene has a softening point of at least about 85°C, and preferably at least about 100°C.

The adhesive composition may also comprise an epoxy component, preferably in an amount of about 0.1 to about 2.0 weight percent on a dry solids basis.

- 10 Additionally, the adhesive composition may contain a pigment component, such as carbon black, titanium oxide, and mixtures thereof. The adhesive composition may also contain further additives such as UV screeners, heat stabilizers, antioxidants, and mixtures thereof.

- Preferably, the adhesive composition is in the form of a film layer. In dried film form, the adhesive layer comprises about 30 to about 70 weight percent
15 chlorinated polyolefin component and about 30 to about 70 weight percent chlorinated polypropylene component. In one embodiment, the adhesive layer comprises about 30 weight percent chlorinated polyolefin and about 70 weight percent chlorinated polypropylene.

- For example, the present invention provides a flexible, weatherable decorative
20 sheet material comprising a decorative paint film and an adhesive layer overlying the inner surface of the decorative paint film, wherein the adhesive layer comprises the chlorinated polypropylene and chlorinated polyolefin components described above. Preferably, the decorative paint film has a 60 degree gloss value of at least 60.

- Further, the decorative sheet material may include a primer layer adhering the
25 inner surface of the decorative paint film to the adhesive layer. Preferably, the primer layer comprises an acrylic polymer composition. The decorative sheet material may further include a thermoformable backing layer adhered to the opposing surface of the adhesive layer. Additionally, the decorative sheet material may include an extensible mask layer releasibly adhered to the outer surface of the paint film to form a protective
30 film overlying the paint film. For example, a mask layer comprising a polymer

selected from the group consisting of polyurethane, polyolefin, polyester, and polyamide may be used.

The present invention also includes a method of making a flexible weatherable decorative sheet material. The method includes the steps of forming a thermoformable decorative paint film and applying a coating of an adhesive composition to the inner
5 surface of the paint film to form an adhesive layer, wherein the adhesive composition comprises the chlorinated components described above. The method may also include the steps of applying a primer layer to the inner surface of the decorative paint film prior to application of the adhesive layer. Also, the method may include the step of
10 applying a thermoformable backing layer to the exposed surface of the adhesive layer, such that the adhesive layer bonds the backing layer to the paint film.

The decorative paint film may be formed by applying at least one coating layer to a smooth flexible casting surface and drying the coating layer on the casting surface to produce a paint film so that the outer surface of the paint film is releasably bonded
15 to the casting surface. The decorative paint film may comprise a single layer of a pigmented polymer or may comprise both a clear coat layer and a pigmented color coat layer.

The decorative sheet material constructed using the method outlined above may be thermoformed into a three-dimensional shape and the exposed surface of the thermoformable backing layer may be bonded to a substrate to form a composite
20 shaped part. The decorative sheet material of the present invention may be inserted into a mold, such as a compression mold or an injection mold, and bonded to the substrate to form the composite shaped part. The decorative sheet material may be inserted into the mold in the form of a substantially flat sheet or after thermoforming
25 the sheet material into a preform.

BRIEF DESCRIPTION OF THE DRAWINGS

Having thus described the invention in general terms, reference will now be made to the accompanying drawings, which are not necessarily drawn to scale, and
30 wherein:

Figure 1 is a perspective view of an automobile illustrating the front fascia of the automobile having a decorative paint film applied thereto;

Figure 2 is a front view of an automobile front fascia having a decorative paint film applied thereto;

5 Figure 3 is a cross-sectional view of the fascia shown in Figure 2 taken along line 3-3 of Figure 2;

Figure 4 is a cross-sectional view of the decorative sheet material of the present invention adhered to a substrate;

10 Figure 5 is a cross-sectional view of the decorative sheet material of the present invention including a clear coat and a color coat layer;

Figure 6 is a cross-sectional view of the decorative sheet material of the present invention having a single paint film layer;

Figure 7 is a schematic illustration of a process for construction of the decorative sheet material of the present invention;

15 Figure 8 is a schematic illustration of a process for applying the mask layer to the outer surface of a decorative paint film;

Figures 9A-9D are schematic illustrations of the steps in a thermoforming process used to construct a preform; and

20 Figures 10A-10C are schematic illustrations of steps in an injection molding process for forming a composite shaped part.

DETAILED DESCRIPTION OF THE INVENTION

The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. Like numbers refer to like elements throughout.

30 Figure 1 illustrates an automobile 10 having a composite shaped part 12. As shown, the composite shaped part 12 is a complex, contoured three-dimensional front

fascia of the automobile 10. The composite shaped part 12 has a decorative sheet material 14 applied thereto. Although not limited to such applications, the decorative sheet material 14 of the present invention is particularly advantageous for providing a decorative surface on a composite shaped part 12 of an automobile 10. However, those skilled in the art will appreciate that the present invention could be used in a variety of applications requiring a weatherable, decorative surface.

Figure 2 is a front view of the composite shaped part 12 having the decorative sheet material 14 applied thereto. Figure 3 is a cross-sectional side view of the composite shaped part 12 comprising a substrate 16 having a decorative sheet material 14 applied thereto. As illustrated in Figure 3, the decorative sheet material 14 undergoes different amounts of elongation at different points along the contoured surface of the composite shaped part 12. In one embodiment, the decorative sheet material 14 of the present invention has a three-dimensional configuration in which certain areas of the sheet material have been subjected to elongation in excess of about 300%, and other areas of the sheet material are substantially non-elongated. However, the difference in gloss value between the elongated areas and the non-elongated areas should be no more than 10 gloss units with a minimum 60 degree gloss value of at least 60. The decorative sheet material 14 of the present invention is capable of maintaining a high level of gloss regardless of the amount of elongation experienced by the decorative sheet material during a thermoforming or molding process.

Figure 4 shows a greatly expanded cross-sectional view of a composite shaped part 12 comprising a decorative sheet material 14 of the present invention adhered to a substrate 16. The decorative sheet material includes a mask layer 20, a clear coat layer 22, a color coat layer 24, a primer layer 26, an adhesive layer 28, and a thermoformable backing layer 30.

The extensible mask layer 20 is designed to maintain gloss and DOI during forming processes and molding processes. Forming processes include, but are not limited to, thermoforming, cold stretching, and vacuum forming. Molding processes include, but are not limited to, injection molding, compression molding, and blow molding. The mask layer 20 also adds strength to the decorative sheet material 14 and improves process uniformity during the thermoforming process. Additionally, the

extensible mask layer **20** protects the underlying layers of the decorative sheet material **14** from scratching or marring until the part is ready for display. The mask layer **20** is capable of stretching up to about 600 percent during thermoforming and has a room temperature elongation at break of at least about 200 percent.

5 The mask layer **20** may be retained as the outer layer of the decorative sheet material **14** during construction of the final product, such as an automobile.

Thereafter, the mask layer **20** may be removed to reveal the underlying decorative paint film **18**. For instance, the extensible mask layer **20** can be maintained as a protective layer and removed only after the vehicle has completed shipment and is
10 ready for delivery to a customer. The extensible mask layer **20** is releasably bonded to the underlying decorative paint film **18** and may be stripped away from the underlying layers in a single piece. In a preferred embodiment, the mask layer **20** is transparent or substantially transparent to permit visual inspection of the part for surface defects without removal of the mask layer.

15 Additionally, the extensible mask layer **20** maintains high gloss and DOI during injection or compression molding, such as thermoplastic or thermoset compression molding, where the mold is roughened or deglossed. Roughened molds are less expensive than highly polished molds and are also functionally superior to highly polished molds because the rough mold surface enhances air removal from the
20 mold as the mold closes. The extensible mask layer **20** protects the paint film **18** from loss of gloss or other damage caused by the mold without resorting to the use of highly polished molds.

Preferably, the extensible mask layer **20** is about 0.3 mils to about 3.0 mils in thickness. The extensible mask layer **20** comprises polyurethane, polyolefin, such as
25 polyethylene and polypropylene, polyester, such as polyethylene terephthalate, or polyamide. Preferably, the mask layer **20** comprises a dried film of an aliphatic or aromatic polyester or polyether polyurethane in the form of a dispersion or a solution. For example, polyurethane polymers QA 5218 and QA 5026, manufactured by Mace Adhesives and Coatings of Dudley, Massachusetts, may be used to form the mask
30 layer **20**. In one embodiment, the mask layer **20** comprises about 85 to about 99.5 weight percent polyurethane water-borne dispersion. Advantageously, a small amount

of surfactant (about 0.05 to about 0.2 weight percent), such as SURFYNOL 104H manufactured by Air Products of Allentown, PA, is added to lower surface tension.

The mask layer **20** composition may include additional additives designed to migrate into the clear coat layer **22** to enhance weatherability or other desirable properties of the clear coat layer or to prevent migration of additives from the clear coat into the mask layer. Migratory additives suitable for use with the present invention include, but are not limited to, hardness enhancers, release agents, ultraviolet light stabilizers, antioxidants, dyes, lubricants, surfactants, catalysts, and slip additives.

More specifically, the migratory additives useful in the present invention include benzophenone, silicones, waxes, triazoles, and triazines. The migratory additives are encouraged to migrate into the outer surface of the clear coat layer **22** by the heat and/or pressure present during thermoforming processes and in-mold processes. Additionally, the presence of these additives in the mask layer **20** prevents migration of additive components from the clear coat layer **22** into the mask layer.

Ultraviolet light stabilizers, such as TINUVIN 1130 and TINUVIN 292, both manufactured by Ciba Geigy of Hawthorne, NY, can be added as migratory additives in the mask layer **20** composition. Silicone additives, such as BYK333 manufactured by BYK Chemie of Wallingford, CT, can be added to lower the coefficient of friction of the clear coat layer **22**. The migratory additives are generally added in amounts ranging from about 0.01 to about 2.0 weight percent, with all additives accounting for no more than about 5.0 weight percent of the mask layer **20** composition.

Figures 5 and 6 are greatly expanded cross-sectional views of two embodiments of the decorative sheet material **14** of the present invention. The decorative paint film **18** may comprise a single layer **25** of a pigmented polymer, as shown in Figure 6, or may comprise multiple layers, as shown in Figures 4 and 5. If a single layer **25** of pigmented polymer is used, the polymer may be selected from the group consisting of urethane polymers, acrylic polymers, fluoropolymers, and alloys of a fluoropolymer and an acrylic polymer. FLUOREX® films manufactured by Rexam are examples of alloys of a fluoropolymer and an acrylic polymer. The single layer **25** of pigmented polymer may also include UV screeners to enhance

weatherability, antioxidants, heat stabilizers, and other conventional additives. The pigmented polymer layer **25** may further include pigments, dyes, and/or flakes to enhance visual appearance.

As shown in Figures 4 and 5, the decorative paint film **18** may also comprise both a clear coat layer **22** and a color coat layer **24**. The clear coat layer **22** is formed from a substantially transparent weatherable polymer composition selected to provide a film which will not significantly fade, peel, crack, or chalk when exposed to the environment for the intended life of the part **12**. Additionally, the clear coat layer **22** must be formable from a two-dimensional surface to a three-dimensional surface without objectionable loss of appearance or performance properties. Advantageously, the clear coat layer **22** is selected from the group consisting of urethane polymers, acrylic polymers, fluoropolymers, and alloys or a fluoropolymer and an acrylic polymer (such as FLUOREX® films). As with the single pigmented polymer layer **25**, the clear coat layer **22** may include UV screeners, antioxidants, heat stabilizers, and other conventional additives. Preferably, the clearcoat layer **22** is about 0.3 to about 3 mils in thickness.

The color coat layer **24** is formed of a polymer composition containing a uniformly dispersed pigment to provide the appearance necessary for exterior automobile use. Preferably, the color coat layer **24** is selected from the group consisting of urethane polymers, acrylic polymers, fluoropolymers, and alloys of a fluoropolymer and acrylic polymer (such as FLUOREX® films). The color coat layer **24** may include pigments, dyes, and/or flakes to enhance visual appearance and improve weatherability. Preferably, the color coat layer **24** is about 0.3 to about 3 mils in thickness.

If desired, a color adjustment layer **27** may be added between the clear coat layer **22** and the color coat layer **24** to enhance visual appearance. The color adjustment layer **27** can be applied in coating form and include pigments, dyes and/or flakes or applied as a graphic design using printing methods such as gravure, rotary screen, flat bed step-and-repeat screen, ink jet, flexographic or other printing techniques.

The primer layer **26** improves adhesion between the color coat layer **24** and the adhesive layer **28**. The primer layer **26** preferably comprises an acrylic polymer prepared in solution using any compatible solvent known in the art, such as toluene. In one embodiment, the primer layer **26** is prepared from a solution comprising about
5 65 to about 85 weight percent acrylic composition and about 5 to about 10 weight percent solvent. An acrylic polymer suitable for use in the primer layer **26** is acrylic adhesive 68070 manufactured by DuPont. The primer layer **26** may be opaque, colored or clear. Opaque is defined as less than 1 percent transmission at a wavelength of less than 400 nm. The primer layer **26** is preferably about 0.2 to about
10 2 mils in thickness. The primer layer **26** may be colored or opaque to protect the underlying thermoformable backing layer **30** from damage caused by UV exposure. Pigments such as carbon black, titanium oxide, and mixtures thereof may be added to impart color to the acrylic polymer composition used in the primer layer **26**. Additionally, additives such as UV screeners, antioxidants, and heat stabilizers may be
15 added to the primer layer **26**.

The adhesive layer **28** adheres the decorative paint film **18** to a thermoformable backing layer **30**. The adhesive layer **28** comprises a mixture or blend of a chlorinated polypropylene and a higher molecular weight chlorinated polyolefin. In one embodiment, the adhesive layer **28** is formed from a mixture of
20 about 5 to about 20 weight percent chlorinated polypropylene and about 1 to about 10 weight percent of a higher molecular weight chlorinated polyolefin formed in solution. A compatible solvent known in the art, such as toluene, is present in an amount of about 60 to about 80 weight percent. After evaporation of the solvent, the dried adhesive layer **28** comprises about 30 to about 70 weight percent chlorinated
25 polyolefin and about 30 to about 70 weight percent chlorinated polypropylene. In one embodiment, the adhesive layer **28** comprises about 30 weight percent chlorinated polyolefin and about 70 weight percent chlorinated polypropylene. A chlorinated polypropylene suitable for use with the present invention is HARDLEN 13-LP manufactured by Advanced Polymer. A higher molecular weight chlorinated
30 polyolefin suitable for use with the present invention is SUPERCHLON 822S manufactured by CP/Phibrochem of Fort Lee, NJ. The adhesive layer **28** should be

capable of stretching about 300 to about 600 percent. Due to the substantial elongation capability of the adhesive layer 28, the adhesive layer maintains the necessary adhesive strength to prevent delamination of the decorative paint film 18 from the thermoformable backing layer 30 over a wide temperature range. The
5 adhesive layer 28 must have good adhesion to the backing layer 30 and the primer layer 26. Additionally, the adhesive layer 28 must exhibit good cohesive strength at 100°C and good elongation properties at thermoforming temperature (about 190° to about 200°C).

The blend of chlorinated polypropylene and higher molecular weight
10 chlorinated polyolefin provides both good adhesion to adjacent film layers and good elongation and cohesive strength over a wide range of temperatures. The chlorinated polypropylene component, such as HARDLEN 13-LP, has a higher softening point than the chlorinated polyolefin component, which enhances the cohesive strength of the adhesive layer 28, particularly at elevated temperatures. The higher molecular
15 weight chlorinated polyolefin component, such as SUPERCHLON 822S, provides good adhesion at room temperature. The two chlorinated components should have comparable chlorine content in order to ensure chemical compatibility. The two chlorinated components preferably have a chlorine content of about 20 to about 40 weight percent, and most preferably, a chlorine content of about 20 to about 30 weight
20 percent.

The higher molecular chlorinated polyolefin should have a peel strength at room temperature of at least about 5 lbs./in., and preferably about 7 lbs./in. Additionally, the chlorinated polyolefin should have a peel strength at 100°C of at least about 0.2 lbs./in., and preferably at least about 0.4 lbs./in. The chlorinated
25 polypropylene should have a peel strength of at least about 0.8 lbs./in at room temperature, and preferably at least about 1.0 lbs./in. Further, the chlorinated polypropylene should have a peel strength at 100°C of at least about 0.8 lbs./in., and preferably at least about 1.0 lbs./in. The softening point of the chlorinated polypropylene component should be at least about 85°C, and preferably at least about
30 100°C. Peel strength at room temperature was measured using Sintech System I manufactured by Sintech, Inc. Peel strength at elevated temperature was measured

using an INSTRON machine, model 4467, coupled with a heating unit that allows temperature control of the sample. Using either machine, peel strength was measured using a 180 degree peel with a cross head speed of 4 inches/minute.

5 An epoxy component, such as EPON 828RS manufactured by Shell Chemical, may be added in small amounts (approximately about 0.1 to about 2.0 weight percent on a dry solids basis) as an acid scavenger. As with the primer layer 26, the adhesive layer 28 may be colored or opaque to protect the underlying thermoformable backing layer 30 from damage caused by UV exposure. Pigments such as carbon black, titanium oxide, and mixtures thereof may be added to impart color to the polymer
10 composition used in the adhesive layer 28. Additives such as UV screeners, antioxidants, and heat stabilizers may be added to the adhesive layer 28. Preferably, the adhesive layer 28 is about 0.2 to about 2 mils in thickness.

The thermoformable backing layer 30 bonds the decorative paint film 18 of the decorative sheet material 14 to the substrate 16. In addition, the backing layer 30
15 provides bulk and/or rigidity for handling the decorative sheet material 14 as a thermoformed preform. The backing layer 30 also provides thickness to prevent glass fibers, fillers or other sources of visual roughening or "orange peel" from the substrate 16 from affecting the visual appearance of the decorative sheet material 14. The backing layer 30 must bond well with both the substrate 16 and the adhesive layer 28.
20 The backing layer 30 may be selected from the group consisting of thermoplastic olefin, acrylonitrile-butadiene-styrene terpolymer, polypropylene, thermoplastic polyimide, polyethylene oxide, polycarbonate, polyvinyl chloride, polystyrene, styrene/polyphenylene oxide (NORYEL), polybutylene terephthalate, nylon, PETG copolyester, and mixtures, laminates and copolymers thereof, depending on the
25 material used as the substrate 16.

Figure 7 illustrates a process for constructing the decorative sheet material 14 of the present invention. As shown, a film carrier 33 is advanced from a supply roll 38 through a series of process steps. The film carrier 33 preferably comprises a polyester casting film having a high gloss surface. The film carrier 33 is important for high
30 gloss applications because it imparts high gloss and DOI to the decorative sheet material 14. Advantageously, the film carrier 33 comprises polyethylene terephthalate

(PET) in a grade without slip additives. The film carrier 33 is about 1 to about 3 mils in thickness, preferably about 2 mils in thickness.

The film carrier 33 passes through a first coating station 40. If a single pigmented layer 25 is used as the decorative paint film 18, the pigmented layer is deposited onto the film carrier 33 using coating station 40 and the resulting film is dried by dryer 46. If a decorative paint film 18 having multiple coatings is desired, the first coating station 40 may deposit the clear coat layer 22. The clear coat layer 22 then passes through a dryer 42. Thereafter, a color coat layer 24 is deposited on the dried clear coat layer 22 using coating station 44. The color coat layer 24 is then dried using dryer 46. Optionally, the dried color coat layer 24 can be subjected to a corona treatment (not shown).

The coating stations 40 and 44 may utilize any conventional coating or casting techniques, such as reverse roll coating or slot die coating techniques. Slot die coating methods are preferred.

The dryers 42 and 46 may utilize any conventional drying technique. Preferably the dryers 42 and 46 are ovens having multiple heating zones wherein each successive heating zone operates at a progressively higher temperature. For example, an oven having four to six heating zones ranging in temperature from about 200 F to about 400 F may be used. Alternatively, dryer 42 may be eliminated from the process such that the color coat 24 is applied to the clear coat 22 while the clear coat is still wet.

After the decorative paint film 18 is applied to the film carrier 33, the film carrier advances to a primer coating station 48, where the primer layer 26 is deposited onto the exposed layer of the decorative paint film 18. The primer layer 26 is then dried using dryer 49. Thereafter, the film carrier advances to an adhesive coating station 50, where the adhesive layer 28 is deposited onto the primer layer 26. Thereafter, the adhesive layer 28 is dried using dryer 51. The primer coating station 48 and adhesive coating station 50 may utilize any conventional coating or casting technique, such as reverse roll coating or slot die coating techniques. The dryers 49 and 51 may utilize any conventional drying technique.

A thermoformable backing layer **30** is advanced from a supply roll **52** and laminated to the adhesive-coated surface of the film carrier **33**. Optionally, the backing layer **30** can be subjected to a corona treatment (not shown) prior to lamination. The resulting laminate is collected by product roll **54**.

5 Figure 8 illustrates a process for preparing a decorative sheet material **14** having a mask layer **20**. A non-extensible carrier **34** is advanced from a supply roll **58**. The carrier **34** may be constructed of the same material used for the film carrier **33**. Preferably, the carrier **34** comprises a polyethylene terephthalate film. The carrier **34** advances through a coating station **60**, where the mask layer **20** is deposited onto a
10 surface of the carrier. The coating station **60** may utilize any coating or casting technique known in the art, such as reverse roll coating or slot die coating techniques. Thereafter, the coated carrier **34** passes through a dryer **62** to form a dried mask layer **20**. As discussed above in connection with dryers **42** and **46** used to dry the decorative paint film **18**, the dryer **62** used to dry the mask layer **20** may utilize any conventional
15 drying technique. Preferably, the dryer **62** comprises an oven with multiple heating stages. The dryer **62** evaporates the solvents present in the mask layer **20** composition.

The layers of the decorative sheet material **14** formed in the process illustrated in Figure 7 are advanced from a supply roll **56**. The film carrier **33** is stripped away
20 from the remaining layers to expose either the single pigmented layer **25** or the clear coat layer **22** of the decorative paint film **18**, depending on the construction of the paint film used. The exposed outer layer of the decorative paint film **18** is laminated and releasably bonded to the mask layer **20** by nipping the two films between two rollers, **64** and **65**, with or without applying heat to the layers. The resulting
25 decorative sheet material **14** is collected by product roll **67**. The non-extensible carrier **34** may be stripped away to expose the mask layer **20** before or after collection of the sheet material **14** by product roll **67**.

In another embodiment, the decorative paint film **18**, primer layer **26**, and adhesive layer **28** are coated directly onto the dried mask layer **20** rather than
30 laminating the coated films together. In a further embodiment, the mask layer is coated onto the clear coat layer **22**. For example, a decorative sheet material **14**

prepared according to Figure 7 could be stripped from carrier 33 so that the mask layer 20 can be coated directly onto the clear coat layer 22.

The decorative sheet material 14 of the present invention can be adhered to a supporting substrate 16 in accordance with known laminating or bonding techniques. Illustrative examples of supporting substrates 16 include metal, wood, and molded polymer substrates. As explained above, exterior automobile parts are particularly suitable as the substrate 16. Suitable polymers for use as the substrate 16 include, for example, thermoplastic olefin, acrylonitrile-butadiene-styrene terpolymer, polypropylene, thermoplastic polyimide, polyethylene oxide, polycarbonate, polyvinyl chloride, polystyrene, styrene/polyphenylene oxide (NORYEL), polybutylene terephthalate, nylon, PETG copolyester, Sheet Molding Compounds (SMC), RIM urethanes, and mixtures, laminates and copolymers thereof.

The decorative sheet material 14 may be applied to the substrate 16 by a variety of methods. These methods include, but are not limited to, compression molding, such as thermoplastic or thermoset compression molding, injection molding and the like. In an injection molding process, the decorative sheet material 14 may be preformed as described below or placed in the mold as a substantially flat sheet. If the sheet material 14 is placed in the mold without performing, the heat and/or pressure of the molding process conforms the sheet material to the desired shape.

Figures 9A-9D illustrate the steps in a thermoforming process. Thermoforming is often used to create a preform in a three-dimensional configuration that roughly approximates the three-dimensional configuration of the final product. The preform is then placed in a mold for in-mold surfacing of a desired substrate 16 to form the final product. Figure 9A shows heating of the decorative sheet material 14 of the present invention by heating elements 70. The heating step softens and increases the extensibility of the decorative sheet material 14 so that the sheet material will readily conform to the contoured outer surface of the mold 74. As shown in Figure 9C, the mold 74 is brought into contact with the heated decorative sheet material 14 and a vacuum is drawn to encourage conformity of the sheet material 14 to the contours of the mold 74. Thereafter, the mold 74 is removed from the decorative sheet

material 14 and the sheet material is allowed to cool and harden into the three-dimensional configuration.

Figures 10A-10C illustrate steps in an in-mold surfacing process. As shown in Figure 10A, the thermoformed decorative sheet material 14 is placed in the mold cavity 78 of an injection mold 76. The decorative sheet material is placed in the mold cavity 78 with the mask layer 20 facing the inner surface of the injection mold 76. Alternatively, the decorative sheet material 14 may be placed in the mold cavity 78 as a flat, two-dimensional insert rather than as a preform. As noted above, the mold 76 may have a roughened inner surface. The injection mold 76 is shut and a moldable polymer 82 is introduced into the mold 76 through the injection mold barrel 80. The polymer 82 bonds to the backing layer 30 and conforms to the contoured shape of the mold cavity 78. Thereafter, the moldable polymer 82 is allowed to cool and harden into a composite shaped part 12 comprising a substrate 16 bonded to a decorative sheet material 14, as shown in Figure 10C. The mask layer 20 of the decorative sheet material may be stripped from the composite shaped part 12 to expose the paint film finish when desired.

EXAMPLE 1

The peel strength data shown in Table 1 illustrates the good balance of adhesion and cohesive strength provided by a blend of chlorinated polypropylene (HARDLEN 13-LP) and a higher molecular weight chlorinated polyolefin (SUPERCHLON 822S). The HARDLEN 13-LP component exhibits good peel strength at 100°C, while the SUPERCHLON 822S component adds good peel strength at room temperature (about 15 to about 30°C). The two chlorinated components have similar chlorine contents: 24.5 weight percent for SUPERCHLON 822S and 26 weight percent for HARDLEN 13-LP.

Table 1

HARDLEN 13-LP (weight %)	SUPERCHLON 822S (weight %)	Peel @ Room Temp (lbs./in)	Peel @ 100°C (lbs./in)
100	0	1-2	1.2
70	30	7-8	0.9
50	50	7-8	0.9-1.0
30	70	7-8	0.8-0.9
0	100	7-8	0.3-0.4

EXAMPLE 2

- An adhesive layer of the present invention was compared to two available adhesives: Eastman 343-1 and Novacote 222. Adhesive layers were formed as described above and subjected to peel strength testing using the peel strength equipment described above. The adhesive layer of the present invention comprised about 30 weight percent SUPERCHLON 822s and about 70 weight percent HARDLEN 13-LP. As shown by the data, the adhesive of the present invention provides a better combination of room temperature and elevated temperature peel strength than the comparative examples.

Table 2

Adhesive	% of Stretch	Peel @ Room Temperature (lbs./in)	Peel @ 100°C (lbs./in)
Adhesive of the present invention	0	7-8	1.1
	approx. 300	6-7	0.9-1.0
Eastman 343-1	0	7-8	0.1-0.2
	approx. 300	7-8	0.1-0.2
Novacote 222	0	7-8	1-2
	approx. 300	1-2	--

Many modifications and other embodiments of the invention will come to mind to one skilled in the art to which this invention pertains having the benefit of the teachings presented in the foregoing descriptions and the associated drawings.

Therefore, it is to be understood that the invention is not to be limited to the specific
5 embodiments disclosed and that modifications and other embodiments are intended to
be included within the scope of the appended claims. Although specific terms are
employed herein, they are used in a generic and descriptive sense only and not for
purposes of limitation.

THAT WHICH IS CLAIMED:

1. A flexible, weatherable decorative sheet material useful in lieu of painting for providing a decorative finish for parts, comprising:
 - 5 a decorative paint film, said paint film having an inner surface and a weatherable outer surface suitable for forming an exterior finish for a part, such as an automobile body part, and
 - an adhesive layer having a first surface and a second surface, said first surface of said adhesive layer overlying said inner surface of said decorative paint
 - 10 film, said adhesive layer comprising
 - a chlorinated polypropylene component having a peel strength of at least about 0.8 lbs./in at 100°C; and
 - a chlorinated polyolefin component having a peel strength of at least about 5 lbs./in at room temperature.
- 15 2. A sheet material according to Claim 1, wherein said adhesive layer comprises about 30 to about 70 weight percent chlorinated polyolefin and about 30 to about 70 weight percent chlorinated polypropylene.
- 20 3. A sheet material according to Claim 2, wherein said adhesive layer comprises about 30 weight percent chlorinated polyolefin and about 70 weight percent chlorinated polypropylene.
- 25 4. A sheet material according to Claim 1, wherein said chlorinated polypropylene component has a peel strength of at least about 1.0 lbs./in at 100°C and said chlorinated polyolefin component has a peel strength of at least about 7 lbs./in at room temperature.
- 30 5. A sheet material according to Claim 1, wherein both said chlorinated polypropylene and said chlorinated polyolefin have a chlorine content of about 20 to about 40 weight percent.

6. A sheet material according to Claim 1, wherein said chlorinated polypropylene has a softening point of at least about 85°C.
- 5 7. A sheet material according to Claim 6, wherein said chlorinated polypropylene has a softening point of at least about 100°C.
8. A sheet material according to Claim 1, wherein said chlorinated polypropylene component has a peel strength of at least about 0.8 lbs./in at room
10 temperature and said chlorinated polyolefin component has a peel strength of at least about 0.2 lbs./in at 100°C.
9. A sheet material according to Claim 8, wherein said chlorinated polypropylene component has a peel strength of at least about 1.0 lbs./in at room
15 temperature and said chlorinated polyolefin component has a peel strength of at least about 0.4 lbs./in at 100°C.
10. A sheet material according to Claim 1, wherein said adhesive layer further comprises about 0.1 to about 2.0 weight percent of an epoxy component on a
20 dry solids basis.
11. A sheet material according to Claim 1, wherein said adhesive layer further comprises a pigment component.
- 25 12. A sheet material according to Claim 11, wherein the pigment component is selected from the group consisting of carbon black, titanium oxide, and mixtures thereof.
13. A sheet material according to Claim 1, wherein said adhesive layer
30 further comprises an additive selected from the group consisting of UV screeners, heat stabilizers, antioxidants, and mixtures thereof.

14. A sheet material according to Claim 1, wherein said outer surface of said decorative paint film has a 60 degree gloss value of at least 60.

5 15. A sheet material according to Claim 1, further comprising a primer layer adhering said inner surface of said decorative paint film to said first surface of said adhesive layer.

10 16. A sheet material according to Claim 15, wherein said primer layer comprises an acrylic polymer composition.

17. A sheet material according to Claim 16, wherein said primer layer is formed from a solution comprising about 65 to about 85 weight percent acrylic polymer composition.

15 18. A sheet material according to Claim 1, further comprising a thermoformable backing layer adhered to said second surface of said adhesive layer.

19. A sheet material according to Claim 18, wherein said thermoformable backing layer is selected from the group consisting of thermoplastic olefin,
20 acrylonitrile-butadiene-styrene terpolymer, polypropylene, thermoplastic polyimide, polyethylene oxide, polycarbonate, polyvinyl chloride, polystyrene, styrene/polyphenylene oxide, polybutylene terephthalate, nylon, PETG copolyester, and mixtures, laminates and copolymers thereof.

25 20. A sheet material according to Claim 1, further comprising an extensible mask layer releasably adhered to said outer surface of said paint film to form a protective film overlying said paint film, said mask layer comprising a polymer selected from the group consisting of polyurethane, polyolefin, polyester, and polyamide.

21. A sheet material according to Claim 1, wherein said paint film comprises a single layer of a pigmented polymer.
22. A sheet material according to Claim 1, wherein said paint film comprises a clear coat layer of a transparent weatherable polymer forming said outer
5 surface and an underlying color coat layer of a pigmented polymer forming said inner surface of the paint film.
23. A flexible, weatherable decorative sheet material useful in lieu of painting for providing a decorative finish for parts, comprising:
a thermoformable decorative paint film, said paint film having an inner
10 surface and a weatherable outer surface suitable for forming an exterior finish for a part, such as an automobile body part, said outer surface having a 60 degree gloss value of at least 60, and said paint film comprising at least one layer which contains a weatherable alloy of a fluoropolymer and an acrylic polymer,
a primer layer comprising an acrylic polymer composition overlying
15 said inner surface of said paint film,
an adhesive layer overlying said primer layer, said adhesive layer comprising about 5 to about 20 weight percent chlorinated polypropylene component having a peel strength of at least about 0.8 lbs./in at 100°C and a peel strength of at least about 0.8 lbs./in at room temperature, and about 1 to about 10 weight percent
20 chlorinated polyolefin component having a peel strength of at least about 5 lbs./in at room temperature and a peel strength of at least about 0.2 lbs./in at 100°C, and
a thermoformable backing layer formed of a thermoplastic olefin composition overlying said adhesive layer.
24. A preform for in-mold surfacing of a part, such as an automobile part,
25 said preform comprising the sheet material according to Claim 23 thermoformed into a three-dimensional configuration.
25. A composite shaped part comprising the preform according to Claim 23, and a substrate of a thermoplastic polymer conforming to the three dimensional configuration of said preform and adhered thereto.

26. A method of making a flexible, weatherable decorative sheet material useful in lieu of painting for providing a decorative finish for parts, comprising:

forming a thermoformable decorative paint film having an inner surface and a weatherable outer surface suitable for forming an exterior finish for a part, such as an automobile body part, and

applying an adhesive layer to the inner surface of the paint film, the adhesive layer comprising a chlorinated polypropylene component having a peel strength of at least about 0.8 lbs./in at 100°C, and a chlorinated polyolefin component having a peel strength of at least about 5 lbs./in at room temperature.

27. A method according to Claim 26, further comprising applying a primer layer to the inner surface of the paint film prior to said step of applying an adhesive layer.

28. A method according to Claim 27, wherein the primer layer comprises an acrylic polymer composition.

29. A method according to Claim 26, wherein the adhesive layer further comprises a pigment component selected from the group consisting of carbon black, titanium oxide, and mixtures thereof.

30. A method according to Claim 26, wherein the adhesive layer further comprising an additive selected from the group consisting of UV screeners, heat stabilizers, antioxidants, and mixtures thereof.

31. A method according to Claim 26, wherein said step of forming a thermoformable decorative paint film comprises applying at least one coating layer to a smooth flexible casting surface, drying said at least one coating layer on said casting surface to produce a paint film with said outer surface releasably bonded to said casting surface and with said inner surface exposed.

32. A method according to Claim 26, wherein said step of forming a thermoformable decorative paint film having an inner surface and a weatherable outer surface comprises coating a pigmented polymer composition on said casting surface and drying said coating composition to form single layer of a pigmented polymer.

5 33. A method according to Claim 26, wherein said step of forming a thermoformable decorative paint film having an inner surface and a weatherable outer surface comprises applying a coating of a transparent weatherable polymer composition to said casting surface to form a clear coat layer and applying a coating of a pigmented polymer composition to said clear coat layer to form a color coat layer.

10 34. A method according to Claim 33, wherein said clear coat layer and said color coat layer are applied wet on wet.

35. A method according to Claim 26, further comprising the step of applying a thermoformable backing layer to the exposed surface of the adhesive layer, the adhesive layer bonding the backing layer to the paint film.

15 36. A method according to Claim 35, further comprising the step of thermoforming the decorative sheet material into a three dimensional shape.

37. A method according to Claim 35, further comprising bonding the exposed surface of the thermoformable backing layer to a substrate to form a composite shaped part.

20

38. A method of making a flexible, weatherable decorative sheet material useful in lieu of painting for providing a decorative finish for parts, comprising:
forming a thermoformable decorative paint film having an inner surface and a weatherable outer surface suitable for forming an exterior finish for a part, such
25 as an automobile body part,

applying a primer layer to the inner surface of the paint film, the primer layer comprising an acrylic polymer composition,

applying a coating of an adhesive composition to the exposed surface of the primer layer to form an adhesive layer, the adhesive composition comprising about 5 to about 20 weight percent chlorinated polypropylene component having a peel strength of at least about 0.8 lbs./in at 100°C and a peel strength of at least about 0.8 lbs./in at room temperature, and about 1 to about 10 weight percent chlorinated polyolefin component having a peel strength of at least about 5 lbs./in at room temperature and a peel strength of at least about 0.2 lbs./in at 100°C, and

applying a thermoformable backing layer to the exposed surface of the adhesive layer, the adhesive layer bonding the backing layer to the paint film.

10

39. A method according to Claim 38, further comprising the steps of:
inserting the decorative sheet material into a mold selected from the group consisting of compression molds and injection molds; and
bonding the decorative sheet material to a substrate to form a composite shaped part.

15

40. An adhesive composition, comprising:
a chlorinated polypropylene component having a peel strength of at least about 0.8 lbs./in at 100°C; and
a chlorinated polyolefin component having a peel strength of at least about 5 lbs./in at room temperature.

20

41. An adhesive composition according to Claim 40, comprising about 1 to about 10 weight percent chlorinated polyolefin and about 5 to about 20 weight percent chlorinated polypropylene.

25

42. An adhesive composition according to Claim 41, further comprising a compatible solvent.

30

43. An adhesive composition according to Claim 40, wherein said chlorinated polypropylene component has a peel strength of at least about 1.0 lbs./in at

100°C and said chlorinated polyolefin component has a peel strength of at least about 7 lbs./in at room temperature.

44. An adhesive composition according to Claim 40, wherein both said
5 chlorinated polypropylene and said chlorinated polyolefin have a chlorine content of about 20 to about 40 weight percent.

45. An adhesive composition according to Claim 40, wherein said
chlorinated polypropylene has a softening point of at least about 85°C.
10

46. An adhesive composition according to Claim 45, wherein said
chlorinated polypropylene has a softening point of at least about 100°C.

47. An adhesive composition according to Claim 40, wherein said
15 chlorinated polypropylene component has a peel strength of at least about 0.8 lbs./in at room temperature and said chlorinated polyolefin component has a peel strength of at least about 0.2 lbs./in at 100°C.

48. An adhesive composition according to Claim 47, wherein said
20 chlorinated polypropylene component has a peel strength of at least about 1.0 lbs./in at room temperature and said chlorinated polyolefin component has a peel strength of at least about 0.4 lbs./in at 100°C.

49. An adhesive composition according to Claim 40, further comprising
25 about 0.1 to about 2.0 weight percent of an epoxy component on a dry solids basis.

50. An adhesive composition according to Claim 40, further comprising a
pigment component.

51. An adhesive composition according to Claim 50, wherein the pigment component is selected from the group consisting of carbon black, titanium oxide, and mixtures thereof.
- 5 52. An adhesive composition according to Claim 40, further comprising an additive selected from the group consisting of UV screeners, heat stabilizers, antioxidants, and mixtures thereof.
53. An adhesive composition according to Claim 40, wherein the adhesive
10 composition is in the form of a film layer.
54. An adhesive composition, comprising:
about 5 to about 20 weight percent chlorinated polypropylene
component having a peel strength of at least about 0.8 lbs./in at 100°C and a peel
15 strength of at least about 0.8 lbs./in at room temperature; and
about 1 to about 10 weight percent chlorinated polyolefin component
having a peel strength of at least about 5 lbs./in at room temperature and a peel
strength of at least about 0.2 lbs./in at 100°C.
- 20 55. An adhesive composition according to Claim 54, wherein both said chlorinated polypropylene and said chlorinated polyolefin have a chlorine content of about 20 to about 40 weight percent.
56. An adhesive composition according to Claim 54, wherein said
25 chlorinated polypropylene has a softening point of at least about 85°C.

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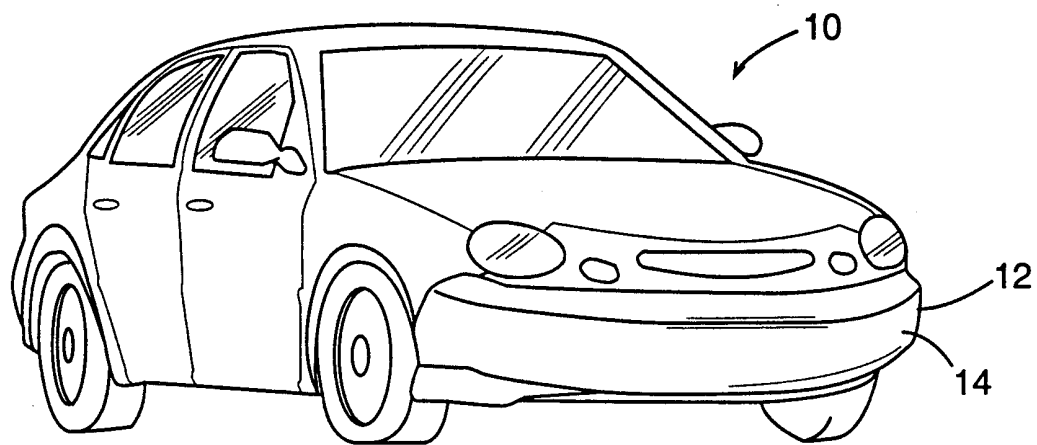


FIG. 1.

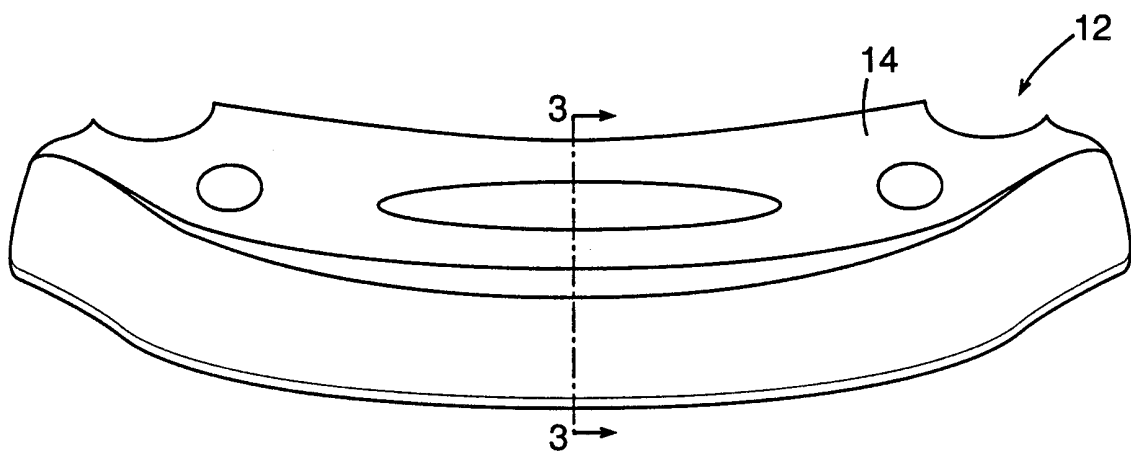


FIG. 2.

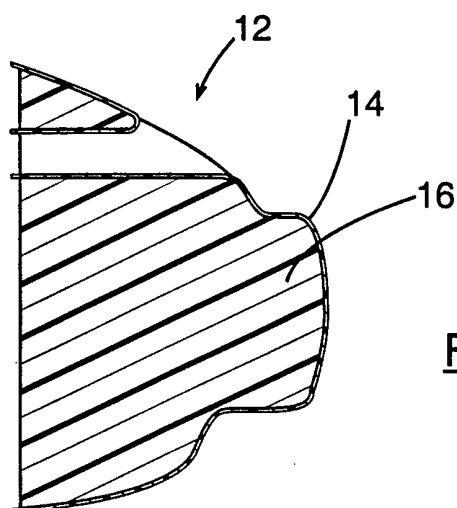


FIG. 3.

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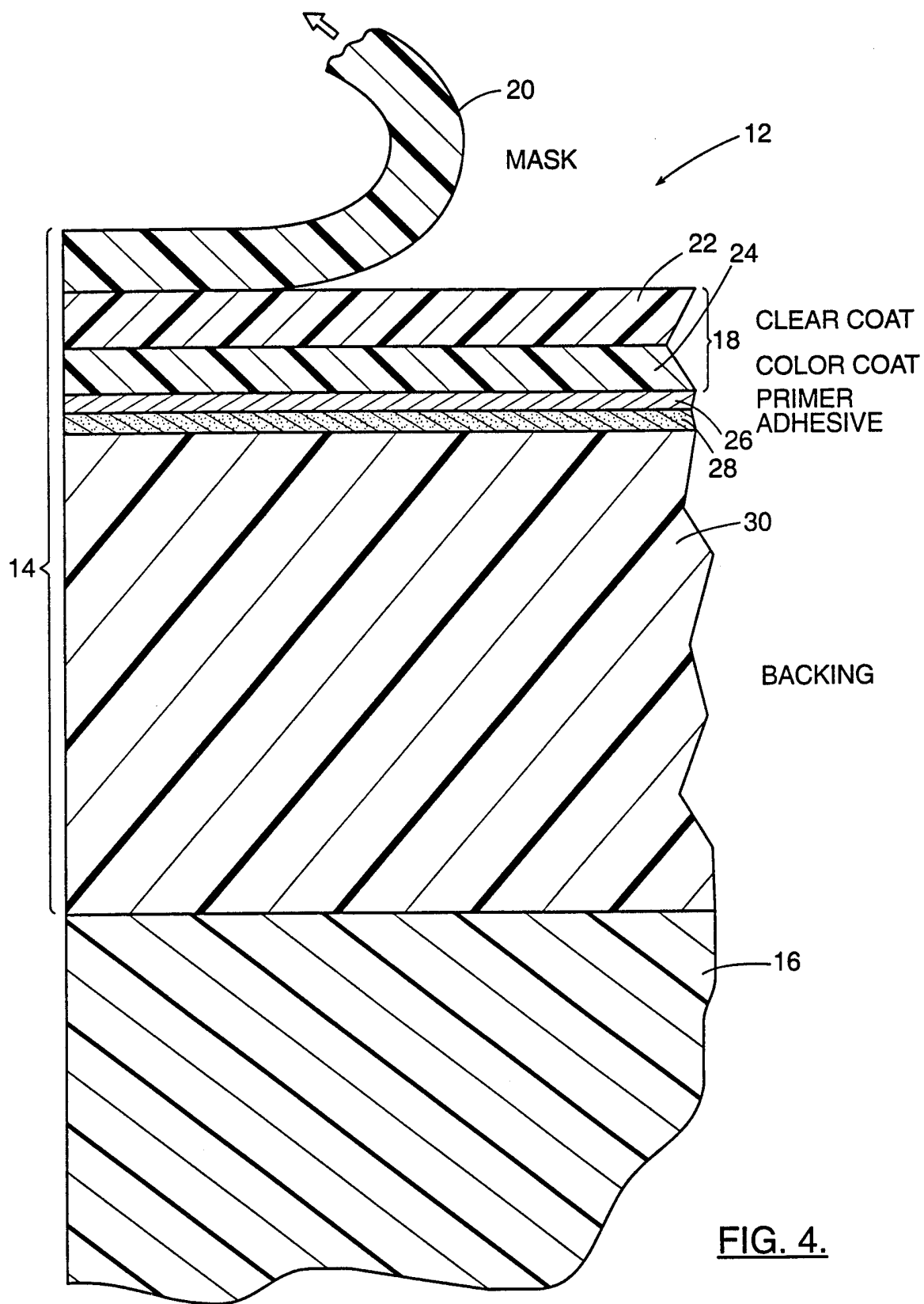
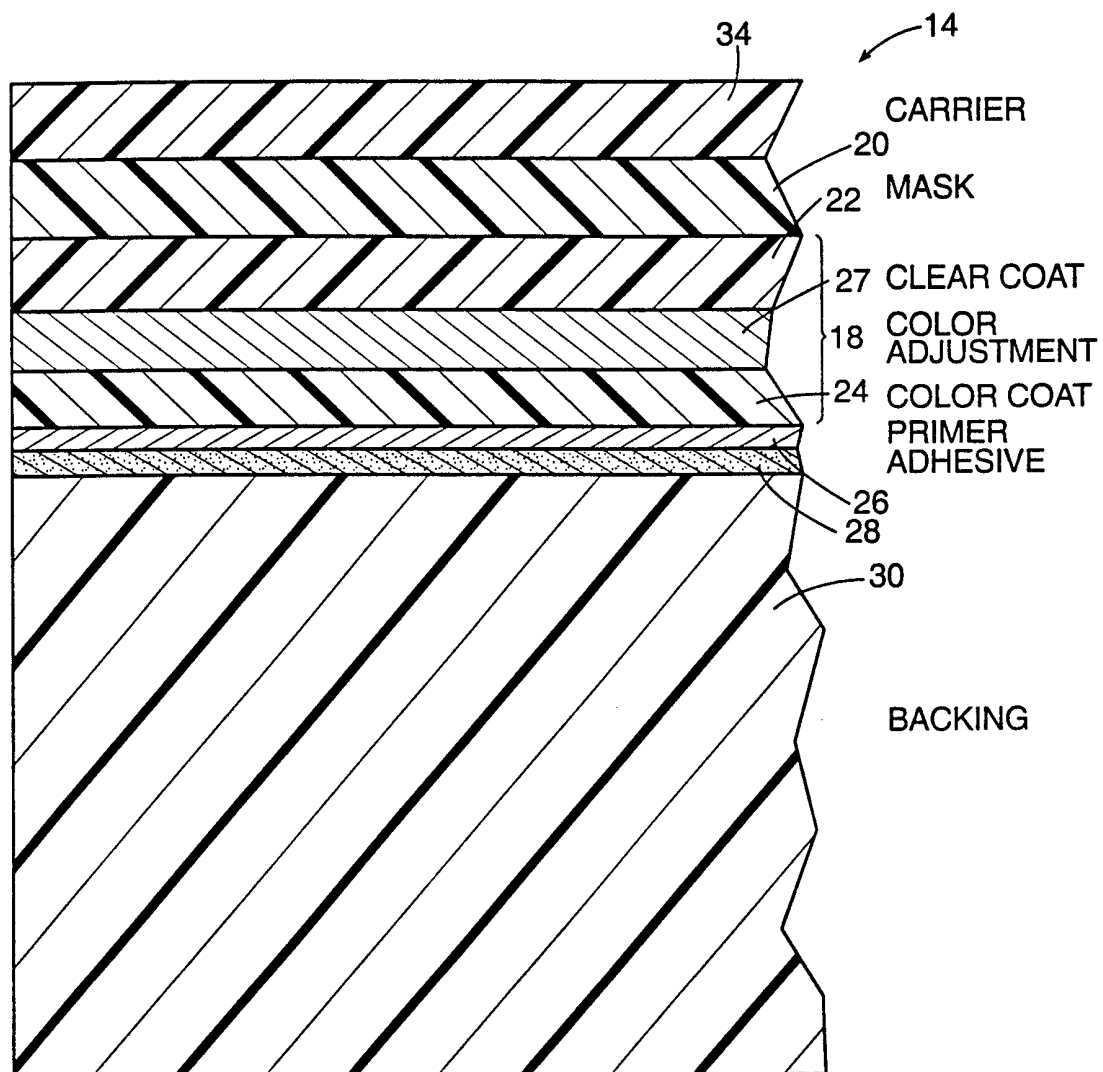
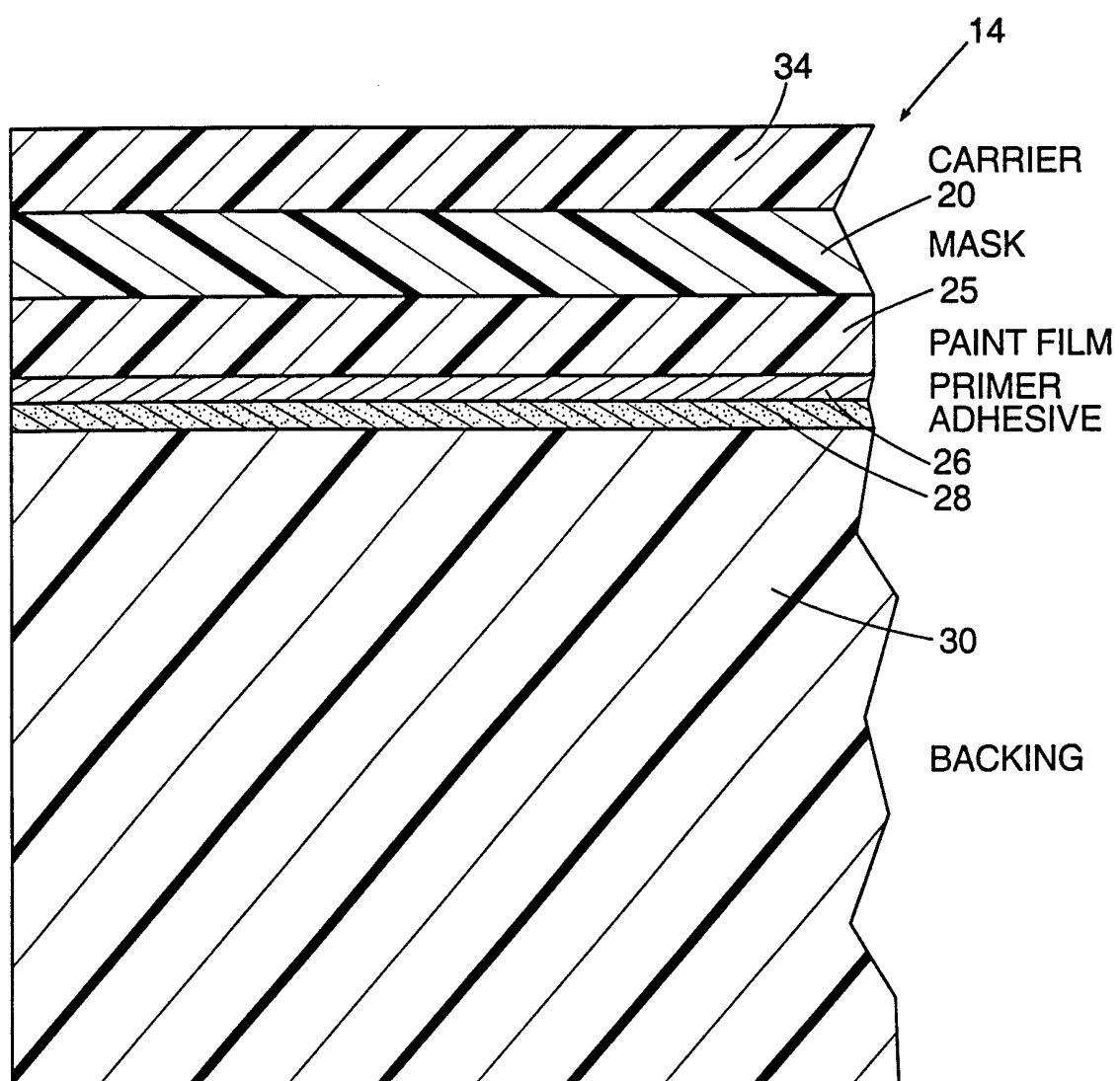


FIG. 4.

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FIG. 5.

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FIG. 6.

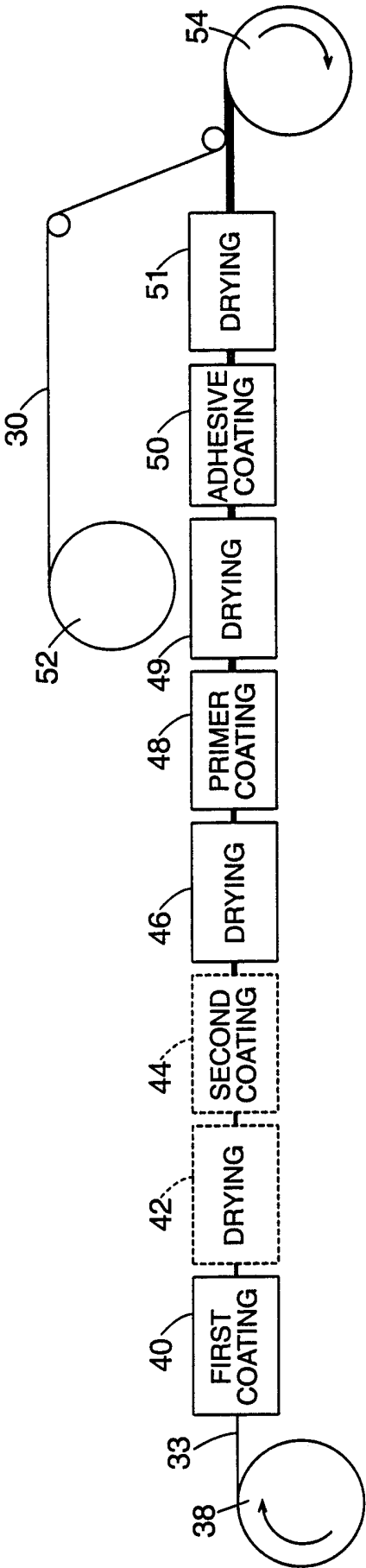


FIG. 7.

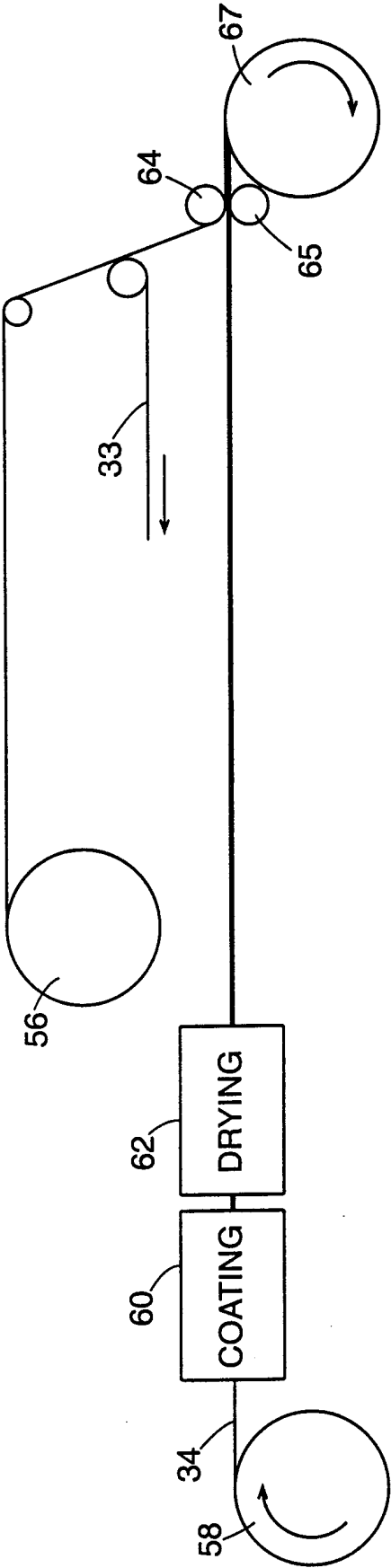


FIG. 8.

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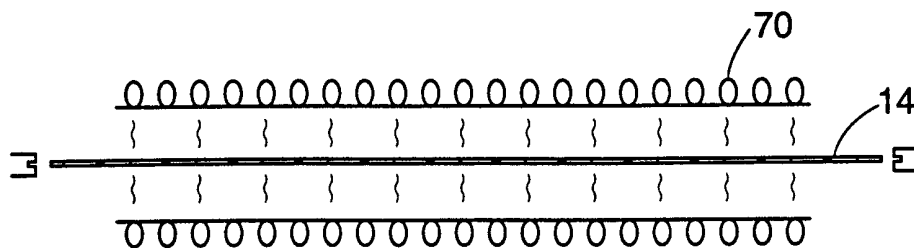


FIG. 9A.

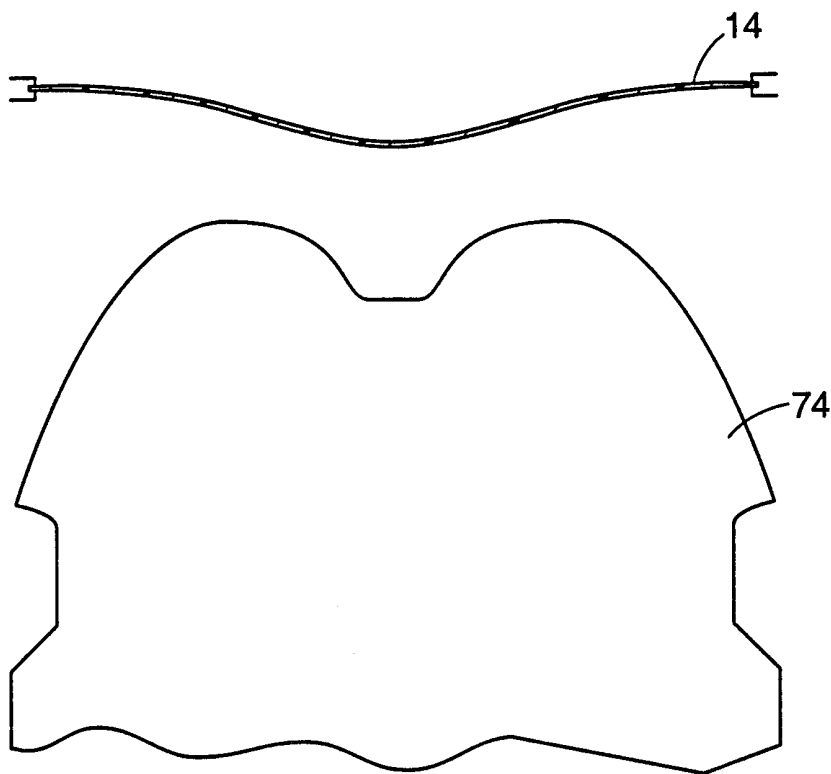


FIG. 9B.

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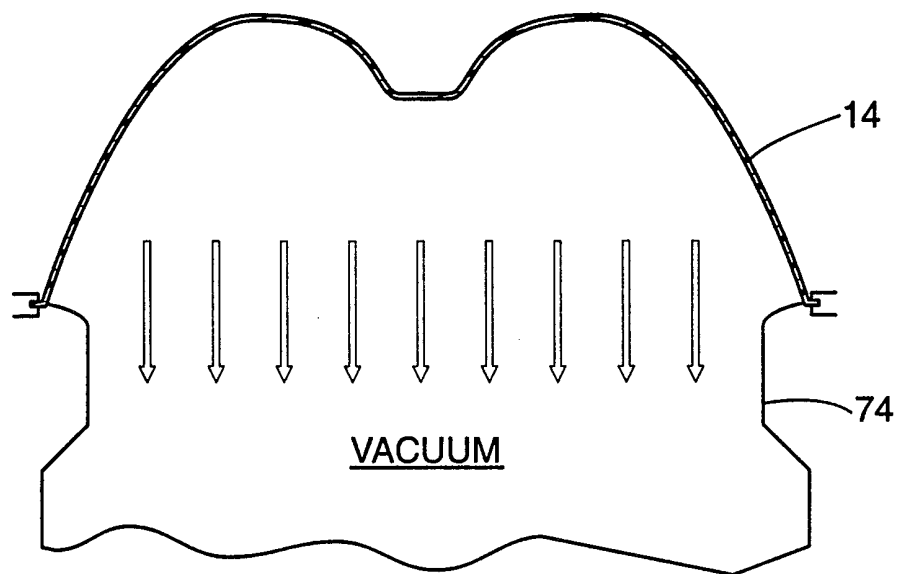


FIG. 9C.

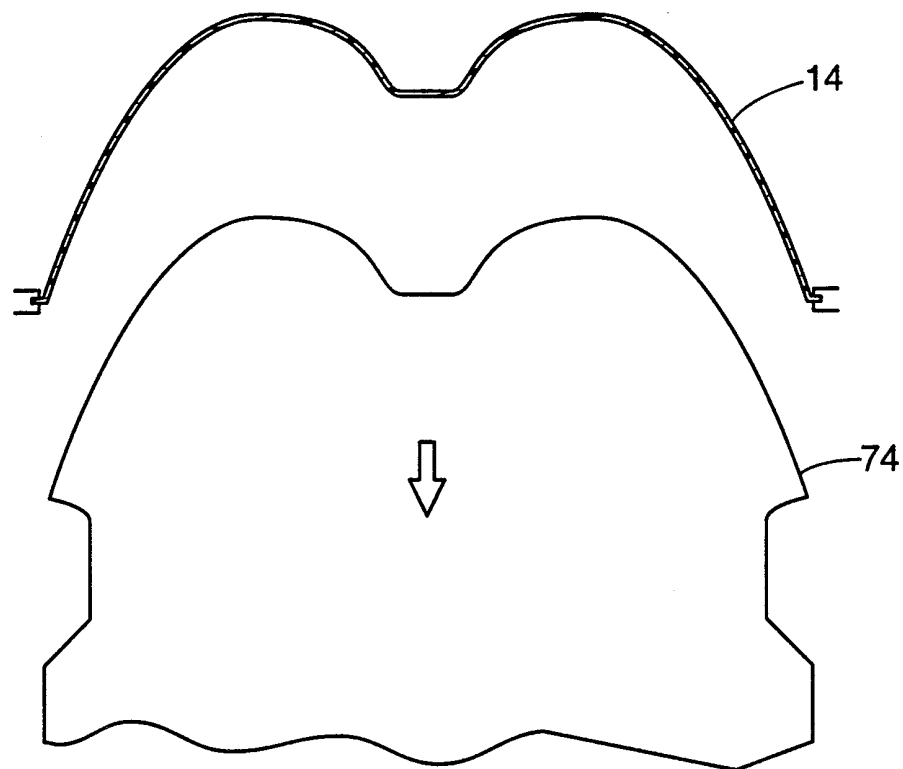


FIG. 9D.

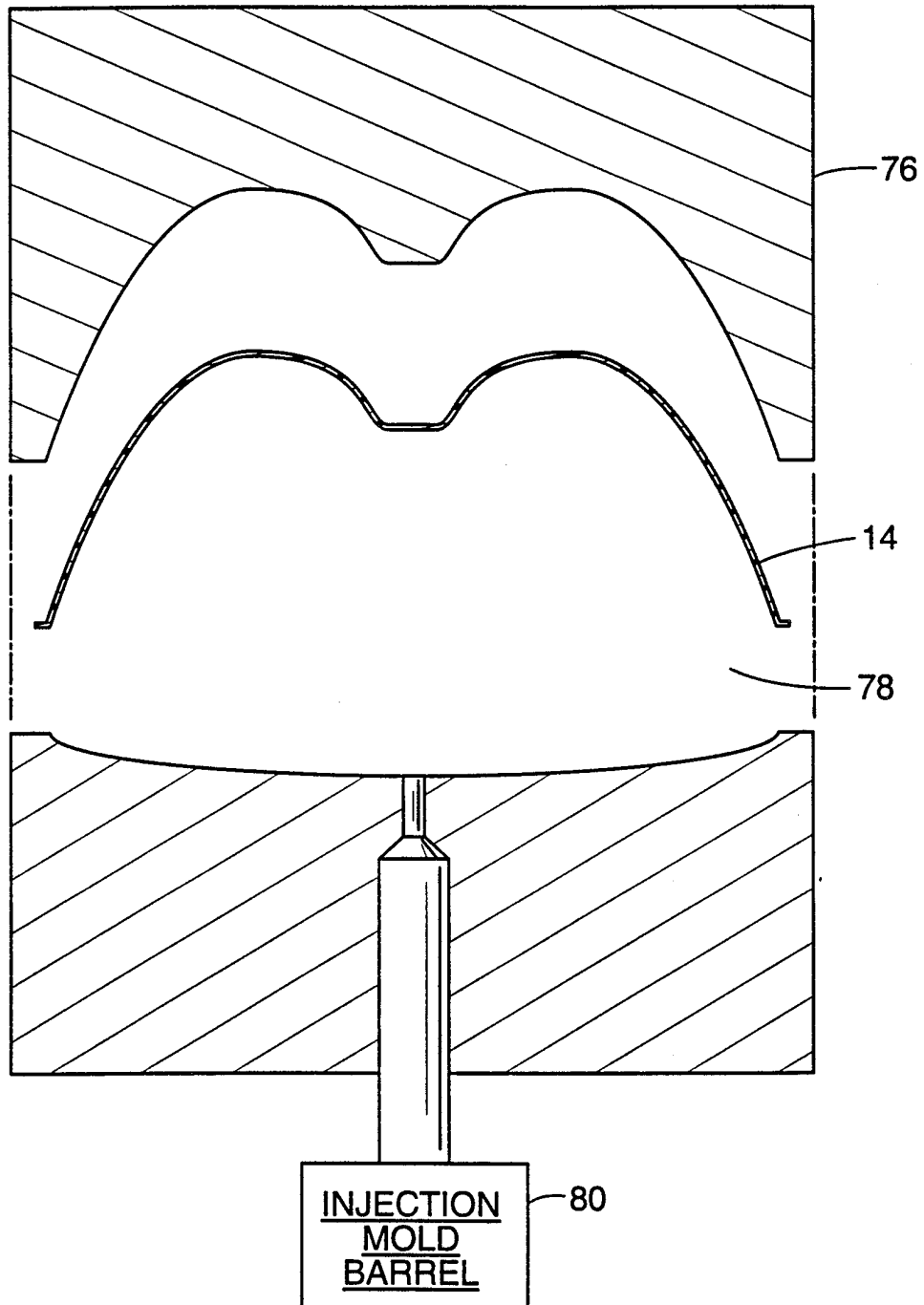


FIG. 10A.

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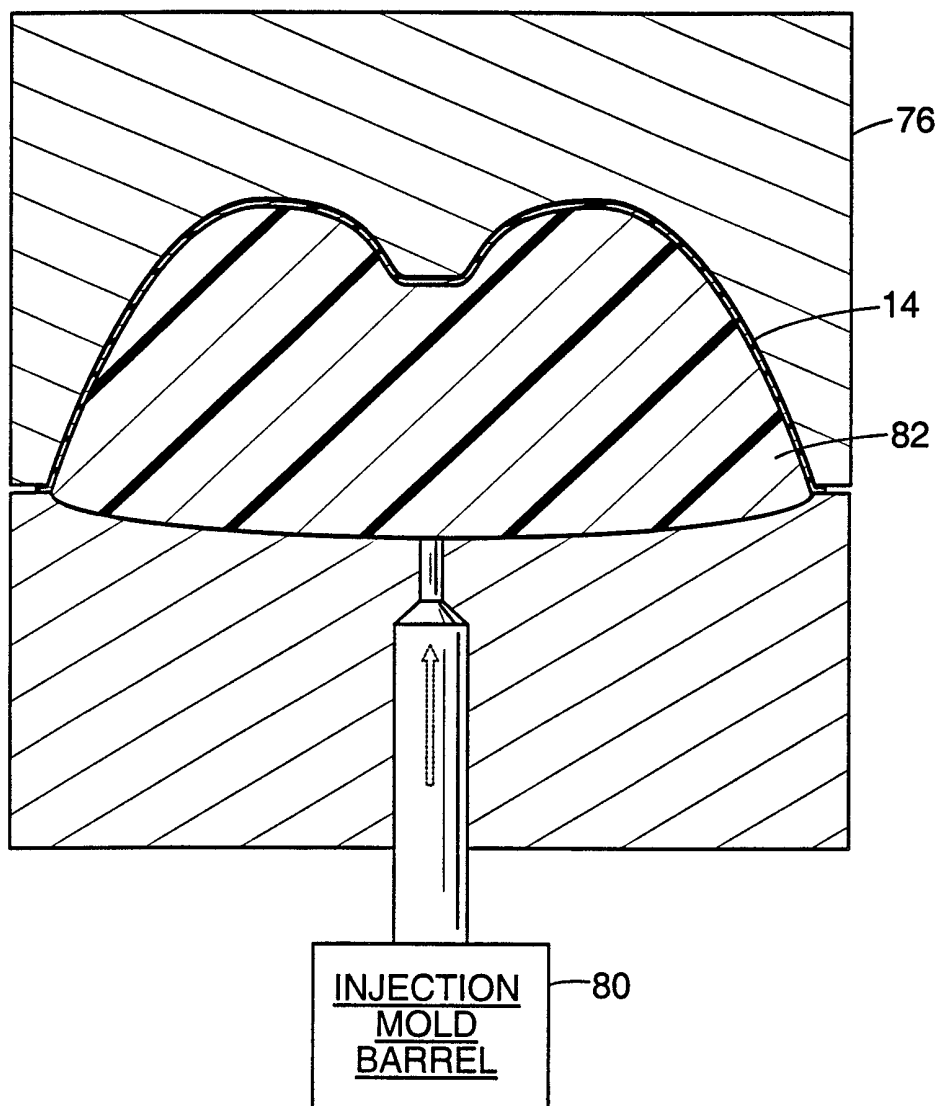


FIG. 10B.

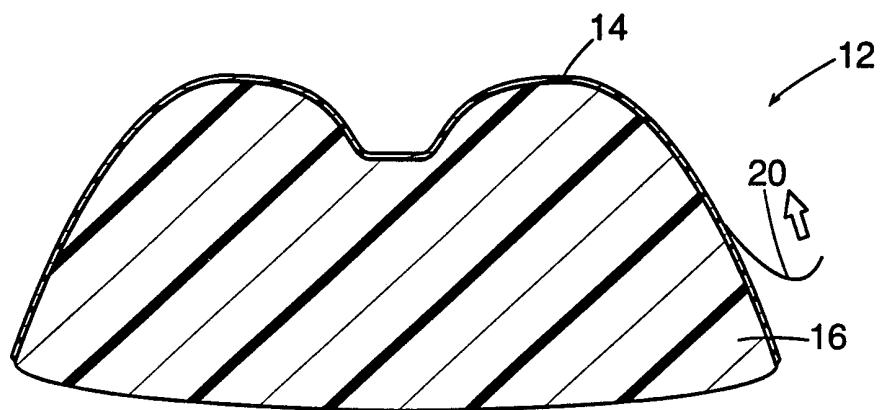


FIG. 10C.