Title: PAINT FILM WITH PROTECTIVE EXTENSIBLE MASK AND PARTS MADE THEREFROM

Abstract: 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 sheet material includes an extensible mask releasably adhered to the outer surface of the paint film to form a protective film overlying the paint film. The mask comprises no more than about 50 mg/m² of N-methyl-2-pyrrolidone, preferably about 6 to about 50 mg/m² of N-methyl-2-pyrrolidone. The mask may comprise a polyester urethane polymer and a polyether urethane polymer, wherein the polyether urethane polymer has a lower concentration of N-methyl-2-pyrrolidone than the polyester urethane polymer. A method of constructing the decorative sheet material and a composite shaped part including the decorative sheet material are also provided.
PAINT FILM WITH PROTECTIVE EXTENSIBLE MASK AND PARTS MADE THEREFROM

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.

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. These types of paint films have been successfully employed for surfacing parts having simple contours, which require a relatively low to moderate degree of forming of the paint film. However, various problems are presented when producing parts with more complex shapes which require much higher degrees of forming and elongation of the paint film.

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). Many of the automotive parts have a complex shape which requires high degrees of elongation of the paint film. Due to differences in the amount of elongation experienced by different areas of the part during the thermoforming and/or molding process, uniformity of appearance has been difficult to achieve with paint films applied prior to molding.

U.S. Patent No. 5, 968,657 discloses a masking film comprising a urethane
layer, wherein the masking film is removably bonded to a paint film. The masking film remains in place while the paint film is thermoformed and/or molded in order to substantially retain the high gloss and DOI of the paint film during such processes. However, the use of urethane-containing mask layers can result in yellowing of the underlying clear coat layer of the paint film, leading to reduced aesthetic quality.

There remains a need for an improved method of providing a paint film finish to complex-shaped molded articles, such as highly contoured automobile body parts, that meets or exceeds the demanding performance and appearance specifications of part manufacturers.

SUMMARY OF THE INVENTION

The present invention provides a decorative paint film that includes a formable protective mask that remains in place on the film during forming or molding operations. The presence of the formable protective mask prevents loss of gloss and DOI during a forming or molding process. The protective mask may be kept in place during construction of the final product, such as an automobile, in order to protect the visual appearance of the paint film finish. The mask may be subsequently stripped off to reveal a high quality, high gloss paint film finish.

It has been discovered that N-methyl-2-pyrrolidone (NMP), which is used as a solvent for certain polymer compositions, can migrate from the mask layer to the underlying clear coat layer of a paint film, causing yellowing of the clear coat layer. The present invention provides a mask having a reduced concentration of NMP, such that yellowing of the clear coat is avoided. Preferably, the low level of NMP is attained by using a blend or mixture of a polyester urethane polymer and a polyether urethane polymer, wherein the polyether urethane polymer has a lower concentration of NMP than the polyester urethane polymer, such that the mask has a lower overall NMP concentration than a mask made solely of the polyester urethane polymer. Alternatively, the mask may comprise at least two layers, a first layer adjacent to the outer surface of the paint film and comprising a blend or mixture of a polyester urethane polymer and a polyether urethane polymer and a second layer overlying the first layer of the mask and comprising a polyester urethane polymer.

In one embodiment, the present invention provides a flexible, weatherable, decorative heat material useful in lieu of painting for providing a decorative finish.
The sheet material comprises a decorative paint film, the 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 sheet material further comprises an extensible mask releasably adhered to the outer surface of the paint film to form a protective film overlying the paint film, the mask comprising no more than about 50 mg/m² of N-methyl-2-pyrrolidone. Preferably, the mask comprises about 6 to about 50 mg/m² of N-methyl-2-pyrrolidone. Most preferably, the mask comprises about 6 to about 20 mg/m² of N-methyl-2-pyrrolidone. In one embodiment, the mask comprises a mixture of about 30 to about 50 weight percent of a polyether urethane polymer and about 50 to about 70 weight percent of a polyester urethane polymer, the polyether urethane polymer having a lower concentration of NMP than the polyester urethane polymer. In another embodiment, the mask comprises at least two layers, a first layer comprising a mixture of a polyester urethane polymer and a polyether urethane polymer, such as the mixture described above, adjacent to the outer surface of the paint film and a second layer comprising a polyester urethane layer overlying the first layer.

The decorative paint film may comprise a single layer of a polymer composition containing pigments, dyes, flakes, or mixtures thereof. Preferably, the paint film comprises a clear coat layer of a transparent weatherable polymer forming the outer surface and an underlying color coat layer of a polymer composition containing at least one of pigments, dyes, flakes or mixtures thereof, the color coat layer forming the inner surface of the paint film.

The sheet material may further include a thermoformable backing layer bonded to the inner surface of the paint film. The thermoformable backing layer may be selected from the group consisting of thermoplastic olefin, polyethylene, 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.

The sheet material may also include an adhesive layer affixing the paint film to the thermoformable backing layer. The adhesive layer comprises one or more layers selected from the group consisting of urethane adhesives, acrylic adhesives, acrylic adhesives with crosslinkers, chlorinated polyolefins and mixtures thereof.
The above-described decorative sheet material may be used to form a preform for in-mold surfacing of a part by thermoforming the decorative sheet material into a three-dimensional configuration. A composite shaped part may also be constructed by adhering the preform to a substrate of a thermoplastic polymer, which conforms to the three-dimensional configuration of the preform and is adhered thereto. In one embodiment, the decorative sheet material of the composite shaped part 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 and wherein the elongated areas and the non-elongated areas have a 60 degree gloss value within 10 gloss units from one another and in excess of 60.

A motor vehicle is also provided comprising a plurality of composite shaped parts wherein the extensible mask remains in place on the parts to protect the paint finish of the vehicle from damage during manufacture and shipment of the vehicle and is subsequently removed upon delivery of the vehicle to a customer.

A method of making a flexible, weatherable decorative sheet material is also provided. The method includes applying a coating comprising a urethane polymer composition onto a casting surface and drying the polymer coating to form a continuous extensible polymer mask releasably adhered to the casting surface and comprising no more than about 50 mg/m² of NMP. In one embodiment, the coating application step comprises applying a coating of a mixture of a polyester urethane polymer and a polyether urethane polymer onto the casting surface. Alternatively, the coating application step may comprise applying a first coating overlying the casting surface and comprising a polyester urethane polymer, and a second coating overlying the first coating and comprising a mixture or blend of a polyether urethane polymer and a polyester urethane polymer. A decorative paint film is formed having an inner surface and a weatherable outer surface suitable for forming an exterior finish for a part. The weatherable outer surface of the paint film is releasably bonded to the exposed surface of the mask. The decorative paint film may be formed by applying at least one coating layer to a smooth flexible casting surface, drying the coating layer on the casting surface to produce a paint film with an outer surface releasably bonded to the casting surface and with the inner surface exposed, and bonding the exposed inner surface of the paint film to a thermoformable backing layer.
The step of releasably bonding the outer surface of the paint film may include stripping the casting surface from the paint film to expose the weatherable outer surface of the paint film, bringing the exposed weatherable outer surface of the paint film into contact with the mask, and bonding the mask and the paint film together.

The bonding may be accomplished by applying pressure and/or heat to the layers.

The decorative sheet material constructed as described above may be thermoformed into a three-dimensional shape while the mask remains in place. Additionally, the thermoformed decorative sheet material may be inserted into an injection mold with the mask facing the mold surface. Thereafter, molten thermoplastic polymer is injected into the mold and hardening of the injected thermoplastic polymer is effected in order to bond the polymer to the decorative sheet material to form a composite shaped part. The mask may be thereafter stripped from the composite shaped part to expose the decorative surface of the sheet material.

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 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;

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;

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;
Figure 8 is a schematic illustration of a process for applying the mask 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;

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

Figure 11 is a cross-sectional view of a multiple layer embodiment of the mask of the present invention; and

Figure 12 is a schematic illustration of a process for construction of another embodiment of the decorative sheet material of the present invention.

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.

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. Examples of composite parts of automobiles include, but are not limited to, hoods, bumpers, roofs, trunk lids, door panels and A, B and C pillars. 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, even after experiencing a high level of elongation, such as in excess of about 300% or even as high as about 600%, 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 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 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 20 also adds strength to the decorative sheet material 14 and improves process uniformity during the thermoforming process. Additionally, the extensible mask 20 protects the underlying layers of the decorative sheet material 14 from scratching or marring until the part is ready for display. The mask 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.

The mask 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 20 may be removed to reveal the underlying decorative paint film 18. For instance, the extensible mask 20 can be maintained as a protective layer and removed only after the vehicle has completed shipment and is ready for delivery to a customer. The extensible mask 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 20 is transparent or substantially transparent to permit visual inspection of the part for surface defects without removal of the mask. In other embodiments, the mask 20 contains pigments or dyes such that the mask exhibits a slight tint so that the presence of the mask can be discerned, but inspection of the underlying paint film 18 is still possible.

Additionally, the extensible mask 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 mold as the mold closes. The extensible mask 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 paint film 18 exhibits a 60 degree gloss value of at least 60, and more preferably at least 65.

Preferably, the extensible mask 20 is about 0.3 mils to about 3.0 mils in thickness. The extensible mask 20 comprises no more than about 50 mg/m² of N-methyl-2-pyrrolidone (NMP). Preferably, the mask comprises about 6 to about 50 mg/m² of NMP, most preferably about 6 to about 20 mg/m² of NMP. These NMP concentrations refer to the final concentrations in the mask 20 after drying of the mask. In one embodiment, the extensible mask 20 comprises a urethane polymer composition. Preferably, the mask 20 comprises a dried film of an aliphatic or aromatic polyester and/or polyether polyurethane in the form of a dispersion or a solution. A preferred mask 20 embodiment comprises a polyester urethane polymer and a polyether urethane polymer, wherein the polyether urethane polymer has a lower concentration of NMP than the polyester urethane polymer, thereby lowering the overall concentration of NMP as compared to a mask made solely using the polyester urethane polymer. The mask 20 may comprise a blend or mixture of the polyester urethane polymer and the polyether urethane polymer, such as a mixture comprising about 50 to about 70 weight percent of the polyester urethane polymer and about 30 to about 50 weight percent of the polyether urethane polymer. Alternatively, as shown in Figure 11, the mask 20 may comprise at least two layers, a first layer 20A adjacent to the outer surface of the paint film and comprising a mixture of a polyester urethane polymer and a polyether urethane polymer, such as the mixture described
above, and a second layer 20B overlying the first layer of the mask and comprising a polyester urethane polymer. The polyester urethane polymer component generally provides better adhesiveness to the underlying paint film and the polyether urethane polymer component provides greater elongation properties, as well as the lower concentration of NMP. A commercially available example of a polyester urethane polymer suitable for use in the present invention is QA 5218 polymer manufactured by Mace Adhesives and Coatings of Dudley, MA. A commercially available embodiment of the polyether urethane polymer suitable for use in the present invention is QA 5545 polymer, also manufactured by Mace Adhesives and Coatings. The mask 20 preferably comprises about 85 to about 99.5 weight percent polyurethane water-borne dispersion. Advantageously, a small amount of surfactant (about 0.05 to about 2.0 weight percent), such as SURFYNOL 104H manufactured by Air Products of Allentown, PA, is added to lower surface tension. Isopropyl alcohol may also be added in small amounts, such as up to about 5% by weight, in order to reduce surface tension.

The mask 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. 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, triazines and combinations thereof. The migratory additives are encouraged to migrate into the outer surface of the clear coat layer 22 by the heat present during thermoforming or molding processes. Additionally, the presence of these additives in the mask 20 prevents migration of additive components from the clear coat layer 22 into the mask.

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 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 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 polymer, as shown in Figure 6, or may comprise multiple layers, as shown in Figures 4 and 5. If a single layer 25 of 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 polymer may also include UV screeners to enhance weatherability, antioxidants, heat stabilizers, and other conventional additives. The polymer layer 25 preferably includes pigments, dyes, flakes, or mixtures thereof 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 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 pigments, dyes, flakes, or mixtures thereof to provide the appearance necessary for exterior automobile use and improve weatherability. Preferably, the color coat layer 24 is selected from the group consisting of urethane polymers, acrylic polymers, fluoropolymers, and alloys or a fluoropolymer and acrylic polymer (such as FLUOREX® films). 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 is an optional layer that 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 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 wavelengths less than 400 nm. The primer layer 26 is preferably about 0.2 to about 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 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 one or more layers selected from the group consisting of urethane adhesives, acrylic adhesives, acrylic adhesives with cross linkers, chlorinated polyolefins and mixtures thereof. Preferably, a mixture of a chlorinated polypropylene and a higher molecular weight chlorinated polyolefin is used. In one embodiment, the adhesive layer 28 is prepared from a mixture of 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. A chlorinated polypropylene suitable for use with the present invention is HARDLEN 13LP manufactured by Advanced Polymer. A higher molecular weight chlorinated
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.

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 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 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. The backing layer 30 may be selected from the group consisting of thermoplastic olefin, polyethylene, 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 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 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 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 using a “wet on wet” coating technique.

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. Alternatively, dryer 49 may be eliminated from the process such that the adhesive layer 28 is applied to the primer layer 26 while the primer layer is still wet using a “wet on wet” coating 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.

Figure 8 illustrates a process for preparing a decorative sheet material 14 having a mask 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 20 is deposited onto a surface of the carrier. As noted above, the mask 20 may comprise more than one layer. For example, the coating station 60 may deposit two layers, a first coating overlying the carrier 34 and comprising a polyester urethane polymer, and a second coating overlying the first coating and comprising a mixture or blend of a polyether urethane polymer and a polyester urethane polymer. 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 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 20 may utilize any conventional drying technique. Preferably, the dryer 62 comprises an oven with multiple heating stages. The dryer 62 evaporates the solvents present in the mask 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 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 20 by nipping the two films between two rollers, 64 and 65, with or without applying heat to the layers. The resulting decorative sheet material 14 is collected by product roll 67. The non-extensible carrier 34 may be stripped away to expose the mask 20 before or after collection of the sheet material 14 by product roll 67.

In another embodiment, a single or multiple layer decorative paint film 18, primer layer 26, and adhesive layer 28 are coated directly onto the dried mask 20.
rather than laminating the coated films together. The resulting multi-layer film is laminated to a backing layer 30 as described above. In a further embodiment, the mask 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 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, polyethylene, 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 preforming, 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 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 20 of the decorative sheet material may be stripped from the composite shaped part 12 to expose the paint film finish when desired.

Figure 12 illustrates a process for forming one preferred embodiment of the decorative paint film of the present invention. In this embodiment, a layer of acrylonitrile-butadiene-styrene terpolymer (ABS) is extruded from extruder 84 onto roller 86. The layer of ABS material passes through a nip created by roller 86 and roller 88 in order to adjust the thickness of the ABS layer. Preferably, the ABS layer is about 60 to about 100 mils in thickness after passing through the nip. The ABS layer then enters a second nip created by rollers 88 and 90. A paint film supplied by supply roll 92 also enters the nip created by rollers 88 and 90. The surface 94 of the paint film is an exposed adhesive layer capable of adhering to a hot layer of ABS. For example, the adhesive layer may comprise a heat-activatable adhesive, such as ELVACITE 2009, or a thin layer of ABS terpolymer. The decorative paint film is nipped to the sheet of ABS and collected on collection roll 96. One or more of the rollers, 86, 88 and 90, may be chilled in order to cool the ABS layer. Using this process, a paint film may be cost-effectively adhered to an ABS backing layer. If desired, the resulting material may then be thermoformed into any desired shape as described in connection with Figures 9A-9D. The decorative paint film used in the process illustrated in Figure 12 may be constructed according to the process described
in connection with Figure 7, with the exception of the addition of the thermoformable backing layer. The extruded ABS layer acts as the backing layer. In certain applications, the sheet material of this embodiment can be used as a composite shaped part without the need for a further substrate layer.

EXAMPLE 1

A mask composition according to the present invention, shown in Table 1, was prepared. As shown, the composition comprised about 56% polyester urethane polymer (QA 5218) and about 36% polyether urethane polymer (QA 5545).

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight</th>
<th>Percent By Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>QA 5218</td>
<td>56.400</td>
<td>56.400%</td>
</tr>
<tr>
<td>QA 5545</td>
<td>36.400</td>
<td>36.400%</td>
</tr>
<tr>
<td>TINUVIN 1130</td>
<td>0.525</td>
<td>0.525%</td>
</tr>
<tr>
<td>TINUVIN 292</td>
<td>0.175</td>
<td>0.175%</td>
</tr>
<tr>
<td>SURFYNOL 104H</td>
<td>1.500</td>
<td>1.500%</td>
</tr>
<tr>
<td>IP Alcohol</td>
<td>5.000</td>
<td>5.000%</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>100.000</strong></td>
<td><strong>100.000%</strong></td>
</tr>
</tbody>
</table>

The above composition was prepared according to the following procedure:

1) Dispense the urethanes, 5218 and 5545, into a 300 gallon vessel and place vessel on mixer having a 16” cowels “F” style high shear mixing blade.

2) Mix at 400 rpm for 5 minutes, adjusting height as required.

3) Add TINUVIN ingredients while mixing, speed up to 500 rpm, mix for 5 minutes.

4) Preblend alcohol and SURFYNOL in a separate container using low shear mixing. Blending should only take about 5 minutes of mixing time.

5) Adjust the mixer speed to a point where there is good vortex but avoiding excessive entrapment of air.
6) While mixing, add the solution of alcohol and SURFYNOL to the mixer slowly, about 10 lbs. per minute.

7) If applicable, slowly add pigments to mixer while mixing.

8) Continue mixing for 15 minutes, then cut mixer off and remove the vessel from the mixer.

9) Filter the batch through 50 micron filter bags using gravity filter technique.

A clear coat and color coat were prepared according to the formulations in Tables 2-4.

**Table 2**

Color Coat Formulation

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent By Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>B14276-M139 Black Dispersion</td>
<td>0.370%</td>
</tr>
<tr>
<td>HK-400 Flatting Agent</td>
<td>0.370%</td>
</tr>
<tr>
<td>29Y499 Transparent Yellow Dispersion</td>
<td>0.730%</td>
</tr>
<tr>
<td>Dimethyl Phthalate</td>
<td>1.820%</td>
</tr>
<tr>
<td>3346 ST Sparkle Silver Flake</td>
<td>4.400%</td>
</tr>
<tr>
<td>DB Acetate</td>
<td>7.270%</td>
</tr>
<tr>
<td>Clear FLUOREX Base (See Table 3)</td>
<td>85.040%</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>100.000%</strong></td>
</tr>
</tbody>
</table>

**Table 3**

Clear FLUOREX Base

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent By Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELVACITE 2042</td>
<td>10.58%</td>
</tr>
<tr>
<td>KYNAR 500</td>
<td>31.75%</td>
</tr>
<tr>
<td>DB Acetate</td>
<td>45.28%</td>
</tr>
<tr>
<td>Dimethyl Phthalate</td>
<td>11.33%</td>
</tr>
<tr>
<td>TINUVIN 900</td>
<td>1.06%</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>100.00%</strong></td>
</tr>
</tbody>
</table>
Table 4

Clear Coat Formulation

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent By Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELVACITE 2042</td>
<td>11.92%</td>
</tr>
<tr>
<td>KYNAR 500</td>
<td>30.65%</td>
</tr>
<tr>
<td>DB Acetate</td>
<td>18.93%</td>
</tr>
<tr>
<td>Dimethyl Phthalate</td>
<td>18.93%</td>
</tr>
<tr>
<td>EXXATE 600 Solvent</td>
<td>18.94%</td>
</tr>
<tr>
<td>TINUVIN 900</td>
<td>0.63%</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>100.00%</strong></td>
</tr>
</tbody>
</table>

The mask composition was coated onto 2 mil PET and dried. The dried mask was laminated to a paint film comprising a 1.9 mil clear coat layer prepared according to Table 4, a 1.9 mil color coat prepared according to Tables 2-3, a 1 mil acrylic primer layer, a .5 mil layer of a urethane adhesive (NC222 made by Novacote Flex Pack), and a 30 mil thermoplastic olefin backing layer. The resulting laminate was thermoformed into a three dimensional preform and the mask was removed. The preform was then submerged in a water bath at a temperature of 40°C for a period of 10 days. The laminate was also subjected to 10 days of heat aging at a temperature of 80°C and 10 days of humidity exposure at 50°C and 95-100% RH. No yellowing of the clear coat was visible after any of these tests.

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 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:
   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 extensible mask having inner and outer surfaces, the inner surface 
   being releasably adhered to said outer surface of said paint film to form a protective 
   film overlying said paint film, said extensible mask comprising a polyester urethane 
   polymer and a polyether urethane polymer.

2. A sheet material according to Claim 1, wherein said mask comprises about 6 to about 50 mg/m² of N-methyl-2-pyrrolidone.

3. A sheet material according to Claim 1, wherein said mask comprises about 6 to about 20 mg/m² of N-methyl-2-pyrrolidone.

4. A sheet material according to Claim 1, wherein said mask comprises a dried film of an aliphatic or aromatic polyurethane solution or dispersion.

5. A sheet material according to Claim 1, wherein said mask comprises a mixture of said polyester urethane polymer and said polyether urethane polymer.

6. A sheet material according to Claim 5, wherein said mixture comprises about 50 to about 70 weight percent of said polyester urethane polymer and about 30 to about 50 weight percent of said polyether urethane polymer.

7. A sheet material according to Claim 1, wherein said polyether urethane 
   polymer has a lower concentration of N-methyl-2-pyrrolidone than said polyester 
   urethane polymer.

8. A sheet material according to Claim 1, wherein said mask comprises at 
   least two layers, a first layer adjacent to the outer surface of the paint film and 
   comprising a mixture of a polyester urethane polymer and a polyether urethane
polymer, and a second layer overlying the first layer of the mask and comprising a polyester urethane polymer.

9. A sheet material according to Claim 8, wherein said mixture comprises about 50 to about 70 weight percent of said polyester urethane polymer and about 30 to about 50 weight percent of said polyether urethane polymer.

10. A sheet material according to Claim 1, wherein said mask has an elongation at break of at least about 200 percent.

11. A sheet material according to Claim 1, wherein said mask has a thickness of about 0.3 mil to about 3 mils.

12. A sheet material according to Claim 1, wherein said paint film comprises a single layer of a polymer composition containing at least one of pigments, dyes, and flakes.

13. A sheet material according to Claim 1, wherein said paint film comprises a clear coat layer of a transparent weatherable polymer forming said outer surface and an underlying color coat layer of a polymer composition containing at least one of pigments, dyes, and flakes, said color coat layer forming said inner surface of the paint film.

14. A sheet material according to Claim 13, further comprising a color adjustment layer between said clear coat layer and said color coat layer.

15. A sheet material according to Claim 1, further comprising a thermoformable backing layer bonded to said inner surface of said paint film.

16. A sheet material according to Claim 15, wherein said thermoformable backing layer is selected from the group consisting thermoplastic olefin, polyethylene, 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.
17. A sheet material according to Claim 15, wherein said thermoformable backing layer comprises acrylonitrile-butadiene-styrene terpolymer.

18. A sheet material according to Claim 17, further comprising an adhesive layer affixing said paint film to said thermoformable backing layer, said adhesive layer selected from the group consisting of heat-activatable adhesives and acrylonitrile-butadiene-styrene terpolymer.

19. A sheet material according to Claim 15, further comprising an adhesive layer affixing said paint film to said thermoformable backing layer.

20. A sheet material according to Claim 19, wherein said adhesive layer comprises one or more layers selected from the group consisting of urethane adhesives, chlorinated polyolefins, acrylic adhesives, and mixtures thereof.

21. A sheet material according to Claim 1, wherein said mask comprises at least one component selected from the group consisting of pigments, dyes and mixtures thereof.

22. A sheet material according to Claim 1, further comprising an adhesive layer overlying said inner surface of said paint film.

23. A sheet material according to Claim 1, wherein said outer surface of said paint film has a 60 degree gloss value of at least 65.

24. A preform for in-mold surfacing of a part, such as an automobile part, said preform comprising the sheet material according to Claim 1 thermoformed into a three-dimensional configuration.

25. A composite shaped part comprising the sheet material according to Claim 1, and a substrate of a thermoplastic polymer adhered thereto.

26. A composite shaped part according to Claim 25, wherein said extensible mask is transparent to permit visual inspection of the part for surface defects without removal of said extensible mask.
27. A motor vehicle comprising a plurality of composite shaped parts, said composite shaped parts comprising a sheet material according to Claim 1 adhered to a substrate of a thermoplastic polymer, and wherein the extensible mask remains in place on said parts to protect the paint finish of the vehicle from damage during manufacture and shipment of the vehicle and is removed upon delivery of the vehicle to a customer.

28. A method of making a flexible, weatherable decorative sheet material useful in lieu of painting for providing a decorative finish for parts, comprising:
   applying a coating comprising a polyester urethane polymer composition and a polyether urethane polymer composition onto a casting surface,
   drying the polymer compositions to form a continuous extensible polymer mask releasably adhered to the casting surface,
   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
   releasably bonding the weatherable outer surface of said paint film to the exposed surface of the mask.

29. A method according to Claim 28, wherein the dried polymer compositions comprise no more than about 50 mg/m² of N-methyl-2-pyrrolidone.

30. A method according to Claim 28, wherein said step of applying a coating comprises applying a coating of a mixture of a polyester urethane polymer and a polyether urethane polymer onto the casting surface.

31. A method according to Claim 30, wherein said applying step comprises applying a coating comprising about 50 to about 70 weight percent of the polyester urethane polymer and about 30 to about 50 weight percent of the polyether urethane polymer onto the casting surface.

32. A method according to Claim 30, wherein the polyether urethane polymer has a lower concentration of N-methyl-2-pyrrolidone than the polyester urethane polymer.
33. A method according to Claim 28, wherein said applying step comprises applying a first coating overlying the casting surface and comprising a polyester urethane polymer, and applying a second coating overlying the first coating and comprising a mixture of a polyether urethane polymer and a polyester urethane polymer.

34. A method according to Claim 28, wherein said step of releasably bonding said outer surface of said paint film comprises stripping said casting surface from the paint film to expose said weatherable outer surface of the paint film, bringing the exposed weatherable outer surface of the paint film into contact with said mask on its casting surface, bonding the mask and said paint film to one another, and removing the casting surface from said mask.

35. A method according to Claim 28, 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, and bonding the exposed inner surface of said paint film to a thermoformable backing layer.

36. A method according to Claim 28, wherein said step of forming a thermoformable decorative paint film having an inner surface and a weatherable outer surface comprises coating a polymer composition containing at least one of pigments, dyes, and flakes, onto a casting surface and drying the coating composition to form a single paint film layer.

37. A method according to Claim 28, 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 a casting surface to form a clear coat layer and applying a coating of a polymer composition containing at least one of pigments, dyes, and flakes, to the clear coat layer to form a color coat layer.
38. A method according to Claim 28, further comprising the step of thermoforming the decorative sheet material into a three dimensional shape while the mask remains in place.

39. A method according to Claim 38, further comprising the steps of:

inserting the thermoformed decorative sheet material into an injection mold with the mask facing the mold surface;

injecting polymer into the mold; and

effecting hardening of the injected polymer to bond the polymer to the decorative sheet material to form a composite shaped part.

40. A method according to Claim 39, further comprising the step of stripping the mask from the composite shaped part following said injecting and hardening steps to expose the decorative surface of the sheet material.