EUROPEAN PATENT SPECIFICATION

Date of publication and mention of the grant of the patent: 15.08.2007 Bulletin 2007/33

Application number: 99927375.8

Date of filing: 11.06.1999

Int Cl.: B32B 27/32 (2006.01) G09F 3/10 (2006.01) B44C 1/17 (2006.01)

International application number: PCT/US1999/012948


MULTILAYERED THERMOPLASTIC FILM AND SIGN CUTTING METHOD USING THE SAME
MEHRSCHICHTIGER THERMOPLASTISCHER FILM UND SEINE VERWENDUNG IM
SCHILDSTANZVERFAHREN
FILM THERMOPLASTIQUE MULTICOUCHES ET PROCEDE DE DECOUPE DE SIGNES UTILISANT
CELUI-CI

Designated Contracting States: BE CH DE FR GB LI LU NL

Priority: 12.06.1998 US 96984

Date of publication of application: 18.04.2001 Bulletin 2001/16

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WO-A-96/21557
US-A-5 468 532

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Description

Technical Field

[0001] This invention relates to a multilayered thermoplastic film, useful as signage films, and to a sign cutting method using the foregoing multilayered film.

Background of the Invention

[0002] Sign cutting methods wherein an image is cut from a polymer film adhered to a pressure sensitive adhesive composite and then transferred to a desired substrate are known. This technique is used to provide a wide variety of signage applications including exterior identification signs as well as decorative or commercial graphics on trucks, cars, boats, and the like. The polymer film that is typically used with these graphic applications is a calendered or dispersion cast polyvinyl chloride (PVC) monolayer film. While the use of these PVC films have met with success in the marketplace, they have also been found to be not entirely acceptable. Neither the PVC films nor the processes for making such films are environmentally friendly. Many of the PVC films employ plasticizers that migrate into the adhesive and degrade the functionality of the adhesive composite. Plasticizer migration is also considered to be related to objectionable spotty film appearance, sometimes referred to as mottle. This problem is especially troublesome in warm weather climates. Many of the processes for making the PVC films are costly. The present invention, which relates to a novel multilayered film structure and to a sign cutting method using the same, overcomes these problems.

[0003] U.S. Patent 4,946,532 discloses composite facestocks and liners made of multilayer polymeric films. The multilayer film is comprised of a coextrudate containing a core or base layer and skin layers overlying each side of the core layer. The core layer contains a filler material.

[0004] U.S. Patent 5,435,963 discloses an oriented polymeric in-mold label film that includes a hot-stretched, annealed, linerless self-wound film lamina. The film is disclosed as having a face layer for printing, a central layer, and a base layer which includes a heat-activatable adhesive. The working examples disclose a label film with the face layer disclosed as being a mixture of an ethylene/vinyl acetate copolymer and a polypropylene homopolymer. The central layer is disclosed as being a mixture of an ethylene/vinyl acetate copolymer, either polypropylene homopolymer or a random polypropylene copolymer, and optionally a titanium dioxide concentrate. The base layer is disclosed as being a mixture of an ethylene/vinyl acetate copolymer, either a polypropylene homopolymer or a low density polyethylene, and optionally a heat-activatable adhesive and an antistat.

Summary of the Invention

[0005] In one aspect, the invention relates to a multilayered thermoplastic film, comprising at least one polyolefin core layer having a first side and a second side, wherein the core layer comprises a polyolefin having a density in the range of 0.89 to 0.97 grams per cubic centimeter and a second thermoplastic material selected from ionomers derived from sodium, lithium or zinc and an ethylene/unsaturated carboxylic acid or anhydride copolymer; at least one abrasion resistant first thermoplastic skin layer overlying the first side of the core layer, and at least one second thermoplastic skin layer overlying the second side of the core layer, wherein the composition of the core layer is different from the composition of the skin layers, and the core layer and the skin layers being characterized by the absence of PVC.

[0006] In another aspect, the invention relates to a sign cutting method, comprising: providing a pressure sensitive adhesive composite, the composite comprising a multilayered thermoplastic film, a layer of a pressure sensitive adhesive and a release liner;

the multilayered thermoplastic film comprising (1) a thermoplastic core layer having a first side and a second side, (2) an abrasion and scuff resistant clear first thermoplastic skin layer overlying the first side of the core layer, and (3) a clear second thermoplastic skin layer overlying the second side of the core layer, the pressure sensitive adhesive layer being positioned between the second thermoplastic skin layer and the release liner, and being preferentially adherent to the second thermoplastic skin layer;

the thermoplastic core layer comprising: (a) a polyolefin having a density in the range of 0.89 to 0.97 grams per cubic centimeter; (b) a second thermoplastic material selected from the group consisting of ethylene acrylic acid copolymers, ethylene-methacrylic acid copolymers, ionomers derived from sodium, lithium or zinc and an ethylene/methacrylic acid copolymer, or combination of two or more thereof, the second thermoplastic material being present at a concentration of 2% to 25% by weight based on the weight of the core layer, and (c) a light stabilizer at a concentration of 1,000 to 10,000 ppm based on the weight of the core layer;

the first thermoplastic skin layer comprising a light stabilizer at a concentration of 2,000 to 20,000 ppm based on the weight of the first skin layer 1;

the second thermoplastic skin layer comprising a light stabilizer at a concentration of 1,000 to 15,000 ppm based on the
weight of the second skin layer;
the composition of the core layer and the skin layers being different, and the core layer and the skin layers being
characterized by the absence of PVC;
cutting an image in the multilayered thermoplastic film; and transferring the image to a substrate.

Brief Description of the Drawings

[0007] In the annexed drawings, like references indicate like parts or features:

Fig. 1 is a schematic illustration of the side view of a multilayered thermoplastic film embodying the present invention in a particular form, the film comprising a thermoplastic core layer having a first side and second side, an abrasion resistant first thermoplastic skin layer overlying the first side of the core layer, and a second thermoplastic skin layer overlying the second side of the core layer.

Fig. 2 is a schematic illustration of the side view of a multilayered thermoplastic film embodying the present invention in another particular form, the film comprising a thermoplastic core layer having a first side and a second side, an abrasion resistant first thermoplastic skin layer overlying the first side of core layer, an intermediate layer overlying the second side of the core layer, and a second thermoplastic skin layer overlying the intermediate layer.

Fig. 3 is a flow sheet illustrating an extrusion process for making the multilayered thermoplastic film illustrated in Fig. 1.

Fig. 4 is a flow sheet illustrating an extrusion process for making the multilayered thermoplastic film illustrated in Fig. 2.

Fig. 5 is a schematic illustration of the side view of a pressure sensitive adhesive composite embodying the present invention in a particular form, the composite comprising a thermoplastic core layer having a first side and a second side, an abrasion resistant first thermoplastic skin layer overlying the first side of the core layer, a second thermoplastic skin layer overlying the second side of the core layer, a layer of a pressure sensitive adhesive overlying the second skin layer, a layer of a release coating overlying the pressure sensitive adhesive, and a backing liner overlying the release coating layer.

Fig. 6 is a schematic illustration of the side view of a pressure sensitive adhesive composite embodying the present invention in another particular form, the composite comprising a thermoplastic core layer having a first side and a second side, an abrasion resistant first thermoplastic skin layer overlying the first side of the core layer, an intermediate layer overlying the second side of the core layer, a second thermoplastic skin layer overlying the intermediate layer, a layer of a pressure sensitive adhesive overlying the second skin layer, a layer of a release coating overlying the pressure sensitive adhesive, and a backing liner overlying the release coating layer.

Fig. 7 is a flow sheet illustrating the inventive sign cutting method in a particular form.

Description of the Preferred Embodiments

[0008] The present invention relates to signage films and multilayer thermoplastic films as described above.

[0009] In one preferred embodiment, the first skin layer is clear.

[0010] In another preferred embodiment, the second skin layer is clear.

[0011] In yet another preferred embodiment, the core layer further comprises at least one third polymeric material selected from ethylene/vinyl acetate copolymers, acid-modified ethylene acrylate polymers, anhydride-modified ethylene acrylate copolymers, anhydride-modified ethylene/vinyl acetate copolymers, acid and acrylate-modified ethylene/vinyl acetate resins, anhydride-modified ethylene/vinyl acetate resins, anhydride-modified high density polyethylene resins, anhydride-modified linear low density polyethylene resins, anhydride modified low density polyethylene resins and anhydride modified polypropylene resins, and combinations thereof.

[0012] In another preferred embodiment, the second thermoplastic material is present at a concentration of 2% to 25% by weight based on the weight of the core layer.

[0013] In yet another preferred embodiment, the core comprises a light stabilizer at a concentration of 1,000 to 10,000 ppm based on the weight of the core layer.

[0014] In another preferred embodiment, the first skin layer is comprised of an ionomer derived from sodium, lithium or zinc and an ethylene/unsaturated carboxylic acid copolymer.

[0015] In yet another preferred embodiment, the polyolefin has a density in the range of 0.89 to 0.97 grams per cubic centimeter; and wherein the core layer further comprises a third polymeric material selected from ethylene/vinyl acetate copolymers, acid-modified ethylene acrylate polymers, anhydride-modified ethylene acrylate copolymers, anhydride-modified ethylene/vinyl acetate copolymers, acid and acrylate-modified ethylene/vinyl acetate resins, anhydride-modified ethylene/vinyl acetate resins, anhydride-modified high density polyethylene resins, anhydride-modified linear low density polyethylene resins, anhydride modified low density polyethylene resins and anhydride modified polypropylene resins and combinations thereof, wherein the second thermoplastic material is present at a concentration of 2% to 25% by weight based on the weight of the core layer, and a light stabilizer at a concentration of 1,000 to 10,000 ppm based on
the weight of the core layer;
and wherein the abrasion resistant first thermoplastic skin layer is scuff resistant and clear and comprises a light stabilizer 
at a concentration of 2,000 to 20,000 ppm based on the weight of the first skin layer; and 
the second thermoplastic skin layer is clear and comprises a light stabilizer at a concentration of 1,000 to 15,000 ppm 
based on the weight of the second skin layer.

[0016] In another preferred embodiment, an intermediate layer is positioned between the core layer and the second 
thermoplastic skin layer, the supplemental core intermediate layer being characterized by the absence of PVC.

[0017] In yet another preferred embodiment, a clear topcoat layer overlies the first thermoplastic skin layer, the clear 
topcoat layer being characterized by the absence of PVC.

[0018] In another preferred embodiment, a layer of a pressure sensitive adhesive overlies the second thermoplastic 
skin layer.

[0019] In yet another preferred embodiment, the pressure sensitive adhesive layer comprises a rubber based adhesive, 
acrylic adhesive, vinyl ether adhesive, silicone adhesive or combination of two or more thereof.

[0020] In another preferred embodiment, a release liner overlies the layer of pressure sensitive adhesive.

[0021] In yet another preferred embodiment, the release liner is comprised of a release coating composition overlying a 
backing liner, the backing liner is comprised of paper, polymeric film or a combination thereof.

[0022] In another preferred embodiment, the release liner is comprised of a release coating composition overlying a 
backing liner, the release coating composition is a silicone release coating composition.

[0023] In yet another preferred embodiment, the release liner is comprised of a release coating composition overlying a 
backing liner, the release coating composition comprising a polyorganosiloxane.

[0024] In another preferred embodiment, each of the skin layers have the same composition.

[0025] In yet another preferred embodiment, the skin layers have different compositions.

[0026] In another preferred embodiment, the core layer and the skin layers comprise a coextrudate.

[0027] In yet another preferred embodiment, the first skin layer is comprised of an ionomer derived from sodium, 
lithium or zinc and an ethylene/methacrylic acid copolymer.

[0028] In another preferred embodiment, the core layer is pigmented.

[0029] In yet another preferred embodiment, the core layer is clear.

[0030] In another preferred embodiment, the overall thickness of the multilayered thermoplastic film is from 1 to 10 
mils, the thickness of the core layer is from 10% to 90% of the overall thickness.

[0031] In yet another preferred embodiment, the core layer further comprises an adhesive material.

[0032] In one preferred embodiment at least one of the skin layers further comprises an adhesive material, antblock 
agent, slip additive, or combination of two or more thereof.

[0033] In another preferred embodiment, the film is an electronic cutting film, and wherein said at least one second 
thermoplastic skin layer comprises an adhesive priming layer disposed over the second side of the core layer.

[0034] The films are characterized as having a core layer which is composed of at least one polyolefin. In another 
preferred embodiment, the core layer further comprises one or more of a light stabilizer, a pigment, one or more other ther-
mosplastic polymers or processing additives, the details of which are discussed below. The films of the present invention 
also include at least one skin layer on the core. The skin layers may be directly in contact with the core or may be 
atached to the core through tie or intermediate layers. At least one skin layer is abrasive resistant. In one aspect, the 
abrasive resistant layer is the first skin layer and may be clear or pigmented, preferably clear. This layer may be prepared 
from blends of polymers and include one or more of light stabilizers, pigments or processing chemicals, the details of 
which are described herein. The second skin may be clear or pigmented. The second skin may be prepared from a 
blend of polymers and may also include one or more of light stabilizers, processing chemicals or pigments, which are 
described herein. The multilayer film may be oriented or unoriented, preferably unoriented. The skin and core may be 
individually oriented or unoriented, preferably unoriented. The material used to make the films of the present invention 
are selected to provide the physical characteristics necessary for signage. In other words, the materials must provide 
effective physical characteristics to provide the needed strength to withstand the cutting process and weatherability for 
sign applications.

[0035] In a preferred embodiment, the inventive multilayered films are characterized by a combination of features.

These include the composition of the core layer being characterized by the combination of a polyolefin having a density 
in the range of about 0.89 to about 0.97 grams per cubic centimeter, and in a most preferred embodiment, a second 
thermoplastic material selected from ionomers derived from sodium, lithium or zinc and an ethylene/unsaturated 
carboxylic acid or anhydride copolymer, such as an ethylene/methacrylic acid copolymer, and combinations thereof, 
the concentration of the second thermoplastic material being from about 1% to about 25% preferably from about 2% to about 
10% by weight based on the weight of the core layer. Unexpectedly, this combination of polyolefin and a second ther-
mosplastic material significantly improves the appearance of the film. This combination is particularly advantageous when 
dark colors (e.g., dark blue, black, etc.) are desired. For example, a film with a charcoal gray appearance is produced 
when only the polyolefin is used, but when the polyolefin is combined with the second thermoplastic material as indicated
above, a deep black color is achieved. It is recognized that the polymer blend is useful in some applications where color is important to the end-user, there are some applications where this is not the case, and the composition of the core need not be a copolymer blend.

In one preferred embodiment, the core layer and each of the skin layers are characterized by relatively high concentrations of light stabilizers. In this regard, the core layer has a light stabilizer concentration of about 1,000 to about 10,000 ppm or from about 2500 to about 8000, the first skin layer has a light stabilizer concentration of about 2,000 to about 20,000 ppm or from about 5000 to about 16,000, and the second skin layer has a light stabilizer concentration of about 1,000 to 15,000, from about 3,000 to about 12,000 ppm. The use of such high levels of light stabilizers provides the inventive multilayered films with outdoor weatherability properties comparable to and in some instances superior to those of the PVE films used in the prior art.

In a most preferred embodiment, the skin layers are clear. This enhances the economics of using the inventive multilayered film when the core layer is pigmented due to the fact that the time involved with changing from one color to another during extrusion of the multilayered film is significantly reduced. While not wishing to be bound by theory, it is believed that this advantage is realized because pigment in extruded polymer compositions tends to adhere to the internal metal parts of the extruder die and other extrusion apparatus downstream of the extruder, and the use of the clear skin layers of the invention prevents or limits contact between the pigmented core layer and the internal metal parts of the foregoing extrusion equipment.

The first skin layer and optionally the second skin layer, of the inventive multilayered film is characterized by the use of an abrasion and scuff resistant polymer. This feature not only provides the inventive multilayered film with enhanced abrasion and scuff resistance properties, but also provides the film with excellent sign cutting and weeding properties.

The inventive multilayered film is characterized by the absence of PVC. The overall composition of the core layer is different than the overall composition of the skin layers.

The inventors have found that the foregoing combination of features provides the inventive multilayered films with properties that make them equivalent to or superior to the PVC films used in the prior art, and yet allows for the use of films that avoid the problems involved with the use of such PVC films.

Useful embodiments of the inventive multilayered film are depicted in Figs. 1 and 2. Referring to Fig. 1, multilayered film 12 has a thermoplastic core layer 16, which has a first side and a second side, an abrasion and scuff resistant clear first thermoplastic skin layer 48 overlying the first side of the core layer 16, and a clear second thermoplastic skin layer 20 overlying the second side of the core layer 16. Skins 18 and 20 may also be pigmented.

Referring to Fig. 2, multilayered film 12A has a thermoplastic core layer 16, which has a first side and a second side, an intermediate layer 17 overlying to the second side of the core layer 16, an abrasion and scuff resistant clear first thermoplastic skin layer 48 overlying the first side of the core layer 16, and a clear second thermoplastic skin layer 20 overlying the intermediate layer 17. Skins 18 and 20 may also be pigmented. The intermediate layer may be a stiffening layer. The stiffening layer is composed of a thermoplastic polymer, such as the polyolefin described herein (e.g. polyethylene, polypropylene, or an ethylene, propylene copolymer). The intermediate layer may be an adhesive layer as well. The intermediate layer may be composed of reground core polymers which include pigments. As an alternative, the intermediate layer may also be an opacifying layer. The opacifying layer contains materials which increase the opacity of the multilayer film.

The core layer 16 is comprised of a blend of a thermoplastic polymer with a second thermoplastic material. The core may also be composed of a thermoplastic polymer, a second thermoplastic material and an adhesive. Of course it is understood that the core may have other processing components and stabilizing components as is discussed below.

This combination is comprised of a polyolefin having a density in the range of about 0.89 to about 0.97 g/cc, and a preferred embodiment about 0.915 to about 0.97 g/cc, and in another preferred embodiment about 0.926 to about 0.945 g/cc. The core includes a second thermoplastic material selected from ionomers derived from sodium, lithium or zinc and ethylene-unsaturated carboxylic acid or anhydride copolymer, such as ethylene/methacrylic acid copolymers, and combinations of two or more thereof. The concentration of the second thermoplastic material is critical and is in the range of about 2% to about 25% by weight based on the weight of the core layer 16. In one preferred embodiment, the concentration of the second thermoplastic material is from about 2% to about 22% by weight, and in a preferred embodiment about 3% to about 20% by weight, and in another preferred embodiment about 3% to about 10% by weight based on the weight of the core layer 16. The combined weight of the polyolefin and second thermoplastic material is at least about 60% by weight based on the weight of the core layer 16, and in one preferred embodiment about 60% to about 95% by weight, and in another preferred embodiment about 70% to about 95% by weight based on the weight of the core layer 16.

The polyolefins that are useful in the core include polyethylene, polypropylene or polybutylene or copolymers of ethylene, propylene or butylene with an alpha olefin. The alpha olefin, is selected from those alpha olefins containing from 3 to about 18 carbon atoms, and in one embodiment 2 to about 12 carbon atoms, and in one embodiment, 3 to
about 8 carbon atoms, including propylene, ethylene, butene, butylene, hexene, 4-methylpentene and octene. The polyolefin core may be made by a blend of polyolefins such as a polyethylene and an ethylene propylene copolymer. Medium density polyolefins and the linear medium density polyolefins are useful. Useful polyolefins include those prepared using a Ziegler-Natta catalyst or a metallocene catalyst. An example of a useful polyolefin is available from Huntsman Products under the trade designation 1080, which is identified as a polyethylene having a density of 0.93 g/cc. Affinity 1030HF, which is a product of Dow Chemical identified as a metallocene catalyst catalyzed octene-ethylene copolymer can also be used. Dowlex 2036A which is a product of Dow identified as linear medium density polyethylene can be used. Quantum 285-003, which is a product of Millenium Petrochemical identified as a polyethylene resin having a density of 0.93 grams per cubic centimeter can be used.

[0046] As described above, the core layer includes a second thermoplastic material selected from ionomers derived from sodium, lithium or zinc and ethylene/unsaturated carboxylic acid or anhydride copolymers, and combinations of two or more thereof. The ionomer resins available from DuPont under the tradename Surlyn can be used. These resins are identified as being derived from sodium, lithium or zinc and copolymers of ethylene and methacrylic acid. Included in this group are the sodium containing ionomers available under the Surlyn name and the following designations: 1601, 1605, 1707, 1802, 1901, AD-8548, 8020, 8140, 8528, 8550, 8660, 8920 and 8940. Also included are the zinc containing ionomers available under the Surlyn name and following designations: 1650, 1652, 1702, 1705-1, 1855, 1857, AD-8547, 9120, 9650, 9730, 9910, 9950 and 9970. The lithium containing ionomers available under the Surlyn name and the following designations are also useful; AD-8546. 7930 and 7940.

[0047] The ethylene/methacrylic acid copolymers that are useful include those available from DuPont under the tradename Nucrel. These include Nucrel 0407, which has a methacrylic acid content of 4% by weight and a melting point of 109°C, and Nucrel 0910, which has a methacrylic acid content of 8.7% by weight and a melting point of 100°C.

[0048] The ethylene/acrylic acid copolymers that are useful include those available from Dow Chemical under the tradename Primacor. These include Primacor 1430, which has an acrylic acid monomer content of 9.5% by weight and a melting point of 97°C.

[0049] The core layer 16 can be pigmented or it can be clear. A clear core layer is one that can be seen through. Preferably, the core layer is pigmented. The pigment can be a metallic pigment, heavy metal-based pigment a heavy-metal free pigment, or an organic pigment A heavy metal is defined herein as being lead, cadmium, chromium, or antimony. The pigments that can be used include titanium dioxide, both rutile and anatase crystal structure. The titanium dioxide may be coated or uncoated (e.g. aluminum oxide coated TiO₂).

[0050] In one preferred embodiment, the pigment is added to the core layer material in the form of a concentrate containing the pigment and a resin carrier. The concentrate may contain, for example, about 20% to about 80% by weight pigment, and about 20% to about 80% by weight resin carrier. The resin carrier can be any thermoplastic polymer having a melting point in the range of about 100°C in about 175°C. Examples include polyethylene, polypropylene, polybutylene, and the like. In one preferred embodiment, a titanium dioxide concentrate is used which is comprised of a blend of about 30% to about 70% by weight polypropylene and about 70% to about 30% by weight titanium dioxide. An example of a commercially available pigment concentrate that can be used is available from A. Schulman Inc. under the tradename Polybatch White P8555 SD, which is identified as a white color concentrate having a coated rutile titanium dioxide concentration of 50% by weight in a polypropylene homopolymer carrier resin. Ampacet 150380, which is a product of Ampacel Corporation identified as a red pigment concentrate, can be used. Ampacet 190303, which is a product of Ampacel Corporation identified as a black pigment concentrate, can be used. Ampacet LR-87132 Orange PE MB, which is a product of Ampacel Corporation identified as a lead molybdate/lead chromate pigment concentrate, can be used. The heavy-metal free pigment concentrates that can be used include Ampacet LR-86813 Yellow UV PE MB, Ampacet LR-86810 Red PE MB. Ampacet LR-86816 Orange PE MB, and Ampacet LR-86789 Red UV PE MB. The concentration of pigment in the core layer can be up to about 25% by weight, and in one preferred embodiment about 5% to about 25% by weight, and in another preferred embodiment about 10% to about 20% by weight.

[0051] As indicated above, the multilayered film 12 or 12A is useful in sign applications and a critical feature of this invention is that the skin layer 18 be abrasion and scuff resistant. Also, in one preferred embodiment, the skin layer 20 is abrasion and scuff resistant. The type of abrading and scuffing that is of concern is the abrading and scuffing that occurs when the film is applied to a substrate. In one preferred embodiment of the invention, the film is applied to with a rubber or plastic applicator which is rubbed against the film surface to smooth out the edges or remove air bubbles trapped between the film and substrate. The air is squeezed out from underneath the film by forcing the bubble of air to the edge. This tends to abrade and/or scuff the film surface leaving an objectionable appearance. Abrasion and scuff resistance can be measured using ASTM D4060-84. For purposes of this invention, a film surface that is "abrasion and scuff resistant" is a film surface that has a 60° gloss reduction of 20 points or less when tested in accordance with ASTM D4060-84 using a No. CS-10 wheel and a 250 gram load after 5 cycles of rotation.

[0052] The skin layer 18 may be clear or pigmented, preferably clear. The term "clear" is used herein to refer to the fact that the skin layer 18 can be seen through. "Clear" films are those through which graphics may be read. These include matte and transparent films. When pigmented, the skin layer may contain one or more of the pigments described
hindered amine light stabilizers may, for example, be derivatives of 2,2,6,6-tetramethyl piperidines or substituted piperizinediones. A number of hindered amine light stabilizers useful in the invention are available commercially such as ultraviolet (UV) light absorbers and/or other light stabilizers. These additives are included to provide the inventive core layer 16 and skin layers 18 and 20 may contain relatively high concentrations of light stabilizers such as ultraviolet (UV) light absorbers and/or other light stabilizers. These additives are included to provide the inventive
hydroxy ethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidine; and Chemissorb 944 which is poly[6-(1,1,3,3-tetramethylbutyl)amino]-s-triazine-2,4-diyl[[2,2,6,6-tetramethyl-4-piperidyl]limino] hexamethylene (2,2,6,6-tetramethyl-4-piperidyl)limino]. A useful stabilizer is available under the tradename Ampacet 10561 which is a product of Ampacet identified as a UV stabilizer concentrate containing 20% by weight of a UV stabilizer and 80% by weight of a low density polyethylene carrier resin; the UV stabilizer in this product is Chemissorb 944. Useful light stabilizers are also provided in Ampacet 150380 and Ampacet 190303, both of which are pigment concentrates discussed above. Ampacet 150380 has a UV stabilizer concentration of 7.5% by weight. Ampacet 190303 has a UV stabilizer concentration of 4% by weight. The UV stabilizer in each of these products is Chemissorb 944. Ampacet LR-89933 is a grey concentrate having a UV stabilizer concentration of 4.5% by weight, the UV stabilizer being Tinuvin 783.

[0057] The skin layers 18 and 20 may contain antiblock and/or slip additives. These additives reduce the tendency of the film to stick together when it is in roll form. The antiblock additives include natural silica, diatomaceous earth, synthetic silica, glass spheres, ceramic particles, etc. The slip additives include primary amides such as stearamide, behenamide, oleamide, erucamide, and the like; secondary amides such as stearyl erucamide, erucyl erucamide, oleyl palmitamide, stearyl stearamide, erucyl stearamide, and the like; ethylene bisamides such as N,N’-ethylenebisstearamide, N,N’-ethylenebisolamide and the like; and combinations of any two or more of the foregoing amides. An example of a useful slip additive is available from Ampacet under the tradename 10061; this product is identified as a concentrate containing 6% by weight of a stearamide slip additive. The antiblock and slip additives may be added together in the form of a resin concentrate. An example of such a concentrate is available from DuPont under the tradename Elvax CE9619-1. This resin concentrate contains 20% by weight silica, 7% by weight of an amide slip additive, and 73% by weight of Elvax 3170 (a product of DuPont identified as an ethylene/vinyl acetate copolymer having a vinyl acetate content of 18% by weight). The antiblock additive can be used at a concentration in the range of up to about 1% by weight, and in one embodiment about 0.01% to about 0.5% by weight. The slip additive can be used at a concentration in the range of up to about 1% by weight, and in one preferred embodiment about 0.01% to about 0.5% by weight.

[0058] Another use for slip additives is to impart scuff resistance to the top skin layer (18) surface. Depending upon how these materials are incorporated in skin layer 18 these materials will migrate to the surface through incorporation in the body of these materials. The skin layer 18 can be applied to the top. The slip can be incorporated in skin layer 18 by polyethylene concentrate form or by direct feeding of these additives through ports in the skin extruder.

[0059] The core layer 18 may contain a minor amount of an adhesive resin to enhance the adhesion of the skin layers 18 and 20 to the core layer 18. Also, or alternatively, tie layers of an adhesive resin can be positioned between the core layer 16 and either or both of the skin layers 18 and 20 for enhancing adhesion. The adhesive resin can be an ethylene/vinyl acetate copolymer. These include the ethylene/vinyl acetate copolymers available from DuPont under the trade designation Elvax. Examples include Elvax 3170 and 3190LG. The adhesive resins available from DuPont under the tradename Bynel can also be used. These include ethylene/vinyl acetate resins available under the trade designation Series 1100, acid-modified ethylene acrylate polymers (Series 2000), anhydride-modified ethylene acrylate copolymers (Series 2100), anhydride-modified ethylene/vinyl acetate copolymers (Series 3000), acid- and acrylate-modified ethylene/vinyl acetate resins (Series 3100), anhydride-modified ethylene/vinyl acetate copolymers (Series 3800), anhydride-modified ethylene/vinyl acetate resins (Series 3900), anhydride-modified high density polyethylene resins (Series 4000), anhydride-modified linear low density polyethylene resins (Series 4100), anhydride modified low density polyethylene resins (Series 4200), and anhydride modified polypropylene resins (Series 5000). Bynel CXA 1123 and Bynel CXA 3101 are specific examples. When included in the core layer, the adhesive resin is used at a concentration of up to about 45%, or up to about 25% by weight, and in one preferred embodiment about 1% to about 15% by weight. In another preferred embodiment, the adhesive resin is present in an amount from about 20% to about 40%, or from about 25% to about 35% by weight. When used in the form of film layers between the core layer and the skin layers; each of such preferred adhesive resin film layers has a thickness of about 5% to about 25% of the thickness of the multilayer film, and in one preferred embodiment about 10% to about 20%. In one preferred embodiment, the adhesive layer has a thickness of about 0.1 to about 0.5, or from about 0.2 to about 0.4 mil.

[0060] In one preferred embodiment, the core layer 16 and/or skin layers 18 and 20 contain an effective amount of a processing aid to facilitate extrusion. While not wishing to be bound by theory, it is believed that these processing aids have a high affinity to metal surfaces and thereby prevent or reduce the tendency of the polymer compositions being extruded from adhering to the inner walls of the extrusion equipment. This makes it easier to purge the extrusion equipment during color changeovers. These processing aids include hexafluorocarbon polymers. An example of a commercially available processing aid that can be used is Ampacet 10919 which is a product of Ampacet Corporate identified as a hexafluoro carbon polymer. The processing aids are typically used at concentrations of up to about 0.25% by weight, and in one preferred embodiment about 0.03% to about 0.15% by weight.

[0061] As indicated above, one preferred embodiment of the invention (Fig. 2) involves providing an intermediate layer 17 between the core layer 16 and the skin layer 20. The intermediate layer 17 may be comprised of the same materials as the core layer 16, skin layer 18 and skin layer 20. In one embodiment, scrap or trim material produced during the process for making these multilayered films can be recycled as the intermediate layer material. An example of a polyolefin
that can be used in the intermediate layer is the polyethylene resin supplied by Huntsman under the trade designation
1080. In one preferred embodiment, the intermediate layer 17 is pigmented so as to be white, black or gray in color.
That is, the pigments used in this intermediate layer 17 are white, black, or a suitable mixture of white and black
to provide a desired shade of gray. In this preferred embodiment, the core layer 16 may contain a colored pigment (e.g.,
red, blue, yellow, etc). This combination enhances the opacity of the inventive multilayered film and provides the film
with deeper and richer colours. With this preferred embodiment, it is of particular advantage to use heavy-metal free
pigments in both the core layer and the intermediate layer. Examples of commercially available heavy-metal free pigments
or organic pigments that can be used include Ampacet LR-86789 which is a red pigmented polyethylene resin concentrate,
Ampacet 190303 which is a black pigmented polyethylene resin concentrate. Ampacet LR-89933 which is a grey con-
centrace, and Ampacet 110235 which is a white pigmented polyethylene concentrate. The intermediate layer 17, when
used, typically has a thickness of about 5% to about 25%, and in one preferred embodiment about 10% to about 15%
of the overall thickness of the multilayered film 12A.

[0062] In one preferred embodiment, a clear topcoat layer overlies skin layer 18. A topcoat layer may be added to any
of the multilayer films described herein. The topcoat layer is applied to the first skin layer and may directly applied or
attached through one or more tie or adhesive (such as the pressure sensitive adhesive described herein) coats. The
topcoat layer is used to provide the inventive multilayered film with enhanced abrasion and scuff resistant properties
and, in one embodiment, enhanced gloss characteristics. The topcoat preferably has a thickness from about 2 to about
6, or from about 3 to about 5 microns. The topcoat layer is made from a thermoplastic polymer composition, the polymer
being an ester, urethane, epoxy, phenoxy, acrylic, or a combination of two or more thereof. The polymer can be a
radiation curable polymer, with UV curable epoxy, acrylic, ester, urethane and phenoxy resins being especially useful.
The polymer can be a heat curable resin with urethane and acrylic resins being especially useful. The polymer composition
may contain diluents (e.g., vinyl ether, limonene dioxide, epoxy oligomers, glycidyl ether), wetting agents or surfactants
which are used to provide a uniform flow resulting in an even topcoating layer, waxes, slip aids, light stabilizers, and the
like. Use of at least one of the foregoing light stabilizers discussed above is critical and any of the light stabilizers
discussed above can be used. The concentration of these light stabilizers is in the range of about 500 about 20,000
ppm, and in one preferred embodiment about 1,000 to about 12,000 ppm, and in another preferred embodiment about
2,000 to about 8,000 ppm. The thickness of the topcoat layer is generally from about 1 to about 12 microns, and in one
preferred embodiment from about 3 to about 6 microns. An example of an acrylic resin based topcoat formulation that
can be used is as follows:

<table>
<thead>
<tr>
<th>Tradename</th>
<th>Supplier</th>
<th>Description</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhoplex B15P</td>
<td>Rohm &amp; Haas</td>
<td>Acrylic Resin</td>
<td>93.9%</td>
</tr>
<tr>
<td>CX 100</td>
<td>Zeneca Resins</td>
<td>Polyaziridine Crosslinker</td>
<td>3.0%</td>
</tr>
<tr>
<td>Disperbyk 182</td>
<td>Byk Chemie</td>
<td>Wetting Agent</td>
<td>1.0%</td>
</tr>
<tr>
<td>DF-75</td>
<td>Air Products</td>
<td>Defoamer</td>
<td>0.1%</td>
</tr>
<tr>
<td>Synflow 178XF</td>
<td>Micro Powders</td>
<td>Wax/Mar Additive</td>
<td>2.0%</td>
</tr>
</tbody>
</table>

An example of an UV curable epoxy resin based topcoat formulation that can be used is as follows:

<table>
<thead>
<tr>
<th>Tradename</th>
<th>Supplier</th>
<th>Description</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyracure UVR-6110</td>
<td>Union Carbide</td>
<td>Epoxy Resin</td>
<td>83.5%</td>
</tr>
<tr>
<td>Tone 301</td>
<td>Union Carbide</td>
<td>Caprolactone Polyol</td>
<td>10.0%</td>
</tr>
<tr>
<td>Cyracure UVI-6974</td>
<td>Union Carbide</td>
<td>Photoinitiator</td>
<td>6.0%</td>
</tr>
<tr>
<td>Silivet L7604</td>
<td>OSI</td>
<td>Wetting Agent</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

An example a UV curable urethane based topcoat formulation is as follows:

<table>
<thead>
<tr>
<th>Tradename</th>
<th>Supplier</th>
<th>Description</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN 963880</td>
<td>Sartomer</td>
<td>urethane acrylate (aliphatic)</td>
<td>75%</td>
</tr>
<tr>
<td>SR 238</td>
<td>Sartomer</td>
<td>1, 6 hexanediol</td>
<td>20.5%</td>
</tr>
<tr>
<td>Irgacure 184</td>
<td>Ciba</td>
<td>photoinitiator</td>
<td>3%</td>
</tr>
<tr>
<td>Tinuvin 1130</td>
<td>Ciba</td>
<td>UV Stabilizer</td>
<td>1%</td>
</tr>
<tr>
<td>Tinuvin 123</td>
<td>Ciba</td>
<td>UV Stabilizer</td>
<td>0.5%</td>
</tr>
</tbody>
</table>
In one preferred embodiment, the topcoat provides the ability to print by any method, such as with electrostatic and thermal transfer printing. The topcoat may be any of the topcoats described herein. Preferably the topcoat is a thermal plastic polyurethane. The printing topcoat is preferably applied at a coat weight of about 5 to about 9, or from about 6 to about 8 gsm. An example of a topcoat for printing is as follows:

<table>
<thead>
<tr>
<th>Tradename</th>
<th>Supplier</th>
<th>Description</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irosect 9827</td>
<td>Morton Chemical</td>
<td>thermoplastic polyurethane</td>
<td>12%</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>Methyl, Ethyl Ketone</td>
<td>38%</td>
</tr>
<tr>
<td>Irganox 1010</td>
<td>Ciba</td>
<td>Antioxidant</td>
<td>0.25%</td>
</tr>
<tr>
<td>Tinuvin 292</td>
<td>Ciba</td>
<td>UV Stabilizer</td>
<td>0.125%</td>
</tr>
<tr>
<td>Tinuvin 328</td>
<td>Ciba</td>
<td>UV Stabilizer</td>
<td>0.125%</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>Toluene</td>
<td>25.5%</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>Isopropyl alcohol</td>
<td>24%</td>
</tr>
</tbody>
</table>

This topcoat is prepared by blending the polyurethane with the ketone to make a first blend which is then mixed with a concentrate prepared from the antioxidant and uv stabilizers. Toluene and isopropyl alcohol are added to the mixture and the mixture is filtered.

The topcoat layer can be applied to the skin layer 18 using known techniques, including multi roll coating, reverse roll coating, blade coating, air knife coating gravure coating, etc.

In one preferred embodiment, the core layer 16, intermediate layer 17, and each of the skin layers 18 and 20, and topcoat layer are characterized by the absence of polyvinyl chloride (PVC).

In another preferred embodiment, and as illustrated by Fig. 2, a multilayer film has core layer 16, abrasive resistant skin layer 18, and intermediate layer 17 which is in contact with an adhesive or adhesive skin layer 20. The core is composed of those polymers described above. In one preferred embodiment, skin layer 18 and intermediate layer 17 have the same composition. In another preferred embodiment intermediate layer 17 is a stiffness adding layer such as one or more of the above polyolefins or second thermoplastic materials described above. Intermediate layer 17, in one preferred embodiment, has a thickness of about 0.05 to about 1.5 mil, preferably from about .1 mil to about 1 mil, or from about 0.15 mil to about 0.65 mil. Applicants have discovered by the inclusion of this intermediate layer, stiffness of the film is improved.

The multilayered thermoplastic films 12 (Fig. 1) and 12A (Fig. 2) may have an overall thickness ranging from about 1 to about 10 mils, and in a preferred embodiment about 1 to about 8 mils, and in another preferred embodiment about 1 to about 5 mils, and in another preferred embodiment about 2 to about 4 mils, and in one preferred embodiment about 3 mils. The thickness of the core layer 16 may range from about 10% to about 90% of the overall thickness of the multilayered film, and in one preferred embodiment from about 20% to about 80%. In one preferred embodiment, the thickness of the skin/core/skin layers is 10%/80%/10%, and in another preferred embodiment it is 20%/60%/20%. The skin layers 18 and 20 may be of the same thickness or they may have different thicknesses. Preferably, the skin layers 18 and 20 have the same or substantially the same thickness which allows the multilayered film to lay flat and avoid curl. Similarly, each of the skin layers 18 and 20 may have the same composition or they may have different compositions.

The multilayered thermoplastic film 12 (Fig. 1) or 12A (Fig. 2) may be made using a polymeric coextrusion process. The coextrudate of polymeric film materials is formed by simultaneous extrusion from two or more extruders and a suitable known type of coextrusion die whereby the core layer 16 (and optional intermediate layer 17) and the skin layers 18 and 20 are adhered to each other in a permanently combined state to provide a unitary coextrudate. The coextrusion processes for making these multilayered films are well known in the art. Examples of such processes are depicted in Figs. 3 and 4.

Often the abrasive resistant polymer will develop a static charge during processing. This charge may collect dust on the surface which is objectionable since sign applications require a clean surface. The charge may be minimized by incorporation of an antistatic materials to the skin layer. The antistatic agents may be added as the concentrate containing 5% of the antistatic agent in a polyethylene concentrate. The concentrate is typically used at a level of 6%. The antistatic agent is typically present in an amount from about 100 ppm to about 15,000 ppm, or about 25,000 ppm to about 10,000 ppm or from about 3,000 to about 6,000 ppm. A preferred antistatic agent is glycerol monoleate. Other useful antistatic agents include alkoxylated amines or amides, such as ethoxylated amines or ethoxylated amides.

Referring to Fig. 3, an extrusion process for making the multilayered film 12 is disclosed. The apparatus used in this process includes extruders 100, 102 and 104, adapter block 106, extrusion die 108, air knife 110, casting roll 112, chill roll 114, nip rolls 116, and take up reel 118. The polymeric material for forming skin layer 18 is extruded from extruder 100 and then advanced to adapter block 106 and extrusion die 108. The polymeric material for forming core layer 16 is
extruded from extruder 102 and then advanced to adapter block 106 and extrusion die 108. The polymeric material for forming skin layer 20 is extruded from extruder 104 and then advanced to adapter block 106 and extrusion die 108. In extrusion die 108 the polymeric materials are combined to form the multilayered film 12. The multilayered film 12 is advanced from extruder 102 and then advanced to adapter block 106 and extrusion die 108. The polymeric material for forming intermediate layer 17 is extruded from extruder 103 and then advanced to adapter block 106 and extrusion die 108. The polymeric material for forming skin layer 20 is extruded from extruder 104 and then advanced to adapter block 106 and extrusion die 108. In extrusion die 108 the polymeric materials are combined to form the multilayered film 12A. The multilayered film 12A is advanced from extrusion die 108, past air knife 110, under casting roll 112, over chill roll 114, through nip rolls 116 to take-up reel 118 where it is wound to provide multilayered film 12A in roll form.

[0071] An extrusion process for making the multilayered film 12A is disclosed in Fig. 4. The apparatus used in this process includes extruders 100, 102, 103 and 104, adapter block 106, extrusion die 108, air knife 110, casting roll 112, chill roll 114, nip rolls 116, and take up reel 118. The polymeric material for forming skin layer 18 is extruded from extruder 100 and then advanced to adapter block 106 and extrusion die 108. The polymeric material for forming core layer 16 is extruded from extruder 102 and then advanced to adapter block 106 and extrusion die 108. The polymeric material for forming intermediate layer 17 is extruded from extruder 103 and then advanced to adapter block 106 and extrusion die 108. The polymeric material for forming skin layer 20 is extruded from extruder 104 and then advanced to adapter block 106 and extrusion die 108. In extrusion die 108 the polymeric materials are combined to form the multilayered film 12A. The multilayered film 12A is advanced from extrusion die 108, past air knife 110, under casting roll 112, over chill roll 114, through nip rolls 116 to take-up reel 118 where it is wound to provide multilayered film 12A in roll form.

[0072] An advantage of the present invention is that the multilayered films 12 and 12A that are employed are easy to process. The presence of the clear skin layers 18 and 20 allows for easy purging and changing of colors during extrusion. These multilayered films sign cut and weed well. They have excellent scuff and abrasion resistant characteristics. They have excellent outdoor weatherability characteristics.

The Pressure Sensitive Adhesive Composite

[0073] In one preferred embodiment, the inventive multilayer thermoplastic film is provided as part of a pressure sensitive adhesive composite wherein the multilayered thermoplastic film has a pressure sensitive adhesive laminate adhered to it. The pressure sensitive adhesive laminate is comprised of a layer of a pressure sensitive adhesive adhered to a release liner. The release liner is comprised of a backing liner and a layer of a cured release coating layer adhered to the backing liner. The release coating is positioned between the pressure sensitive adhesive and the backing liner. The pressure sensitive adhesive layer is positioned between the second skin layer of the multilayered thermoplastic film and the release coating layer and is preferentially adherent to the second skin layer. Useful embodiments are depicted in Figs. 5 and 6.

[0074] Referring to Fig. 5, a pressure sensitive adhesive composite 10 is disclosed which includes multilayered thermoplastic film 12 and a pressure sensitive adhesive laminate 14. The multilayered film 12 has thermoplastic core layer 16, which has a first side and a second side, an abrasion resistant clear first thermoplastic skin layer 18 overlying the first side of the core layer 16 and second clear thermoplastic skin layer 20 overlying the second side of the core layer 16. The adhesive laminate 14 has a layer of a pressure sensitive adhesive 30 adhered to the skin layer 20. A layer of the release coating 32 overlying and adhered to the pressure sensitive adhesive 30, and the backing liner 34 overlying the release coating layer 32. The release coating layer 32 and backing liner 34 combine to form release liner 35.

[0075] Referring to Fig. 6, a pressure sensitive adhesive composite 10A is disclosed which includes a multilayered thermoplastic film 12A and a pressure sensitive adhesive laminate 14. The multilayered film 12A has thermoplastic core layer 16, which has a first side and a second side, intermediate layer 17 overlying and adhered to the second side of the core layer 16, abrasion resistant clear first thermoplastic skin layer 18 overlying the first side of the core layer 16, and clear second thermoplastic skin layer 20 overlying the intermediate layer 17. The adhesive laminate 14 has a layer of a pressure sensitive adhesive 30 adhered to the skin layer 20, a layer of a release coating 32 overlying and adhered to the pressure sensitive adhesive 30, and a backing liner 34 overlying the release coating layer 32. The release coating layer 32 and backing liner 34 combine to form release liner 35.

[0076] The release coating composition 32 can be any release coating composition known in the art. Silicone release coating compositions are preferred, and any of the silicone release coating compositions which are known in the art can be used. The major component of the silicone release coating is a polyorganosiloxane and more often polydimethylsiloxane. The silicone release coating compositions used in this invention may be room temperature cured, thermally cured, or radiation cured. Generally, the room temperature and thermally curable compositions comprise at least one polyorganosiloxane and at least one catalyst (or curing agent) for such polyorganosiloxane(s). Such compositions may also contain at least one cure accelerator and/or adhesivity promoter. As is known in the art, some materials have the capability of performing both functions, i.e., the capability of acting as a cure accelerator to increase the rate, reduce the curing temperature, etc., and also as an adhesivity promoter to improve bonding of the silicone composition to the substrate. The use of such dual function additives where appropriate is within the purview of the invention.

[0077] The release coating composition 32 is applied to the backing liner 34 using known techniques. These include gravure, reverse gravure, offset gravure, roller coating, brushing, knife-over roll, metering rod, reverse roll coating, doctor knife, dipping, die coating, spraying curtain coating, and the like. The coat weight is in the range of about 0.1 to about
The backing liner 34 may comprise paper, polymer film, or a combination thereof. Paper liners are useful because of the wide variety of applications in which they can be employed. Paper is also relatively inexpensive and has desirable properties such as antiblocking, antistatic, dimensional stability, and can potentially be recycled. Any type of paper having sufficient tensile strength to be handled in conventional paper coating and treating apparatus can be employed as the substrate material. Thus, any type of paper can be used depending upon the end use and particular personal preferences. Included among the types of paper which can be used are clay coated paper, glassine, polymer coated paper, hemp, and similar cellulose materials prepared by such processes as the soda, sulfite or sulfate (Kraft) processes, the neutral sulfide cooking process, alkali-chlorine processes, nitric acid processes, semi-chemical processes, etc. Although paper of any weight can be employed as a substrate material, paper having weights in the range of from about 30 to about 120 pounds per ream are useful, and papers having weights in the range of from about 60 to about 100 pounds per ream are presently preferred. The term "ream" as used herein equals 3000 square feet.

Alternatively, the backing liner 34 may be a polymer film, and examples of polymer films include polyolefin, polyester, and combinations thereof. The polyolefin films may comprise polymer and copolymers of monoolefins having from 2 to about 12 carbon atoms, and in one embodiment from 2 to about 8 carbon atoms, and in one preferred embodiment 2 to about 4 carbon atoms per molecule. Examples of such homopolymers include polyethylene, polypropylene, poly-1-butene, etc. The examples of copolymers within the above definition include copolymers of ethylene with from about 1% to about 10% by weight of propylene, copolymers of propylene with about 1% to about 10% by weight of ethylene or 1-butene, etc. Films prepared from blends of copolymers or blends of copolymers with homopolymers also are useful. The films may be extruded in mono or multilayers.

Another type of material which can be used as the backing liner 34 is a polycoated kraft liner which is basically comprised of a kraft liner that is coated on either one or both sides with a polymer coating. The polymer coating, which can be comprised of high, medium, or low density polyethylene, propylene, polyester, and other similar polymer films, is coated onto the substrate surface to add strength and/or dimensional stability to the liner. The weight of these types of liners ranges from about 30 to about 100 pounds per ream, with about 94 to about 100 pounds per ream representing a typical range. In total, the final liner is comprised of between 10% and 40% polymer and from 60% to 90% paper. For two sided coatings, the quantity of polymer is approximately evenly divided between the top and bottom surface of the paper.

The pressure-sensitive adhesive 30 can be any pressure sensitive adhesive known in the art. These include rubber based adhesives, acrylic adhesives, vinyl ether adhesives, silicone adhesives, and mixtures of two or more thereof. Included are the pressure sensitive adhesive materials described in "Adhesion and Bonding", Encyclopedia of Polymer Science and Engineering, Vol. 1, pages 476-546, Interscience Publishers, 2nd Ed 1985, the disclosure of which is hereby incorporated by reference. The pressure sensitive adhesive materials that are useful may contain as a major constituent an adhesive polymer such as acrylic type polymers, block copolymers, natural, reclaimed or styrene butadiene rubbers, tackified natural or synthetic rubbers, random copolymers of ethylene and vinyl acetate, ethylene-vinyl-acrylic terpolymers, polyisobutylene, poly(vinyl ether), etc. The pressure sensitive adhesive materials are typically characterized by glass transition temperatures in the range of about -70°C to about 10°C.

Other materials in addition to the foregoing resins may be included in the pressure sensitive adhesive materials. These include solid tackifying resins, liquid tackifiers (often referred to as plasticizers), antioxidants, fillers, pigments, waxes, etc. The adhesive materials may contain a blend of solid tackifying resins and liquid tackifying resins (or liquid plasticizers).

The layer of pressure sensitive adhesive 30 generally has a thickness of about 0.2 to about 2.5 mils, and in one embodiment about 0.5 to about 1.5 mils. In one preferred embodiment, the coat weight of the pressure sensitive adhesive is in the range of about 10 to about 50 grams per square meter (gsm), and in one embodiment about 20 to about 35 gsm.

The pressure sensitive adhesive 30 can be applied to the skin layer 20 of the multilayered film, or to the cured release coating layer 32 of the release liner 35 using known techniques. These include gravure, reverse gravure, offset gravure, roller coating, brushing, knife-over roll, metering rod, reverse roll coating, doctor knife, dipping, die coating, spraying, curtain coating, and the like. When the adhesive 30 is applied to the multilayered thermoplastic film 12 or 12A, the pressure sensitive adhesive composite 10 or 10A is assembled by contacting the release liner 35 and the adhesive 30 using known techniques. When the adhesive 30 is applied to the release liner 35, the pressure sensitive adhesive composite 10 or 10A is assembled by contacting the multilayered thermoplastic film 12 or 12A and the adhesive 30 using known techniques. In the assemblage pressure sensitive adhesive composite 10 or 10A, the pressure sensitive adhesive 30 is positioned between the multilayered thermoplastic film 12 or 12A and the cured release coating 32, and is preferentially adhered to the multilayered thermoplastic film 12 or 12A. The cured release coating 32 is positioned between the pressure sensitive adhesive 30 and the backing liner 34, and is preferentially adhered to the backing liner 34.
In one embodiment, the pressure sensitive adhesive composite 10 or 10A has a thickness in the range of about 5 to about 25 mils, and in one embodiment about 8 to about 20 mils.

The following examples are provided to further disclose the invention. In these examples as well as throughout the specification and in the claims, unless otherwise indicated, all parts and percentages are by weight.

### Example 1

The multilayered film 12 comprised of core layer 16 and skin layers 18 and 20 is coextruded. The core layer 16 has the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huntsman 1080</td>
<td>83%</td>
</tr>
<tr>
<td>Ampacet Black 190303</td>
<td>12%</td>
</tr>
<tr>
<td>Surlyn 1605</td>
<td>3%</td>
</tr>
<tr>
<td>Ampacet 10919</td>
<td>2%</td>
</tr>
</tbody>
</table>

Core layer 16 has a UV light stabilizer concentration of 4,800 ppm which is provided with the Ampacet Black 190303. The UV light stabilizer is Chemisorb 944. Skin layer 18 has the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surlyn 1605</td>
<td>93%</td>
</tr>
<tr>
<td>Ampacet 10561</td>
<td>7%</td>
</tr>
</tbody>
</table>

Skin layer 18 has a UV light stabilizer concentration of 14,000 ppm which is provided with the Ampacet 10561. Skin layer 20 has the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huntsman 1080</td>
<td>95%</td>
</tr>
<tr>
<td>Ampacet 10561</td>
<td>3%</td>
</tr>
<tr>
<td>Ampacet 10919</td>
<td>2%</td>
</tr>
</tbody>
</table>

Skin layer 20 has a UV light stabilizer concentration of 6,000 ppm which is provided by the Ampacet 10561.

### Example 2

The multilayered film 12 comprised of core layer 16 and skin layers 18 and 20 is coextruded. Core layer 16 has the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dowlex 2036A</td>
<td>77%</td>
</tr>
<tr>
<td>Ampacet Black 190303</td>
<td>10%</td>
</tr>
<tr>
<td>Quantum 285-003</td>
<td>10%</td>
</tr>
<tr>
<td>Surlyn 1605</td>
<td>3%</td>
</tr>
</tbody>
</table>

Core layer 16 has a UV light stabilizer concentration of 4,000 ppm which is provided by the Ampacet Black 190303. The UV light stabilizer is Chemisorb 944. Each of the skin layers 18 and 20 have the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surlyn 1605</td>
<td>91%</td>
</tr>
<tr>
<td>Ampacet 10561</td>
<td>5%</td>
</tr>
<tr>
<td>Ampacet 10061</td>
<td>4%</td>
</tr>
</tbody>
</table>

Each of the skin layers 18 and 20 has a UV light stabilizer concentration of 10,000 ppm which is provided by the Ampacet 10561.

### Example 3

The multilayered film 12, which is comprised of core layer 16 having a thickness of 2.4 mils, skin layer 18 having a thickness of 0.3 mil, and skin layer 20 having a thickness of 0.3 mil, is coextruded. The core layer 16 has the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huntsman 1080</td>
<td>83%</td>
</tr>
<tr>
<td>Ampacet Black 190303</td>
<td>12%</td>
</tr>
<tr>
<td>Surlyn 1605</td>
<td>3%</td>
</tr>
<tr>
<td>Ampacet 10919</td>
<td>2%</td>
</tr>
</tbody>
</table>

77% Dowlex 2036A
10% Ampacet Black 190303
10% Quantum 285-003
3% Surlyn 1605

Core layer 16 has a UV light stabilizer concentration of 4,000 ppm which is provided by the Ampacet Black 190303. The UV light stabilizer is Chemisorb 944. Each of the skin layers 18 and 20 have the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surlyn 1605</td>
<td>91%</td>
</tr>
<tr>
<td>Ampacet 10561</td>
<td>5%</td>
</tr>
<tr>
<td>Ampacet 10061</td>
<td>4%</td>
</tr>
</tbody>
</table>

Each of the skin layers 18 and 20 has a UV light stabilizer concentration of 10,000 ppm which is provided by the Ampacet 10561.
composition:

- Core layer 16 has a UV light stabilizer concentration of 4,800 ppm. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet Black 190303. Skin layer 18 has the following composition:
  - 92% Surlyn 9120
  - 8% Ampacet 10561

- Skin layer 18 has a UV light stabilizer concentration of 16,000 ppm. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet 10561. Skin layer 20 has the following composition:
  - 92% Huntsman 1080
  - 5% Ampacet 10561
  - 3% Ampacet 10919

- Skin layer 20 has a UV light stabilizer concentration of 10,000 ppm. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet 10561.

**[0090]** Abrasion tests are conducted on the foregoing multilayer film-following the procedure provided for in ASTM D4060-84. The abrasive wheel is No. CS-10 and the arm weight is 250 grams. The test is conducted by varying the grinding cycles to produce scuffing that can be read with a glossometer. The 60° angle gloss readings are as follows:

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Gloss Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (Zero Cycles)</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>78</td>
</tr>
<tr>
<td>10</td>
<td>69</td>
</tr>
<tr>
<td>25</td>
<td>59</td>
</tr>
<tr>
<td>50</td>
<td>46</td>
</tr>
<tr>
<td>100</td>
<td>23</td>
</tr>
</tbody>
</table>

**[0091]** The foregoing multilayered film is tested for outdoor weatherability using a Xenon Arc weather-o-meter supplied by Atlas. The Xenon Arc weather-o-meter program used was Automotive Test Method SAE J 1960. The criteria for failure is $\Delta E>5$ for color failure and a 25 point drop in gloss for 60° gloss. The number of xenon hours to color failure is 2677 hours, and the number of xenon hours to gloss failure is 2677 hours. These values are significant due to the fact that it is generally considered that 2000 hours of Xenon Arc simulated weather-o-meter testing is roughly equivalent to 5 years of vertical outdoor exposure in North America.

**Example 4**

**[0092]** The multilayered film 12, which is comprised of core layer 16 having a thickness of 2.4 mils, skin layer 18 having a thickness of 0.3 mil, and skin layer 20 having a thickness of 0.3 mil, is coextruded. The core layer 16 has the following composition:

- 77% Dowlex 2036A
- 10% Quantum 285-003
- 10% Ampacet Black 190303
- 3% Surlyn 1605

Core layer 16 has a UV light stabilizer concentration of 4,000 ppm. The UV light stabilizer is Chemisorb 944 and is
Skin layers 18 and 20 have the following composition:

- 91% Surlyn 1605
- 5% Ampacet 10561
- 4% Ampacet 10061

Skin layers 18 and 20 have UV light stabilizer concentrations of 10,000 ppm. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet 10561.

The foregoing thermoplastic film is tested for outdoor weatherability using the procedure described in Example 3. The number of xenon hours to color failure is 3544 hours. The number of xenon hours to gloss failure is 2677 hours.

Example 5

The multilayered film 12, which is comprised of core layer 16 having a thickness of 2.4 mils, skin layer 18 having a thickness of 0.3 mil, and skin layer 20 having a thickness of 0.3 mil, is coextruded. The core layer 16 has the following composition:

- 83% Huntsman 1080
- 12% Ampacet Black 190303
- 3% Surlyn 1605
- 2% Ampacet 10919

Core layer 16 has a UV light stabilizer concentration of 4,800 ppm. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet Black 190303. Skin layer 18 has the following composition:

- 93% Surlyn 1605
- 7% Ampacet 10561

Skin layer 18 has a UV light stabilizer concentration of 14,000 ppm. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet 10561. Skin layer 20 has the following composition:

- 95% Huntsman 1080
- 3% Ampacet 10561
- 2% Ampacet 10919

Skin layer 20 has a UV light stabilizer concentration of 6,000. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet 10651.

Color measurements are conducted on the foregoing multilayer film using a Hunter Lab MiniScan Spectrocolormeter Model MS 4500L with a geometry of 45°/0°, a viewing area of large, an illuminant of D65 and 10° standard observer with the result being an L number of 7.5. This value for the L number is significant. The L number is from the L, a, b optical scale. An L number of zero corresponds to absolute black and for black films the lower the L number the better. L numbers typically observed for conventional black polyolefin films are in the range of about 10-12. On the other hand, L numbers typically observed for dispersion cast black vinyl films used in the industry are in the range of about 5-7. Thus, the L number of 7.5 observed for the tested sample closely approximates the values typically observed for dispersion case black vinyl films.

Example 6

The multilayered film 12, which is comprised of core layer 16 having a thickness of 2.4 mils, skin layer 18 having a thickness of 0.3 mil, and skin layer 20 having a thickness of 0.3 mil, is coextruded. The core layer 16 has the following composition:

- 79% Huntsman 1080
- 12% Ampacet Black 190303
- 5% Surlyn 9120
Core layer 16 has a UV light stabilizer concentration of 4,800 ppm. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet Black 190303. Skin layer 18 has the following composition:

- 92% Surlon 9120
- 8% Ampacet 10561

Skin layer 18 has a UV light stabilizer concentration of 16,000 ppm. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet 10561. Skin layer 20 has the following composition:

- 92% Huntsman 1080
- 5% Ampacet 10561
- 3% Ampacet 10919

Skin layer 20 has a UV light stabilizer concentration of 10,000 ppm. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet 10561.

Color measurements on the foregoing thermoplastic film are conducted in the same manner as indicated in Example 5 with the result being a Hunter color L number of 6.6.

Example 7

The multilayered film 12, which is comprised of core layer 16 having a thickness of 2.4 mils, skin layer 18 having a thickness of 0.3 mil, and skin layer 20 having a thickness of 0.3 mil, is coextruded. The core layer 16 has the following composition:

- 74% Huntsman 1080
- 12% Ampacet Black 190303
- 10% Surlon 9120
- 4% Ampacet 10919

Core layer 16 has a UV light stabilizer concentration of 4,800 ppm. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet Black 190303. Skin layer 18 has the following composition:

- 92% Surlon 9120
- 8% Ampacet 10561

Skin layer 18 has a UV light stabilizer concentration of 16,000 ppm. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet 10561. Skin layer 20 has the following composition:

- 92% Huntsman 1080
- 5% Ampacet 10561
- 3% Ampacet 10919

Skin layer 20 has a UV light stabilizer concentration of 10,000 ppm. The UV light stabilizer is Chemisorb 944 and is provided with the Ampacet 10561.

Color measurements on the foregoing thermoplastic film are conducted in the same manner as indicated in Example 5 with the result being a Hunter color L number 6.9.

Example 8

The multilayered film 12, which is comprised of core layer 16 having a thickness of 2.4 mils, skin layer 18 having
a thickness of 0.3 mil, and skin layer 20 having a thickness of 0.3 mil, is coextruded. The core layer 16 has the following composition:

<table>
<thead>
<tr>
<th>Percentage</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>64%</td>
<td>Huntsman 1080</td>
</tr>
<tr>
<td>12%</td>
<td>Ampacet Black 190303</td>
</tr>
<tr>
<td>20%</td>
<td>Surlyn 9120</td>
</tr>
<tr>
<td>4%</td>
<td>Ampacet 10919</td>
</tr>
</tbody>
</table>

Core layer 16 has a UV light stabilizer concentration of 4,800 ppm. The UV light stabilizer is Chemissorb 944 and is provided with the Ampacet Black 190303. Skin layer 18 has the following composition:

<table>
<thead>
<tr>
<th>Percentage</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>92%</td>
<td>Surlyn 9120</td>
</tr>
<tr>
<td>8%</td>
<td>Ampacet 10561</td>
</tr>
</tbody>
</table>

Skin layer 18 has a UV light stabilizer concentration of 16,000 ppm. The UV light stabilizer is Chemissorb 944 and is provided with the Ampacet 10561. Skin layer 20 has the following composition:

<table>
<thead>
<tr>
<th>Percentage</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>92%</td>
<td>Huntsman 1080</td>
</tr>
<tr>
<td>5%</td>
<td>Ampacet 10561</td>
</tr>
<tr>
<td>3%</td>
<td>Ampacet 10919</td>
</tr>
</tbody>
</table>

Skin layer 20 has a UV light stabilizer concentration of 10,000 ppm. The UV light stabilizer is Chemissorb 944 and is provided with the Ampacet 10561.

Example 9

The multilayered film 12A comprised of core layer 16, supplemental core layer 17, and skin layers 18 and 20 is coextruded. The core layer 16 has a thickness of 2.1 mils and the following composition:

<table>
<thead>
<tr>
<th>Percentage</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>81%</td>
<td>Huntsman 1080</td>
</tr>
<tr>
<td>12%</td>
<td>Ampacet LR 86813 Yellow UV PE MB</td>
</tr>
<tr>
<td>4%</td>
<td>Ampacet 10919</td>
</tr>
<tr>
<td>3%</td>
<td>Surlyn 1605</td>
</tr>
</tbody>
</table>

Core layer 16 has a UV light stabilizer concentration of 9000 ppm which is provided with the Ampacet LR 86813 Yellow UV PE MB. The UV light stabilizer is Tinuvin 783. Intermediate layer 17 has a thickness of 0.3 mil and the following composition:

<table>
<thead>
<tr>
<th>Percentage</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>85%</td>
<td>Huntsman 1080</td>
</tr>
<tr>
<td>11%</td>
<td>Ampacet Grey LR 89933</td>
</tr>
<tr>
<td>4%</td>
<td>Ampacet 10919</td>
</tr>
</tbody>
</table>

Intermediate layer 17 has a UV light stabilizer concentration of 4950 ppm. The UV light stabilizer is Tinuvin 783 and it is provided with the Ampacet Grey LR 89933. Skin layer 18 has a thickness of 0.3 mil and the following composition:

<table>
<thead>
<tr>
<th>Percentage</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>90%</td>
<td>Surlyn 9120</td>
</tr>
<tr>
<td>8%</td>
<td>Ampacet 10561</td>
</tr>
<tr>
<td>2%</td>
<td>Ampacet 10919</td>
</tr>
</tbody>
</table>

Skin layer 18 has a UV light stabilizer concentration of 16,000 ppm which is provided with the Ampacet 10561. The UV light stabilizer is Chemissorb 944. Skin layer 20 has a thickness of 0.3 mil and the following composition:
Skin layer 20 has a UV light stabilizer concentration of 6,000 ppm. The UV light stabilizer is Chemissorb 944. It is provided with the Ampacet 10561.

Example 10

**[0103]** The multilayered film 12A comprised of core layer 16, intermediate layer 17, and skin layers 18 and 20 is coextruded. The core layer 16 has a thickness of 2.1 mils and the following composition:

<table>
<thead>
<tr>
<th></th>
<th>Percentage</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Huntsman 1080</td>
<td>81%</td>
<td></td>
</tr>
<tr>
<td>Ampacet LR 86810 Red PE MB</td>
<td>12%</td>
<td></td>
</tr>
<tr>
<td>Ampacet 10919</td>
<td>4%</td>
<td></td>
</tr>
<tr>
<td>Surlyn 1605</td>
<td>3%</td>
<td></td>
</tr>
</tbody>
</table>

Core layer 16 has a UV light stabilizer concentration of 9,000 ppm which is provided with the Ampacet LR 86810 Red PE MB. The UV light stabilizer is Tinuvin 783. Intermediate layer 17 has a thickness of 0.3 mil and the following composition:

<table>
<thead>
<tr>
<th></th>
<th>Percentage</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Huntsman 1080</td>
<td>85%</td>
<td></td>
</tr>
<tr>
<td>Ampacet Grey LR 89933</td>
<td>11%</td>
<td></td>
</tr>
<tr>
<td>Ampacet 10919</td>
<td>4%</td>
<td></td>
</tr>
</tbody>
</table>

Intermediate layer 17 has a UV light stabilizer concentration of 4950 ppm. The UV light stabilizer is Tinuvin 783. It is provided with the Ampacet Grey LR 89933. Skin layer 18 has a thickness of 0.3 mil and the following composition:

<table>
<thead>
<tr>
<th></th>
<th>Percentage</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Surlyn 9120</td>
<td>90%</td>
<td></td>
</tr>
<tr>
<td>Ampacet 10561</td>
<td>8%</td>
<td></td>
</tr>
<tr>
<td>Ampacet 10919</td>
<td>2%</td>
<td></td>
</tr>
</tbody>
</table>

Skin layer 18 has a UV light stabilizer concentration of 16,000 ppm which is provided with the Ampacet 10561. The UV light stabilizer is Chemissorb 944. Skin layer 20 has a thickness of 0.3 mil and the following composition:

<table>
<thead>
<tr>
<th></th>
<th>Percentage</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Huntsman 1080</td>
<td>94%</td>
<td></td>
</tr>
<tr>
<td>Ampacet 10561</td>
<td>3%</td>
<td></td>
</tr>
<tr>
<td>Ampacet 10919</td>
<td>3%</td>
<td></td>
</tr>
</tbody>
</table>

Skin layer 20 has a UV light stabilizer concentration of 6,000 ppm which is provided by the Ampacet 10561.

Example 11

**[0104]** Part A: The multilayered film 12, which is comprised of core layer 16 having a thickness of 2.4 mils, skin layer 18 having a thickness of 0.3 mil, and skin layer 20 having a thickness of 0.3 mil, is coextruded. The core layer 16 has the following composition:

<table>
<thead>
<tr>
<th></th>
<th>Percentage</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Huntsman 1080</td>
<td>83%</td>
<td></td>
</tr>
<tr>
<td>Ampacet Black 190303</td>
<td>12%</td>
<td></td>
</tr>
<tr>
<td>Surlyn 9120</td>
<td>8%</td>
<td></td>
</tr>
<tr>
<td>Ampacet 10919</td>
<td>2%</td>
<td></td>
</tr>
</tbody>
</table>
Core layer 16 has a UV light stabilizer concentration of 4,800 ppm. The UV light stabilizer is Chemissorb 944 and is provided with the Ampacet Black 190303. Skin layer 18 has the following composition:

- 93% Surlyn 9120
- 7% Ampacet 10561

Skin layer 18 has a UV light stabilizer concentration of 14,000 ppm. The UV light stabilizer is Chemissorb 944 and is provided with the Ampacet 10561. Skin layer 20 has the following composition:

- 95% Huntsman 1080
- 3% Ampacet 10561
- 2% Ampacet 10919

Skin layer 20 has a UV light stabilizer concentration of 6,000. The UV light stabilizer is Chemissorb 944 and is provided with the Ampacet 10651.

Part B: The multilayered film from Part A has a topcoat layer adhered to skin layer 18. The topcoat layer has a thickness of 6 microns and has the following composition:

<table>
<thead>
<tr>
<th>Tradename</th>
<th>Supplier</th>
<th>Description</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyracure UVR-6110</td>
<td>Union Carbide</td>
<td>Epoxy Resin</td>
<td>87.7</td>
</tr>
<tr>
<td>Cyracure UVR-6974</td>
<td>Union Carbide</td>
<td>Photoinitiator</td>
<td>8.0</td>
</tr>
<tr>
<td>Tone 301</td>
<td>Union Carbide</td>
<td>Caprolactone Polyl</td>
<td>4.3</td>
</tr>
</tbody>
</table>

The topcoat layer is cured using a seven-roll coater run at a speed of 600 feet per minute using two banks of 600 watts per inch fusion bulbs, type H, in air.

Part B films from Parts A and B are tested for gloss, and abrasion and scuff resistance using the procedure described in Example 3 with the following results:

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Part A Film</th>
<th>Part B Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (Zero Cycles)</td>
<td>88</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>77.8</td>
<td>87.5</td>
</tr>
<tr>
<td>10</td>
<td>68.8</td>
<td>84.3</td>
</tr>
<tr>
<td>25</td>
<td>58.8</td>
<td>76.8</td>
</tr>
<tr>
<td>50</td>
<td>45.8</td>
<td>74.8</td>
</tr>
</tbody>
</table>

Example 12

A series of 3.0 mil monolayer, unstabilized, metallocene polyethylene cast extrusion films formed stress cracks after 800 hours of artificial weathering in the Xenon weather-o-meter which is programmed for an automotive cycle. A hindered amine stabilizer (HAS) was incorporated into the film mix to improve the film durability. Black and white pigmented metallocene polyethylene films using a (HAS) were made.

Mono layer films of Dow metallocene ethylene-octene (Affinity 1030 HF) copolymers containing approximately 1400 ppm of HAS (Ampacet Black Concentrate with Chemissorb 944) lasted 3771 hours of Xenon exposure with no gloss reduction. Black vinyl film showed a 20 point gloss reduction which is noticeable for the same time exposure as the Affinity 1030 HF film.

Black Pigmented Film Formulation:

- 7.0 % Ampacet Black 190303 (contains 2.0 % U.V. stabilizer Chemissorb 944)
- 93.0 % Dow Metallocene Affinity 1030 HF (LMDPE - Linear Medium Density PE.)
The extrusion cast films were made on an extrusion line having the capability of using three (3) extruders and three (3) or more layer(s) capability. More layers can be made by utilizing a different selector plug and splitting the melt streams.

**Example 13**

A three layer, 3.0 mil multilayer film was prepared where the same skin layer on each side of the core layer. The core layer has a thickness 2.4 and the skin layer have a thickness of 0.3 mil each.
(A) Olympic Blue Film - 3 Layer Coextrusion with ABA structure:

Pigmented or Core Layer Formulation
13.5 % Ampacet Olympic Blue LR 86732
86.5 % Dow Metallocene Affinity 1030 HF (LMDPE)

Skin Layer Composition: Same for both layers
95.0 % Dow Metallocene Affinity 1030 HF (LMDPE)
5.0 % Ampacet 10561

(B) Dark Green Film - 3 Layer Coextrusion with ABA structure:

Core or Pigmented Layer Formulation
12.0 % Ampacet Dark Green LR 86800
88.0 % Dow Metallocene Affinity 1030 HF (LMDPE)

Skin Layer Composition: Same for both layers
95.0 % Dow Metallocene Affinity 1030 HF (LMDPE)
5.0 % Ampacet 10561

Extruder #1 (Skin Layer) - Extruder RPM: 13.5
Extruder Zone Temperatures:
Adapter Temperature: 420° F
Extruder #2 (Skin Layer): Extruder RPM: 18.5
Extruder Zone Temperatures:
Adapter Temperature: 420° F
Main or Core Extruder: Extruder RPM: 341
Extruder Zone Temperatures:
Adapter Temperature: 420° F
Feedblock Zone Temperature: 400° F
Die Zone Temperatures:

Physical Properties:

<table>
<thead>
<tr>
<th>Hunter Color Lab Data</th>
<th>L</th>
<th>a</th>
<th>b</th>
<th>60° Gloss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olympic Blue</td>
<td>43.9</td>
<td>-18.5</td>
<td>-41.7</td>
<td>80</td>
</tr>
<tr>
<td>Dark Green</td>
<td>24.9</td>
<td>-20.7</td>
<td>5.4</td>
<td>80</td>
</tr>
</tbody>
</table>
Example #14

22. Pigmented three layer films were prepared by coextruding a 2.5 mil thick core layer and two skins layer each of which is 0.25 mil. *White Pigmented Fi-m* - 3 Layer Coextrusion with ABA structure:

| Pigmented or Core Layer Formulation | 22.0 % Ampacet White 110233 | 78.0 % Dow Metallocene Affinity 1030 HF (LMDPE) |

Skin Layer Composition: Same for both layers

95.0 % Dow Metallocene Affinity 1030 HF (LMDPE)

5.0 % Ampacet 10561 U.V. PE Concentrat *Black Pigmented Fi-m* - 3 Layer Coextrusion with ABA structure:

| Core or Pigmented Layer Formulation | 8.5 % Ampacet Black 190303 |

| 91.5 % Dow Metallocene Affinity 1030 HF (LMDPE) |

Skin Layer Composition: Same for both layers

95.0 % Dow Metallocene Affinity 1030 HF (LMDPE)

5.0 % Ampacet 10561
(C) Cardinal Red Pigmented Film - 3 Layer Coextrusion with ABA structure:

Core or Pigmented Layer Formulation
16.0 % Ampacet Cardinal Red 150380 (LR 87075)
84.0 % Dow Metallocene Affinity 1030 HF (LMDPE)

Skin Layer Composition: Same for both layers
95.0 % Dow Metallocene Affinity 1030 HF (LMDPE)
5.0 % Ampacet 10561

(D) Sapphire Blue Pigmented Film - 3 Layer Coextrusion with ABA structure:

Core or Pigmented Layer Formulation
12.0 % Ampacet Sapphire Blue LR 86804
88.0 % Dow Metallocene Affinity 1030 HF (LMDPE)

Skin Layer Composition: Same for both layers
95.0 % Dow Metallocene Affinity 1030 HF (LMDPE)
5.0 % Ampacet 10561 U.V. PE Conc) Canary Yellow Pigmented Film - 3 Layer Coextrusion with ABA structure:

Core or Pigmented Layer Formulation
12.0 % Ampacet Canary Yellow LR 87085
88.0 % Dow Metallocene Affinity 1030 HF (LMDPE)

Skin Layer Composition: Same for both layers
95.0 % Dow Metallocene Affinity 1030 HF (LMDPE)
5.0 % Ampacet 10561

<table>
<thead>
<tr>
<th>Hunter Color Lab Data</th>
<th>L</th>
<th>A</th>
<th>b</th>
<th>60° Gloss (MD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>White</td>
<td>93.8</td>
<td>-1.3</td>
<td>0.9</td>
<td>86.0</td>
</tr>
<tr>
<td>Black</td>
<td>11.0</td>
<td>-0.2</td>
<td>0.0</td>
<td>83.9</td>
</tr>
<tr>
<td>Cardinal Red</td>
<td>29.7</td>
<td>49.1</td>
<td>17.1</td>
<td>86.0</td>
</tr>
<tr>
<td>Sapphire Blue</td>
<td>19.1</td>
<td>2.9</td>
<td>-36.6</td>
<td>87.0</td>
</tr>
<tr>
<td>Canary Yellow</td>
<td>74.3</td>
<td>15.8</td>
<td>44.3</td>
<td>82.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Xenon Durability</th>
<th>Delta E &gt; 5.0</th>
<th>Gloss Reduction &gt; 25 pts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>White</td>
<td>6733 hrs.</td>
<td>5730 hrs.</td>
</tr>
<tr>
<td>Black</td>
<td>6570 hrs.</td>
<td>5425 hrs.</td>
</tr>
</tbody>
</table>
Example # 15

A series of 3 layer coextrusions with clear skin layers and 5 different color pigments were coextruded with two types of PE resins: Dow Metallocene LMDPE and Quantum MDPE. The core layer consisted of a single PE resins component and pigmented concentrate. The Xenon weather-o-meter results show that properly stabilize the Quantum MDPE is as durable as the Dow Metallocene LMDPE with one exception: the MDPE sign cuts and weeds better than the Met. LMDPE and does well at small letters (1/4 inch).

The following information relates to using a one component system of MDPE in the core or pigmented layer with clear skins of MDPE on adjacent sides of the film. The films made were made in the following colors: white, black, canary yellow, sapphire blue and cardinal red. These films cut and weeded well even at ¼ inch size letters on the Gerber Edge and Roland sign cutting units and had excellent durability compared to Cast PVC films but slightly less durability than the Dow Metallocene Affinity 1030 HF films. For the signage application the durability is acceptable.

One can observe from the following Table that in most cases the 3 layer coextruded pigmented MDPE films are comparable and in most cases better than Vinyl (PVC) pigmented films of the same color. This is significant and the trick is to find a material that will give scuff resistance and minimize the milkiness appearance without sacrificing sign cutting & weeding and outdoor durability.

<table>
<thead>
<tr>
<th>Hunter Color Lab Data</th>
<th>L</th>
<th>A</th>
<th>b</th>
<th>60° Gloss (MD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>White</td>
<td>94.3</td>
<td>-1.3</td>
<td>0.7</td>
<td>81.9</td>
</tr>
<tr>
<td>Canary Yellow</td>
<td>73.6</td>
<td>17.2</td>
<td>44.7</td>
<td>91.3</td>
</tr>
<tr>
<td>Cardinal Red</td>
<td>28.2</td>
<td>50.4</td>
<td>16.9</td>
<td>87.6</td>
</tr>
<tr>
<td>Sapphire Blue</td>
<td>18.5</td>
<td>3.2</td>
<td>-36.5</td>
<td>85.2</td>
</tr>
<tr>
<td>Black</td>
<td>9.2</td>
<td>0</td>
<td>0.4</td>
<td>86.6</td>
</tr>
</tbody>
</table>

One can observe from the following Table that in most cases the 3 layer coextruded pigmented MDPE films are comparable and in most cases better than Vinyl (PVC) pigmented films of the same color. This is significant and the trick is to find a material that will give scuff resistance and minimize the milkiness appearance without sacrificing sign cutting & weeding and outdoor durability.

<table>
<thead>
<tr>
<th>Xenon Durability</th>
<th>Delta E &gt; 5.0</th>
<th>Gloss Reduction &gt; 25 pts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>White</td>
<td>6464 hrs.</td>
<td>6049 hrs.</td>
</tr>
<tr>
<td>White (PVC)</td>
<td>3718 hrs.</td>
<td>2086 hrs.</td>
</tr>
<tr>
<td>Canary Yellow</td>
<td>5130 hrs.</td>
<td>6442 hrs.</td>
</tr>
</tbody>
</table>
Example # 16

[0119] A 3.0 mil multilayer film was prepared with Packaging grade Surlyn resins. The films were evaluated for improved abrasion resistance and improvement in clarity which would give a less milky appearance. The core layer was 2.4 mils and each skin layer was 0.3 mil. The films were made by coextrusion:

A) Black Pigmented Film Formulation - 3 Layer Coextrusion with ABA structure

<table>
<thead>
<tr>
<th></th>
<th>Xenon Durability</th>
<th>Delta E &gt; 5.0</th>
<th>Gloss Reduction &gt; 25 pts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canary Yellow (PVC)</td>
<td>2259 hrs.</td>
<td>2259 hrs.</td>
<td></td>
</tr>
<tr>
<td>Cardinal Red</td>
<td>6417 hrs.</td>
<td>6253 hrs.</td>
<td></td>
</tr>
<tr>
<td>Cardinal Red (PVC)</td>
<td>2931 hrs.</td>
<td>2369 hrs.</td>
<td></td>
</tr>
<tr>
<td>Sapphire Blue</td>
<td>2656 hrs.</td>
<td>2656 hrs.</td>
<td></td>
</tr>
<tr>
<td>Sapphire Blue (PVC)</td>
<td>2752 hrs.</td>
<td>2938 hrs.</td>
<td></td>
</tr>
<tr>
<td>Black (Invention)</td>
<td>6130 hrs.</td>
<td>3879 hrs.</td>
<td></td>
</tr>
<tr>
<td>Black (PVC)</td>
<td>3906 hrs.</td>
<td>4740 hrs.</td>
<td></td>
</tr>
</tbody>
</table>

Skin Layers A on both surfaces of the Core

93.0 % DuPont Surlyn (Packaging Grade) 1802
6% Ampacet 10561 U.V. in concentrate
5% Ampacet Slip Agent 10061

12000 ppm UV Light stabilizer Chemisorb 944 in layer

Core or Pigmented Layer

94% Dow Metallocene Affinity 1030 HF
6% Ampacet Black 190303 (contains U.V. in concentrate)

Hunter Color Lab Data

<table>
<thead>
<tr>
<th></th>
<th>L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black (invention)</td>
<td>9.2</td>
</tr>
<tr>
<td>Black (PVC)</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Example # 17

[0120] Multilayer films with Packaging grade Surlyn resins were evaluated for improved abrasion resistance and improvement in clarity which would give a less milky appearance. The films were 3.0 mil thick with a 2.4 mil core and each skin layer being 0.3 mil. A) Black Pigmented Film Formulation - 3 Layer Coextrusion with ABC structure

Skin Layer A

93.0 % DuPont Surlyn (Packaging Grade) 1802
7% Ampacet 10561

contains 12000 ppm UV Light stabilizer Chemisorb
Example # 18

A film formulated with a Surlyn top layer was used along with single component polyethylene resins in the pigmented core layer. Non-pigmented Surlyn layers would be coextruded on both adjacent sides of a pigmented core layer with contained a single component polyethylene resin such as Dow Affinity 1030 HF polyethylene resin and blends of Dow Metallocene Afffinity 1030 HF and Quantum MDPE resin.

The following formulations were made comprising clear (non-pigmented) Surlyn skin layers on both adjacent sides of a pigmented core layer. This film contained a single component PE resin in the core and the adjacent Surlyn skin layer that would be in contact with the pressure sensitive adhesive would act as a adhesive side layer for the film to bond to the pressure sensitive adhesive. The multilayer film (ABA type structure) has a thickness of 3.9 mil, with the core layer being 2.4 mils, each skin layer being 0.3 mil.

22. A) ABA Type Film

[0123] Surlyn Skin Layer Formulation:

89.0% DuPont Surlyn 1802 (Pkg Grade Surlyn)
Change in color of delta EE > 5.0 is considered a failure and a reduction in 60° gloss by 25 points or higher from initial reading is considered a failure. Fail gloss criteria at 1130 hours. Fail color Delta E > 5.0) at 848 hrs. Vinyl film failed the Durability test for color at 3906 hrs and failed the 60° gloss test at 4740 hrs.

Several second generation films were made, having different single component polyethylene resin (Dowlex and Affinity) in the pigmented core layer along with a small amount of Surlyn in the core layer for inter-layer adhesion. A noticeable improvement in the appearance of the jetness of the black was observed with the addition of a small amount of Surlyn in the core layer. ABA Type Structure with Surlyn in the "A" skin layers.

Core Layer Blend:
89.0 % Dowlex 2036A LMDPE resin
7.0 % Ampacet Black 190303
3.0 % DuPont Surlyn 160.0 % Ampacet PE Slip Concentrate # 10061

Skin Layer Thickness:
92.0 % DuPont Surlyn 1605
4.0 % Ampacet 10061
4.0 % Ampacet 10561

(C) ABA Type Structure with Surlyn in the "A" skin layers

Core Layer Blend:
89.0 % Dow Metallocene Affinity LMDPE 1030 HF resin
7.0 % Ampacet Black 190303
3.0 % DuPont Surlyn 160.0 % Ampacet PE Slip Concentrate # 10061

<table>
<thead>
<tr>
<th>Hunter Color Lab Data</th>
<th>L</th>
<th>a</th>
<th>b</th>
<th>60° Gloss (MD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black #1</td>
<td>7.7</td>
<td>0.1</td>
<td>0.4</td>
<td>83.4</td>
</tr>
<tr>
<td>Black #2</td>
<td>8.6</td>
<td>0.2</td>
<td>0.7</td>
<td>84.9</td>
</tr>
<tr>
<td>Black (PVC)</td>
<td>6.7</td>
<td>0.0</td>
<td>0.5</td>
<td>98.0</td>
</tr>
</tbody>
</table>
This film structure was made by switching from Dow Metallocene Affinity LMDPE or Dowlex or blends of these with conventional MDPE (either MDPE made by Quantum, now EQUISTAR, or Huntsman now made by Huntsman), a single component MDPE resin was used to improve the sign cutting characteristics of the film so that the film would cut and weed at ¼ inch size letters.

A higher loading (e.g. 14,000 ppm) of U.V. stabilizer was used in the Surlyn skin layer. Another feature that was incorporated into the film was that the bottom clear skin layer was now change to contain MDPE and U.V. stabilizer in place of Surlyn. The total film thickness is 3.0 mils, with a 2.4 mil core and 0.3 mil each skin layers. The film was a ABC type (A is Surlyn Layer, C is PSA - MDPE Layer, B is pigmented Core Layer).

**Example #19**

<table>
<thead>
<tr>
<th>Xenon Durability</th>
<th>DELTA E &gt; 5.0</th>
<th>Gloss Reduction &gt; 25 pts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black #1</td>
<td>2415 hrs.</td>
<td>1726 hrs.</td>
</tr>
<tr>
<td>Black #2</td>
<td>3809 hrs.</td>
<td>1726 hrs.</td>
</tr>
<tr>
<td>Black (PVC)</td>
<td>4740 hrs.</td>
<td>3906 hrs.</td>
</tr>
</tbody>
</table>

**Core Layer Blend:**
- 83.0% Quantum (now EQUISTAR) NA 285-003 MDPE resin
- 12.0% Ampacet Black PE Color Concentrate 190303
- 3.0% DuPont Surlyn 1605 Packaging Grade Surlyn
- 2.0% Ampacet # 10919

**Surlyn (scuff resistant) Skin Layer Blend:**
- 93.0% DuPont Surlyn 1605
- 7.0% Ampacet # 10561

**Pressure Sensitive Adhesive Side Skin Layer Blend:**
- 95.0% Quantum (now EQUISTAR) NA 285-003 MDPE resin
- 3.0% Ampacet # 10561
- 2.0% Ampacet 10919

**Core Layer Blend:**
- 83.0% Huntsman (now Huntsman) PE-1080 MDPE resin
- 12.0% Ampacet Black 190303
- 3.0% DuPont Surlyn 1605 Packaging Grade Surlyn
- 2.0% Ampacet # 10919

**Surlyn (scuff resistant) Skin Layer Blend:**
- 93.0% DuPont Surlyn 1605
- 7.0% Ampacet # 10561

**Pressure Sensitive Adhesive Side Skin Layer Blend:**
- 95.0% Huntsman (now Huntsman) PE-1080 MDPE resin
- 3.0% Ampacet # 10561
Example #20

A series of three layer (ABC) films were made with skin layer that varied the amount of Surlyn. The films had a thickness of 3.0 mils, with the core layer being 2.4 mils and each skin layer being 0.3 mil. The film is an ABC type film where A is Surlyn Layer, C is PSA-MDPE Layer, B is pigmented Core Layer.

<table>
<thead>
<tr>
<th>Hunter Color Lab Data</th>
<th>L</th>
<th>a</th>
<th>b</th>
<th>60 Gloss (MD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black #1</td>
<td>7.4</td>
<td>0.6</td>
<td>0.9</td>
<td>84.3</td>
</tr>
<tr>
<td>Black #2</td>
<td>7.6</td>
<td>0.2</td>
<td>0.8</td>
<td>85.8</td>
</tr>
<tr>
<td>Black (PVC)</td>
<td>6.7</td>
<td>0.0</td>
<td>0.5</td>
<td>98.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Xenon Durability</th>
<th>DELTA E &gt; 5.0</th>
<th>Gloss Reduction &gt; 25 pts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black #1</td>
<td>&gt;3461 hrs.</td>
<td>&gt;3461 hrs.</td>
</tr>
<tr>
<td>Black #2</td>
<td>&gt;3461 hrs.</td>
<td>&gt;3461 hrs.</td>
</tr>
<tr>
<td>Black (PVC)</td>
<td>4740 hrs.</td>
<td>3906 hrs.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Taber Abrasion</th>
<th>60° Gloss Readings (Cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black #2</td>
<td>83 72 67 50 27</td>
</tr>
<tr>
<td>Black (PVC)</td>
<td>95 77 69 60 54</td>
</tr>
</tbody>
</table>

Core Layer Blend:
86.0 % Huntsman (now Huntsman) PE-1080 MDPE resin
12.0 % Ampacet Black # 190303
2.0 % Ampacet # 10919

Pressure Sensitive Adhesive Skin Layer Blend:
95.0 % Huntsman PE-1080 MDPE resin
3.0 % Ampacet # 10561
2.0 % Ampacet # 10919

Surlyn Skin Layer Film Blends:
(1) 93.0 % DuPont Surlyn 9120 7.0 % Ampacet # 10561
(2) 93.0 % DuPont Surlyn 8140 7.0 % Ampacet # 10561
(3) 93.0 % DuPont Surlyn AD8546 7.0 % Ampacet # 10561
(4) 93.0 % DuPont Surlyn AD8547 7.0 % Ampacet # 10561
(5) 93.0 % DuPont Surlyn AD8548 7.0 % Ampacet # 10561
(6) 93.0 % DuPont Surlyn 1707 7.0 % Ampacet # 10561
(7) 93.0 % DuPont Surlyn 1605 7.0 % Ampacet # 10561
Another series of three layer ABC films were prepared with various amounts of Surlyn in the pigmented core layer. The ABC film had a thickness of 3.0 mils, where the core layer had a thickness of 2.4 mil and the skin layers are each 0.3 mil. The file is a ABC type film where A is Surlyn Layer, C is PSA - MDPE Layer, and B is pigmented Core Layer.

Core Layer Blend:
92.0 % DuPont Surlyn 1920 " Golf Ball " Grade resin
8.0 % Ampacet 700840
Pressure Sensitive Adhesive Skin Layer Blend:
95.0 % Huntsman PE-1080 MDPE resin
3.0 % Ampacet # 10561
2.0 % Ampacet # 10919

Surlyn Skin Layer Film Blends:

[0130]

Control
84.0 % Huntsman PE-1080 MDPE
12.0 % Ampacet Black # 190303
4.0 % Ampacet # 10919
(No Surlyn in Core)

5 % Surlyn in Core
79.0 % Huntsman PE-1080 MDPE
12.0 % Ampacet Black # 190303
4.0 % Ampacet # 10919
5.0 % DuPont Surlyn 9120

10 % Surlyn in Core
74.0 % Huntsman PE-1080 MDPE
12.0 % Ampacet Black # 190303
4.0 % Ampacet # 10919
10.0 % DuPont Surlyn 9120

20 % Surlyn in Core
64.0 % Huntsman PE-1080 MDPE
12.0 % Ampacet Black # 190303
4.0 % Ampacet # 10919
20.0 % DuPont Surlyn 9120

40 % Surlyn in Core
54.0 % Huntsman PE-1080 MDPE
12.0 % Ampacet Black # 190303
4.0 % Ampacet # 10919
40.0 % DuPont Surlyn 9120

Hunter Color Lab Data (% Surlyn in Core layer) L  A  b  60° Gloss (MD)

<table>
<thead>
<tr>
<th>% Surlyn in Core</th>
<th>L</th>
<th>A</th>
<th>b</th>
<th>60° Gloss (MD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %</td>
<td>8.7</td>
<td>0.2</td>
<td>1.8</td>
<td>89.6</td>
</tr>
<tr>
<td>5 %</td>
<td>6.7</td>
<td>0.4</td>
<td>1.0</td>
<td>89.0</td>
</tr>
<tr>
<td>10 %</td>
<td>6.9</td>
<td>0.4</td>
<td>0.9</td>
<td>89.9</td>
</tr>
<tr>
<td>20 %</td>
<td>7.2</td>
<td>0.3</td>
<td>0.9</td>
<td>89.1</td>
</tr>
</tbody>
</table>
It is seen that 5.0% Surlyn in the core gives the lowest L number of all the blends.

Example #22

[0131] A three layer, 3.0 mil film has a core layer (2.4 mils) and two skin layers (0.3 mil each). -

Peelable Skin Layer

100% polypropylene resin

Skin Layer A

91.0% DuPont Surlyn (golf ball Grade) 9120 (19% MAA)
8% Ampacet 10561
contains 16000 ppm UV Light stabilizer Chemissorb 944
1% Ampacet 10919 Processing Aid

Core or Pigmented Layer

49% Huntsman MDPE PE-1080 resin
20% Ampacet Black 190671
5% DuPont Surlyn 9120
1% Ampacet 10919 Processing Aid
22% Equistar EVA
3% Ampacet U.V. 10561
contains 6000 ppm light stabilizer Chemissorb 944

Example #23

[0132] A four layer film is made which has a structure of ABAC. The film is 3.0 mils thick with a 2.4 mils thick core, 0.2 mil skin layer, 0.2 mil intermediate layer, and 0.2 mil adhesive skin layer.

Outside Surlyn Layer

85.0% DuPont Surlyn 1605
6.0% Amacet Antistatic Conc. # 100320 (6.0% GMS loading)
8.0% Ampacet U.V. Conc. # 195.0% Ampacet Process Aid
Conc. 10919
Example 24

[0133] A 2.7 mil, two layer film is prepared by coextruding a 2.4 mils core layer with a 0.3 mil skin layer.

Core layer
84.0 parts Huntsman PE-1080 MDPE
12.0 parts Ampacet Black 190303

Skin layer
85.0 parts DuPont Surlyn 1605
6.0 parts Ampacet Antistatic Conc. 100320 (6.0 % GMS loading)

Example 25

[0134] A 3.0 mils, three layer film is prepare by coextruding a 2.4 mils core layer with a 0.3 mil first skin layer and a 0.3 mil second skin layer.

Core Layer
84.0 parts Huntsman PE-1080 MDPE
12.0 parts Ampacet Black 190303

First Skin layer
85.0 parts DuPont Surlyn 1605
6.0 parts Ampacet Antistatic Conc. 100320 (6.0 % GMS loading)
Example 26

A 3.0 mils, three layer film is prepare by coextruding a 2.4 mils core layer with a 0.3 mil first skin layer and a 0.3 mil second skin layer.

Core Layer
84.0 parts Huntsman PE-1080 MDPE
12.0 parts Ampacet Black 190303

First Skin layer
85.0 parts DuPont Surlyn 1605
6.0 parts Ampacet Antistatic Conc. 100320 (6.0 % GMS loading)

Second Skin layer
84.0 parts Huntsman PE-1080 MDPE
12.0 parts Ampacet Black 190303

Example 27

Topcoated films are prepared by roll coating the film of Example 26 with
A) a UV curable epoxy topcoat of the following:

<table>
<thead>
<tr>
<th>Tradename</th>
<th>Supplier</th>
<th>Description</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyracure UVR-6110</td>
<td>Union Carbide</td>
<td>Epoxy Resin</td>
<td>83.5%</td>
</tr>
<tr>
<td>Tone 301</td>
<td>Union Carbide</td>
<td>Caprolactone Polyol</td>
<td>10.0%</td>
</tr>
<tr>
<td>Cyracure UVI-6974</td>
<td>Union Carbide</td>
<td>Photoinitiator</td>
<td>6.0%</td>
</tr>
<tr>
<td>Silivet L7604</td>
<td>OSI</td>
<td>Wetting Agent</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

B) a UV curable urethane based topcoat formulation of the following:

<table>
<thead>
<tr>
<th>Tradename</th>
<th>Supplier</th>
<th>Description</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN 963B80</td>
<td>Sartomer</td>
<td>urethane acrylate</td>
<td>75%</td>
</tr>
<tr>
<td>SR 238</td>
<td>Sartomer</td>
<td>1. 6 hexanediol</td>
<td>20.5%</td>
</tr>
<tr>
<td>Irgacure 184</td>
<td>Ciba</td>
<td>photoinitiator</td>
<td>3%</td>
</tr>
<tr>
<td>Tinuvin 1130</td>
<td>Ciba</td>
<td>UV Stabilizer</td>
<td>1%</td>
</tr>
<tr>
<td>Tinuvin 123</td>
<td>Ciba</td>
<td>UV Stabilizer</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

c) a thermal plastic polyurethane topcoat of the following:

<table>
<thead>
<tr>
<th>Tradename</th>
<th>Supplier</th>
<th>Description</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irostit 9827</td>
<td>Morton Chemical</td>
<td>thermoplastic polyurethane</td>
<td>12%</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>methyl, ethyl ketone</td>
<td>38%</td>
</tr>
<tr>
<td>Irganox 1010</td>
<td>Ciba</td>
<td>Antioxidant</td>
<td>0.25%</td>
</tr>
<tr>
<td>Tinuvin 292</td>
<td>Ciba</td>
<td>UV Stabilizer</td>
<td>0.125%</td>
</tr>
</tbody>
</table>
Sign Cutting Method

[0137] The inventive sign cutting method involves providing a pressure sensitive adhesive composite, the composite being comprised of the foregoing multilayered thermoplastic film adhered to a pressure sensitive adhesive laminate, cutting an image in the multilayered film, and transferring the image from the pressure sensitive adhesive composite to a substrate to provide for the desired graphic application. The inventive method is useful for providing signage applications involving a wide range of substrates and surface contours. These include long-term exterior identification signs, as well as decorative or commercial graphics on cars, trucks, boats, and the like. The image can be in any form including print, designs, and combinations thereof. The image can be clear, black, white or any desired color or combination of colors.

[0138] In one preferred embodiment, the inventive sign cutting method involves the steps of: (A) providing the foregoing pressure sensitive adhesive composite; (B) cutting the multilayered thermoplastic film in the form of a desired image to provide needed portions of the multilayered film and unneeded portions of the multilayered film; (C) removing the unneeded portions of the multilayered film from the composite; (D) placing a pressure sensitive adhesive mask over the composite in contact with the needed portions with sufficient pressure to adhere the needed portions to the mask, the mask being in contact with the first thermoplastic skin layer of the needed portions; (E) separating the mask and the needed portions from the composite, the separated needed portions having the pressure sensitive adhesive adhered to the second thermoplastic skin layer of the needed portions; (F) placing the mask and the needed portions against the substrate to which the image is to be adhered, the pressure sensitive adhesive adhered to the second thermoplastic skin layer of the needed portions being in contact with the substrate; and (G) removing the mask from the needed portions leaving the needed portions adhered to the substrate.

[0139] Step (A) of the inventive method involves providing the pressure sensitive adhesive composite 10 or 10A discussed above. The composite is provided in the size required for the desired application. The film is often provided in roll form and can have any length required for the desired application. For example, lengths of 1 foot, 10 feet, 25 feet, 50 feet, 100 feet, 200 feet, or more can be used. The width is dependent upon the particular graphics machine being used and can be, for example, up to about 48 inches, or up to about 60 inches.

[0140] The cutting step (B) is performed using any technique known in the art for cutting an image from a thermoplastic film adhered to a pressure sensitive adhesive composite. This cutting step is typically performed using an appropriate graphics machine or sign making machine. Examples of suitable graphics machines or sign making machines that can be used include those available from Gerber under the trade designation GSP Graphix 4 and Rolland under the trade designations PNC-910, PNC-950, PNC-960, PNC-1210, PNC-1410 or PNC-1860. In cutting the desired image, the cutting knife or tool is set to cut the pressure sensitive adhesive composite 10 or 10A to a sufficient depth so that the multilayered thermoplastic film 12 or 12A as well as the pressure sensitive adhesive layer 30 attached to the multilayered film 12 or 12A are cut leaving the release liner 35 uncut. Establishing the proper depth of the cut is within the skill of the art. The cutting step is continued until the appropriate image has been cut in the composite. The cutting results in the formation of needed portions of the multilayered film forming the desired image adhered to the release liner, and unneeded portions comprising the remainder of the multilayered film adhered to the release liner.

[0141] Step (C) of the inventive method involves removing the unneeded portions of the multilayered film 12 or 12A and pressure sensitive adhesive 30 from the release liner 35, leaving only the needed portions of the multilayered film 12 or 12A and adhesive layer 30 adhered to the release liner 35. The remaining needed portions form the image that is ultimately desired. This removal step is sometimes referred to in the art as "weeding." Weeding involves peeling the unneeded portions of the multilayered film from the release liner leaving only the needed portions representing the final image adhered to the release liner.

[0142] Step (D) of the inventive method involves placing a pressure sensitive adhesive mask over the needed portions of the multilayered film 12 or 12A that remain adhered to the release liner 35. The pressure sensitive adhesive mask is comprised of a substrate with a pressure sensitive adhesive layer overlying one side of the substrate. The pressure sensitive adhesive mask can be comprised of any of the pressure sensitive adhesives and liner materials (i.e., paper, polymer film, and combinations thereof) discussed above with the proviso that the pressure sensitive adhesive must be of sufficient strength to be able to separate the needed portions of the multilayered film from the release liner, but be of sufficient weakness to allow the needed portions of the multilayered film to adhere to the substrate to which the image is to be adhered during step (G). An example of a commercially available pressure sensitive adhesive mask that can
be used is available from American Built-Rite under the trade designation 6792 Premask.

[0143] Step (E) involves separating the pressure sensitive adhesive premask and the needed portions of the multilayered film 12 or 12A and adhesive layer 30 from the release liner 35. The pressure sensitive adhesive mask is adhered to the first thermoplastic skin layer 18 of the needed portions. The pressure sensitive adhesive 30, which is adhered to the second thermoplastic skin layer 20 of the needed portions, remains adhered to the second skin layer 20 and is exposed.

[0144] Step (F) involves placing the mask with the adhered needed portions over the substrate to which the image is to be adhered with the needed portions in the position to which they are to be adhered. Typically, the mask is applied with sufficient pressure to ensure that the needed portions are securely adhered to the substrate.

[0145] Step (G) involves removing the pressure sensitive adhesive mask from the adhered needed portions leaving the needed portions adhered to the substrate in the form of the desired image. The pressure sensitive adhesive mask is typically pulled away slowly so as to not disturb the position of the needed portions on the substrate. The mask can then be discarded or used in subsequent applications.

[0146] The inventive method will now be described with reference to Fig. 7. Fig. 7 is comprised of illustrations labeled (a) through (j) disclosing the sequence of steps involved with the inventive method. Step (A) is depicted by illustration (a) of Fig. 7. Step (B) is depicted by illustration (b). Step (C) is depicted by illustrations (c) and (d). Step (D) is depicted by illustration (e). Step (E) is depicted by illustrations (f) and (g). Step (F) is depicted by illustration (h). Step (G) is depicted by illustrations (i) and (j). The pressure sensitive adhesive composite 10 illustrated in Fig. 1 is also depicted in illustration (a) of Fig. 7. The pressure sensitive adhesive composite 10 is comprised of a multilayered thermoplastic film 12 adhered to a pressure sensitive adhesive laminate 14. The multilayered film 12 has a thermoplastic core layer 16, which has a first side and a second side, and thermoplastic skin layer 18 overlying the first side of the core layer 16 and second thermoplastic skin layer 20 overlying the second side of the core layer 16. The adhesive laminate has a layer of a pressure sensitive adhesive 30 adhered to the skin layer 20, a layer of a release coating 32 overlying the pressure sensitive adhesive 30 and a backing liner 34 overlying the release coating layer 32. Release coating layer 32 and backing liner 34 combine to form release liner 35. The cutting step (B) is performed using a knife 60 and results in the formation of needed portion 62 and an unneeded portion 64 being formed in multilayered film 12. The unneeded portion 64 of the multilayered film 12 is separated from the release liner 35 as depicted in illustration (c) leaving needed portion 62 adhered to release liner 35 as depicted in illustration (d). Step (D) involves placing a pressure adhesive mask 40 over needed portion 62 as depicted in illustration (e). The pressure sensitive adhesive mask is comprised of substrate 42 and pressure sensitive adhesive layer 44 underlaying substrate 42. The pressure sensitive adhesive mask 40 is applied to the skin layer 18 of the needed portion 62 with sufficient pressure so as to adhere to it. Step (E) involves separating the release liner 35 from the needed portion 62 and pressure sensitive adhesive mask 40 leaving the needed portion 62 adhered to the pressure sensitive adhesive mask 40 as depicted in illustration (f). The release liner 35 that is separated from the needed portion 62 as depicted in illustration (f) can be discarded. The pressure sensitive adhesive mask 40 with the needed portion 62 adhered to it as depicted in illustration (g) is placed over the substrate 50 upon which it is desired to place the desired image as depicted in illustration (h). Sufficient pressure is applied to the pressure sensitive adhesive mask 40 and needed portion 62 in order to adhere the needed portion 62 to the substrate 50. The pressure sensitive adhesive layer 30 adhered to the thermoplastic skin layer 20 of needed portion 62 contacts substrate 50 and secures needed portion 62 to substrate 50 as depicted in illustration (i). The pressure sensitive adhesive mask 40 is then separated from the needed portion 62 and substrate 50 as depicted in illustration (j) and either discarded or used again with subsequent procedures.

[0147] In one preferred embodiment, the method further comprises positioning an intermediate layer between the core layer and the second thermoplastic skin layer, the core intermediate layer being characterized by the absence of PVC.

[0148] In one particularly preferred embodiment, the multilayer film is unoriented.

Claims

1. A multilayer thermoplastic film, comprising:

- at least one polyolefin core layer having a first side and a second side, wherein the core layer comprises a polyolefin having a density in the range of 0.89 to 0.97 grams per cubic centimeter and a second thermoplastic material selected from ionomers derived from sodium, lithium or zinc and an ethylene/unsaturated carboxylic acid or anhydride copolymer;
- at least one abrasion resistant first thermoplastic skin layer overlying the first side of the core layer, and
- at least one second thermoplastic skin layer overlying the second side of the core layer, wherein the composition of the core layer is different from the composition of the skin layers, and the core layer and the skin layers being characterized by the absence of PVC.
2. The film of claim 1 wherein the first skin layer is clear.

3. The film of claim 1 wherein the second skin layer is clear.

4. The film of claim 1 wherein the core layer further comprises at least one third polymeric material selected from ethylene/vinyl acetate copolymers, acid-modified ethylene acrylate polymers, anhydride-modified ethylene acrylate copolymers, anhydride-modified ethylene/vinyl acetate copolymers, acid and acrylate-modified ethylene/vinyl acetate resins, anhydride-modified ethylene/vinyl acetate resins, anhydride-modified high density polyethylene resins, anhydride-modified linear low density polyethylene resins, anhydride-modified low density polyethylene resins and anhydride-modified polypropylene resins, and combinations thereof.

5. The film of claim 1 wherein the second thermoplastic material is present at a concentration of 2% to 25% by weight based on the weight of the core layer.

6. The film of claim 1 wherein the core comprises a light stabilizer at a concentration of 1,000 to 10,000 ppm based on the weight of the core layer.

7. The film of claim 1 wherein the first skin layer is comprised of an ionomer derived from sodium, lithium or zinc and an ethylene/unsaturated carboxylic acid copolymer.

8. The film of claim 1, wherein the polyolefin has a density in the range of 0.89 to 0.97 grams per cubic centimeter; and wherein the core layer further comprises a third polymeric material selected from ethylene/vinyl acetate copolymers, acid-modified ethylene acrylate polymers, anhydride-modified ethylene acrylate copolymers, anhydride-modified ethylene/vinyl acetate copolymers, acid and acrylate-modified ethylene/vinyl acetate resins, anhydride-modified high density polyethylene resins, anhydride-modified linear low density polyethylene resins, anhydride-modified low density polyethylene resins and anhydride-modified polypropylene resins and combinations thereof, wherein the second thermoplastic material is present at a concentration of 2% to 25% by weight based on the weight of the core layer, and a light stabilizer at a concentration of 1,000 to 10,000 ppm based on the weight of the core layer; and wherein the abrasion resistant first thermoplastic skin layer is scuff resistant and clear and comprises a light stabilizer at a concentration of 2,000 to 20,000 ppm based on the weight of the first skin layer; and the second thermoplastic skin layer is clear and comprises a light stabilizer at a concentration of 1,000 to 15,000 ppm based on the weight of the second skin layer.

9. The film of any preceding claim wherein an intermediate layer is positioned between the core layer and the second thermoplastic skin layer, the supplemental care intermediate layer being characterized by the absence of PVC.

10. The film of any preceding claim wherein a clear topcoat layer overlies the first thermoplastic skin layer, the clear topcoat layer being characterized by the absence of PVC.

11. The film of any preceding claim wherein a layer of a pressure sensitive adhesive overlies the second thermoplastic skin layer.

12. The film of claim 11 wherein the pressure sensitive adhesive layer comprises a rubber-based adhesive, acrylic adhesive, vinyl other adhesive, silicone adhesive or combination of two or more thereof.

13. The film of claim 11 wherein a release liner overlies the layer of pressure sensitive adhesive.

14. The film of claim 13 wherein the release liner is comprised of a release coating composition overlying a backing liner, the backing liner is comprised of paper, polymeric film or a combination thereof.

15. The film of claim 13 wherein the release liner is comprised of a release coating composition overlying a backing liner, the release coating composition is a silicone release-coating composition.

16. The film of claim 13 wherein the release liner is comprised of a release coating composition overlying a backing liner, the release coating composition comprising a polyorganosiloxane.
17. The film of any preceding claim wherein each of the skin layers have the same composition.

18. The film of any preceding claim wherein the skin layers have different compositions.

19. The film of any preceding claim wherein the core layer and the skin layers comprise a coextrudate.

20. The film of any preceding claim wherein the first skin layer is comprised of an ionomer derived from sodium, lithium or zinc and an ethylene/methacrylic acid copolymer.

21. The film of any preceding claim wherein the core layer is pigmented.

22. The film of any preceding claim wherein the core layer is clear.

23. The film of any preceding claim wherein the overall thickness of the multilayered thermoplastic film is from 1 to 10 mils, the thickness of the core layer is from 10% to 90% of the overall thickness.

24. The film of any preceding claim wherein the core layer further comprises an adhesive material.

25. The film of any preceding claim wherein at least one of the skin layers further comprises an adhesive material, antiblock agent, slip additive, or combination of two or more thereof.

26. A multilayer thermoplastic film as in any one of claims 1-25 wherein the film is an electronic cutting film, and wherein said at least one second thermoplastic skin layer comprises an adhesive priming layer disposed over the second side of the core layer.

27. A multilayer thermoplastic film as in any of claims 1-25 wherein the film is unoriented.

28. A sign cutting method, comprising:

   providing a pressure sensitive adhesive composite, the composite comprising a multilayered thermoplastic film, a layer of a pressure sensitive adhesive and a release liner;
   the multilayered thermoplastic film comprising (1) a thermoplastic core layer having a first side and a second side, (2) an abrasion and scuff resistant clear first thermoplastic skin layer overlying the first side of the core layer, and (3) a clear second thermoplastic skin layer overlying the second side of the core layer, the pressure sensitive adhesive layer being positioned between the second thermoplastic skin layer and the release liner and being preferentially adherent to the second thermoplastic skin layer;
   the thermoplastic core layer comprising: (a) a polyolefin having a density in the range of 0.89 to 0.97 grams per cubic centimeter; (b) a second thermoplastic material selected from the group consisting of ethylene acrylic acid copolymers, ethylene-methacrylic acid copolymers, ionomers derived from sodium, lithium or zinc and an ethylene/methacrylic acid copolymer, or combination of two or more thereof, the second thermoplastic material being present at a concentration of 2% to 25% by weight based on the weight of the core layer; and (c) a light stabilizer at a concentration of 1,000 to 10,000 ppm based on the weight of the core layer;
   the first thermoplastic skin layer comprising a light stabilizer at a concentration of 2,000 to 20,000 ppm based on the weight of the first skin layer;
   the second thermoplastic skin layer comprising a light stabilizer at a concentration of 1,000 to 15,000 ppm based on the weight of the second skin layer;
   the composition of the core layer and the skin layers being different, and the core layer and the skin layers being characterized by the absence of PVC;
   cutting an image in the multilayered thermoplastic film; and transferring the image to a substrate.

29. The sign cutting method of claim 28, wherein the step of cutting an image provides needed portions of the multilayered film and unneeded portions of the multilayered film; and wherein the method further comprises removing the unneeded portions of the multilayered film from the composite; placing a pressure sensitive adhesive mask over the composite in contact with the needed portions with sufficient pressure to adhere the needed portions to the mask, the mask is in contact with the first thermoplastic skin layer of the needed portions;
separating the mask and the needed portions from the composite, the separated needed portions having the pressure sensitive adhesive adhered to the second thermoplastic skin layer of the needed portions;
placing the mask and the needed portions against the substrate to which the image is to be adhered, the pressure sensitive adhesive adhered to the second thermoplastic skin layer of the needed portions is in contact with the substrate; and
removing the mask from the needed portions leaving the needed portions adhered to the substrate.

30. The method of either of claims 28 or 29 further comprising positioning an intermediate layer between the core layer and the second thermoplastic skin layer, the core intermediate layer being characterized by the absence of PVC.

31. A method as in any of claims 28-30 wherein the multilayer film is unoriented.

Patentansprüche

1. Mehrlagiger thermoplastischer Film, welcher folgendes aufweist:

- wenigstens eine Polyolefin-Kernlage bzw. -schicht mit einer ersten Seite und einer zweiten Seite, wobei die Kernlage ein Polyolefin mit einer Dichte im Bereich von 0,89 bis 0,97 Gramm pro Kubikzentimeter und ein zweites thermoplastisches Material, ausgewählt aus Ionomeren, abgeleitet von Natrium, Lithium oder Zink, und ein Ethylen/ungesättigte Carbonsäure- oder Anhydrid-Copolymer beinhaltet,
- wenigstens eine gegen Abrieb beständige erste thermoplastische Decklage bzw. -schicht, die auf der ersten Seite der Kernlage aufliegt, und
- wenigstens eine zweite thermoplastische Decklage, die auf der zweiten Seite der Kernlage aufliegt, wobei die Zusammensetzung der Kernlage eine andere ist als die Zusammensetzung der Decklagen und die Kernlage und die Decklagen durch das Fehlen bzw. Nichtvorliegen von PVC gekennzeichnet sind.

2. Film nach Anspruch 1, wobei die erste Decklage klar bzw. durchsichtig ist.

3. Film nach Anspruch 1, wobei die zweite Decklage klar bzw. durchsichtig ist.


5. Film nach Anspruch 1, wobei das zweite thermoplastische Material in einer Konzentration von 2 Gew.-% bis 25 Gew.-% basierend auf dem Gewicht der Kernlage, vorliegt.

6. Film nach Anspruch 1, wobei der Kern einen Lichtstabilisator in einer Konzentration von 1.000 bis 10.000 ppm, basierend auf dem Gewicht der Kernlage, beinhaltet.

7. Film nach Anspruch 1, wobei die erste Decklage aus einem Ionomer, abgeleitet von Natrium, Lithium oder Zink, und einem Ethylen/ungesättigtem Carbonsäure-Methacrylsäure-Copolymer zusammengesetzt ist.

und wobei die gegen Abrieb beständige erste thermoplastische Decklage abnutzungsbeständig und klar bzw. durchsichtig ist und einen Lichtstabilisator in einer Konzentration von 2.000 bis 20.000 ppm, basierend auf dem Gewicht der ersten Decklage, beinhaltet und die zweite thermoplastische Decklage klar bzw. durchsichtig ist und einen Lichtstabilisator in einer Konzentration von 1.000 bis 15.000 ppm, basierend auf dem Gewicht der zweiten Decklage, beinhaltet.

9. Film nach einem der vorangegangenen Ansprüche, wobei eine Zwischenlage zwischen der Kernlage und der zweiten thermoplastischen Decklage angeordnet ist, wobei die zusätzliche Kernzwischenlage durch das Fehlen von PVC gekennzeichnet ist.

10. Film nach einem der vorangegangenen Ansprüche, wobei eine klare bzw. durchsichtige Deckschichtlage die erste thermoplastische Decklage überlagert, wobei die durchsichtige Deckschichtlage durch das Fehlen von PVC gekennzeichnet ist.

11. Film nach einem der vorangegangenen Ansprüche, wobei eine Lage aus druckempfindlichem Klebemittel auf der zweiten thermoplastischen Decklage aufliegt.

12. Film nach Anspruch 11, wobei die druckempfindliche Klebemitteldecke ein Klebemittel auf Gummibasis, ein Acrylklebemittel, ein Vinyletherklebemittel, ein Silikonklebemittel oder eine Kombination von zwei oder mehreren davon beinhaltet.

13. Film nach Anspruch 11, wobei eine Freigabedeckschicht die Lage aus druckempfindlichem Klebemittel überlagert.

14. Film nach Anspruch 13, wobei die Freigabedeckschicht aus einer Freigabe-Beschichtungs zusammensetzung, die auf einer Stützschicht aufliegt, zusammengesetzt ist, wobei die Stützschicht aus Papier, Polymerfilm oder einer Kombination davon besteht.

15. Film nach Anspruch 13, wobei die Freigabedeckschicht aus einer Freigabe-Beschichtungs zusammensetzung, die auf einer Stützschicht aufliegt, zusammengesetzt ist, wobei die Freigabe-Beschichtungs zusammensetzung eine Freigabe-Beschichtungs zusammensetzung aus Silikon ist.

16. Film nach Anspruch 13, wobei die Freigabedeckschicht aus einer Freigabe-Beschichtungs zusammensetzung, die auf einer Stützschicht aufliegt, zusammengesetzt ist, wobei die Freigabe-Beschichtungs zusammensetzung ein Polyorganosiloxan enthält.

17. Film nach einem der vorangegangenen Ansprüche, wobei jede der Decklagen die gleiche Zusammensetzung hat.

18. Film nach einem der vorangegangenen Ansprüche, wobei die Decklagen unterschiedliche Zusammensetzungen haben.

19. Film nach einem der vorangegangenen Ansprüche, wobei die Kernlage und die Decklagen ein Coextrudat enthalten.

20. Film nach einem der vorangegangenen Ansprüche, wobei die erste Decklage aus einem Ionomer, abgeleitet von Natrium, Lithium oder Zink, und einem Ethylen/Methacrylsäure-Copolymer zusammengesetzt ist.

21. Film nach einem der vorangegangenen Ansprüche, wobei die Kernlage pigmentiert ist.

22. Film nach einem der vorangegangenen Ansprüche, wobei die Kernlage klar bzw. durchsichtig ist.

23. Film nach einem der vorangegangenen Ansprüche, wobei die Gesamtdicke des mehrlagigen thermoplastischen Films 1 bis 10 Milli-Inch beträgt und die Dicke der Kernlage 10% bis 90% der Gesamtdicke ausmacht.

24. Film nach einem der vorangegangenen Ansprüche, wobei die Kernlage weiterhin ein Klebematerial beinhaltet.

25. Film nach einem der vorangegangenen Ansprüche, wobei wenigstens eine der Decklagen weiterhin ein Klebematerial, ein Antihaftmittel, ein Gleitmittel oder Kombinationen von zwei oder mehreren davon beinhaltet.

26. Mehrlagiger thermoplastischer Film nach einem der Ansprüche 1 bis 25, wobei der Film ein Elektronik-Schneldefilm
ist und wobei die wenigstens eine zweite thermoplastische Decklage eine klebende Grundierungslage beinhaltet, die über der zweiten Seite der Kernlage angeordnet ist.

27. Mehlagiger thermoplastischer Film nach einem der Ansprüche 1 bis 25, wobei der Film nicht ausgerichtet ist.

28. Schilderstanzverfahren, welches folgendes umfaßt:

Bereitstellen eines druckempfindlichen klebenden Verbundstoffs, wobei der Verbundstoff einen mehrlagigen thermoplastischen Film, eine Lage eines druckempfindlichen Klebemittels und eine Freigabedeckschicht beinhaltet, wobei der mehrlagige thermoplastische Film (1) eine thermoplastische Kernlage mit einer ersten Seite und einer zweiten Seite, (2) eine gegen Abrieb und Abnutzung beständige durchsichtige bzw. klare erste thermoplastische Decklage, die auf der ersten Seite der Kernlage aufliegt, und (3) eine klare bzw. durchsichtige zweite thermoplastische Decklage, die auf der zweiten Seite der Kernlage aufliegt, beinhaltet, wobei die Lage aus druckempfindlichem Klebemittel zwischen der zweiten thermoplastischen Decklage und der Freigabedeckschicht angeordnet ist und vorzugsweise an der zweiten thermoplastischen Decklage haftet, wobei die thermoplastische Kernlage folgendes beinhaltet: (a) ein Polyolefin mit einer Dichte im Bereich von 0,89 bis 0,97 Gram pro Kubikzentimeter, (b) ein zweites thermoplastisches Material, ausgewählt aus der Gruppe, bestehend aus Ethylen-Acrylsäure-Copolymeren, Ethylen-Methacrylsäure-Copolymeren, Ionomeren, abgeleitet von Natrium, Lithium oder Zink, und einem Ethylen/Methacrylsäure-Copolymer oder einer Kombination von zwei oder mehreren davon, wobei das zweite thermoplastische Material in einer Konzentration von 2 Gew.-% bis 25 Gew.-%, basierend auf dem Gewicht der Kernlage, vorliegt, und (c) einen Lichtstabilisator in einer Konzentration von 1.000 bis 10.000 ppm, basierend auf dem Gewicht der Kernlage, wobei die erste thermoplastische Decklage einen Lichtstabilisator in einer Konzentration von 2.000 bis 20.000 ppm, basierend auf dem Gewicht der ersten Decklage, beinhaltet, wobei die zweite thermoplastische Decklage einen Lichtstabilisator in einer Konzentration von 1.000 bis 15.000 ppm, basierend auf dem Gewicht der zweiten Decklage, beinhaltet, wobei die Zusammensetzung der Kernlage und der Decklagen unterschiedlich ist und die Kernlage und die Decklagen durch das Fehlen von PVC gekennzeichnet sind, Schneiden eines Bildes in den mehrlagigen thermoplastischen Film und Übertragen des Bildes auf ein Substrat.

29. Schilderstanzverfahren nach Anspruch 28, wobei der Schritt des Schneidens eines Bildes benötigte Abschnitte des mehrlagigen Films und nicht benötigte Abschnitte des mehrlagigen Films bereitstellt, und wobei das Verfahren weiterhin folgendes umfaßt:

Entfernen der nicht benötigten Abschnitte des mehrlagigen Films aus dem Verbundstoff, Inkontaktbringen einer druckempfindlichen Klebemaske über dem Verbundstoff mit den benötigten Abschnitten mit ausreichendem Druck, um die benötigten Abschnitte an die Maske anzukleben, wobei die Maske mit der ersten thermoplastischen Decklage der benötigten Abschnitte in Kontakt ist, Trennen der Maske und der benötigten Abschnitte von dem Verbundstoff, wobei in den getrennten benötigten Abschnitten das druckempfindliche Klebemittel an die zweite thermoplastische Decklage der benötigten Abschnitte angeklebt ist, Aufbringen der Maske und der benötigten Abschnitte auf das Substrat, an welches das Bild geklebt werden soll, wobei das druckempfindliche Klebemittel, das an die zweite thermoplastische Decklage geklebt ist, mit dem Substrat in Kontakt ist, und Entfernen der Maske von den benötigten Abschnitten, wodurch die benötigten Abschnitte an das Substrat angeklebt bleiben.

30. Verfahren nach einem der Ansprüche 28 oder 29, welches weiterhin das Anordnen einer Zwischenlage zwischen der Kernlage und der zweiten thermoplastischen Decklage umfaßt, wobei die Kernzwischenlage durch das Fehlen von PVC gekennzeichnet ist.

31. Verfahren nach einem der Ansprüche 28 bis 30, wobei der mehrlagige Film nicht ausgerichtet ist.

Revendications

1. Film thermoplastique multicouche, comprenant:
au moins une couche centrale polyoléfinique ayant une première face et une seconde face, la couche centrale comprenant une polyoléfine ayant une masse volumique comprise dans l’intervalle de 0,89 à 0,97 gramme par centimètre cube et une seconde matière thermoplastique choisie parmi des ionomères dérivés du sodium, du lithium ou du zinc et d’un copolymère éthylène/acidé ou anhydride carboxylique insaturé ;
au moins une première pellicule thermoplastique, résistante à l’abrasion, recouvrant la première face de la couche centrale, et
au moins une seconde pellicule thermoplastique, recouvrant la seconde face de la couche centrale, dans lequel la composition de la couche centrale est différente de la composition des pellicules, et la couche centrale et les pellicules sont caractérisées par l’absence de PVC.

2. Film suivant la revendication 1, dans lequel la première pellicule est transparente.

3. Film suivant la revendication 1, dans lequel la seconde pellicule est transparente.

4. Film suivant la revendication 1, dans lequel la couche centrale comprend en outre au moins une troisième matière polymère choisie entre des copolymères éthylène/acidé de vinyle, des polymères éthylène-acrylate modifiés avec un acide, des copolymères éthylène-acrylate modifiés avec un anhydride, des copolymères éthylène/acidé de vinyle modifiés avec un anhydride, des résines éthylène/acidé de vinyle modifiées avec un acide et un acrylate, des résines éthylène/acétate de vinyle modifiées avec un anhydride, des résines de polyéthylène halte densité modifiées avec un anhydride, des résines de polyéthylène linéaire basse densité modifiées avec un anhydride, des résines de polyéthylène basse densité modifiées avec un anhydride et des résines de polypropylène modifiées avec un anhydride, et leurs associations.

5. Film suivant la revendication 1, dans lequel la seconde matière thermoplastique est présente à une concentration de 2 % à 25 % en poids sur la base du poids de la couche centrale.

6. Film suivant la revendication 1, dans lequel la couche centrale comprend un photostabilisant à une concentration de 1000 à 10 000 ppm sur la base du poids de la couche centrale.

7. Film suivant la revendication 1, dans lequel la première pellicule est constituée d’un ionomère dérivé du sodium, du lithium ou du zinc et d’un copolymère éthylène/acidé carboxylique insaturé.

8. Film suivant la revendication 1, dans lequel la polyoléfine a une masse volumique comprise dans l’intervalle de 0,89 à 0,97 gramme par centimètre cube; et dans lequel la couche centrale comprend en outre une troisième matière polymère choisie entre des copolymères éthylène/acidé de vinyle, des polymères éthylène-acrylate modifiés avec un acide, des copolymères éthylène-acrylate modifiés avec un anhydride, des copolymères éthylène/acidé de vinyle modifiés avec un anhydride, des résines éthylène/acidé de vinyle modifiées avec un acide et un acrylate, des résines éthylène/acétate de vinyle modifiées avec un anhydride, des résines de polyéthylène haut densité modifiées avec un anhydride, des résines de polyéthylène linéaire basse densité modifiées avec un anhydride, des résines de polyéthylène basse densité modifiées avec un anhydride et des résines de polypropylène modifiées avec un anhydride et leurs associations, dans lequel la seconde matière thermoplastique est présente à une concentration de 2 % à 25 % en poids sur la base du poids de la couche centrale ; et un photostabilisant à une concentration de 1000 à 10 000 ppm sur la base du poids de la couche centrale ;
et dans lequel la première pellicule thermoplastique résistante à l’abrasion est résistante à l’usure et transparente et comprend un photostabilisant à une concentration de 2000 à 20 000 ppm sur la base du poids de la première pellicule ; et
la seconde pellicule thermoplastique est transparente et comprend un photostabilisant à une concentration de 1000 à 15 000 ppm sur la base du poids de la seconde pellicule.

9. Film suivant l’une quelconque des revendications précédentes, dans lequel une couche intermédiaire est positionnée entre la couche centrale et la seconde pellicule thermoplastique, la couche intermédiaire centrale supplémentaire étant caractérisée par l’absence de PVC.

10. Film suivant l’une quelconque des revendications précédentes, dans lequel une couche de finition transparente recouvre la première pellicule thermoplastique, la couche de finition transparente étant caractérisée par l’absence de PVC.

11. Film suivant l’une quelconque des revendications précédentes, dans lequel une couche d’un adhésif sensible à la
pression recouvre la seconde pellicule thermoplastique.

12. Film suivant la revendication 11, dans lequel la couche d’adhésif sensible à la pression comprend un adhésif à base de caoutchouc, un adhésif acrylique, un adhésif à base d’éther vinylique, un adhésif à base de silicone ou une association de deux ou plus de deux d’entre eux.

13. Film suivant la revendication 11, dans lequel un revêtement de séparation recouvre la couche d’adhésif sensible à la pression.

14. Film suivant la revendication 13, dans lequel le revêtement de séparation est constitué d’une composition de revêtement de séparation recouvrant un revêtement de renforcement, le revêtement de renforcement étant constitué de papier, d’un film polymère ou d’une de leurs associations.

15. Film suivant la revendication 13, dans lequel le revêtement de séparation est constitué d’une composition de revêtement de séparation recouvrant un revêtement de renforcement, la composition de revêtement de séparation étant une composition de revêtement de séparation à base de silicone.

16. Film suivant la revendication 13, dans lequel le revêtement de séparation est constitué d’une composition de revêtement de séparation recouvrant un revêtement de renforcement, la composition de revêtement de séparation comprenant un polyorganosiloxane.

17. Film suivant l’une quelconque des revendications précédentes, dans lequel chacune des pellicules possède la même composition.

18. Film suivant l’une quelconque des revendications précédentes, dans lequel les pellicules ont des compositions différentes.

19. Film suivant l’une quelconque des revendications précédentes, dans lequel la couche centrale et les pellicules comprennent un co-extrudat.

20. Film suivant l’une quelconque des revendications précédentes, dans lequel la première pellicule est constituée d’un ionomère dérivé du sodium, du lithium ou du zinc et d’un copolymère éthylène/acide méthacrylique.

21. Film suivant l’une quelconque des revendications précédentes, dans lequel la couche centrale est pigmentée.

22. Film suivant l’une quelconque des revendications précédentes, dans lequel la couche centrale est transparente.

23. Film suivant l’une quelconque des revendications précédentes, dans lequel l’épaisseur totale du film thermoplastique multicouche est de 1 à 10 mil, l’épaisseur de la couche centrale étant de 10 % à 90 % de l’épaisseur totale.

24. Film suivant l’une quelconque des revendications précédentes, dans lequel la couche centrale comprend en outre une matière adhésive.

25. Film suivant l’une quelconque des revendications précédentes, dans lequel au moins une des pellicules comprend en outre une matière adhésive, un agent antibloquant, un additif de glissement ou une association de deux ou plus de deux de ces agents.

26. Film suivant l’une quelconque des revendications 1 à 25, le film étant un film de coupe électronique, et dans lequel ladite au moins une seconde pellicule thermoplastique comprend une couche d’apprêt adhésive placée sur la seconde face de la couche centrale.

27. Film suivant l’une quelconque des revendications 1 à 25, dans lequel le film est non orienté.

28. Procédé pour la coupe de signes, comprenant les étapes consistant :

à fournir un composite adhésif sensible à la pression, le composite comprenant un film thermoplastique multicouche, une couche d’un adhésif sensible à la pression et un revêtement de séparation ;
le film thermoplastique multicouche comprenant (1) un couche centrale thermoplastique ayant une première
face et une seconde face, (2) une première pellicule thermoplastique transparente, résistante à l’abrasion et à l’usure, recouvrant la première face de la couche centrale, et (3) une seconde pellicule thermoplastique transparente, recouvrant la seconde face de la couche centrale, la couche d’adhésif sensible à la pression étant positionnée entre la seconde pellicule thermoplastique et le revêtement de séparation et adhérant préférentiellement à la seconde pellicule thermoplastique ;

la couche centrale thermoplastique comprenant : (a) une polyoléfine ayant une masse volumique comprise dans l’intervalle de 0,89 à 0,97 gramme par centimètre cube ; (b) une seconde matière thermoplastique choisie dans le groupe consistant en des copolymères éthylène-acide acrylique, des copolymères éthylène-acide méthacrylique, des ionomères dérivés du sodium, du lithium ou du zinc et d’un copolymère éthylène/acide méthacrylique, ou une association de deux ou plus de deux d’entre eux, la seconde matière thermoplastique étant présente à une concentration de 2 % à 25 % en poids sur la base du poids de la couche centrale et (c) un photostabilisant à une concentration de 1000 à 10 000 ppm sur la base du poids de la couche centrale ;

la première pellicule thermoplastique comprenant un photostabilisant à une concentration de 2000 à 20 000 ppm sur la base du poids de la première pellicule ;

la seconde pellicule thermoplastique comprenant un photostabilisant à une concentration de 1000 à 15 000 ppm sur la base du poids de la seconde pellicule ;

la composition de la couche centrale et les compositions des pellicules étant différentes, et la couche centrale et les pellicules étant caractérisées par l’absence de PVC ;

à couper une image dans le film thermoplastique multicouche ; et à transférer l’image à un substrat.

29. Procédé pour la coupe de signes suivant la revendication 28, dans lequel l’étape de coupe d’une image fournit des portions requises du film multicouche et des portions inutiles du film multicouche ;

procédé qui comprend en outre les étapes consistant à :

éliminer les portions inutiles du film multicouche du composite ;

placer un masque adhésif sensible à la pression sur le composite en contact avec les portions requises avec une pression suffisante pour faire adhérer les portions requises au masque, le masque étant en contact avec la première pellicule thermoplastique des portions requises ;

séparer le masque et les portions requises du composite, les portions requises séparées comprenant l’adhésif sensible à la pression adhérant à la seconde pellicule thermoplastique des portions requises ;

placer le masque et les portions requises contre le substrat auquel l’image doit être amenée à adhérer, l’adhésif sensible à la pression adhérant à la seconde pellicule thermoplastique des portions requises étant en contact avec le substrat ; et

éliminer le masque des portions requises, en laissant les portions requises adhérant au substrat.

30. Procédé suivant la revendication 28 ou 29, comprenant en outre le positionnement d’une couche intermédiaire entre la couche centrale et la seconde pellicule thermoplastique, la couche intermédiaire centrale étant caractérisée par l’absence de PVC.

31. Procédé suivant l’une quelconque des revendications 28 à 30, dans lequel le film multicouche est non orienté.
REFERENCES CITED IN THE DESCRIPTION

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