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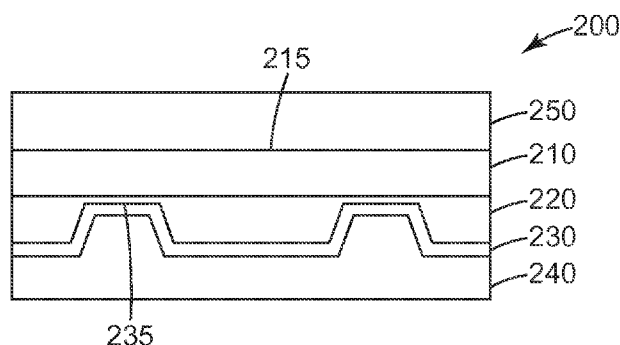
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(54) Title: METHOD FOR PREPARING STRUCTURED ADHESIVE ARTICLES



**Fig. 2**

(57) Abstract: Methods of forming laminating adhesive articles include providing a multi-layer article, an embossing tool with a structured surface, and a support surface tool. The multi-layer articles include a substrate, an adhesive layer, and a liner or may just include an adhesive layer and a liner. The multi-layer article is placed between the structured surface of the embossing tool and the support surface tool. The embossing tool is pressed against the liner and the support surface tool is simultaneously pressed against the substrate by applying pressure or a combination of pressure and heat. The pressing causes the structures on the surface of the embossing tool to distort the liner and the adhesive layer and the support surface tool modifies the surface of the substrate. The distortion in the liner is retained upon release of the applied pressure. Upon removal of the liner from the adhesive layer, the structures on the adhesive layer are unstable, but do not immediately collapse.



## METHOD FOR PREPARING STRUCTURED ADHESIVE ARTICLES

### Field of the Disclosure

This disclosure relates to structured laminating adhesive articles, and methods for making structured laminating adhesive articles, including microstructured laminating adhesive articles.

### Background

Microstructured adhesive articles have been prepared by applying a flowable pressure sensitive adhesive to the surface of a microstructured release liner or the surface of a microstructured molding tool. The process results in the creation of an adhesive having a microstructured surface. When the resulting articles are dry laminated under pressure to substrates such as glass or polymer films, the microstructured features created in the adhesive surface allow air to escape from the bonding interface, thereby minimizing or preventing the formation of bubbles and pinholes.

During lamination, the microstructured features may flatten out and wet the substrate surface. Typically, applied pressure is used to collapse the structures during lamination and form the adhesive bond. However, this process introduces stresses into the adhesive as the adhesive relaxes and tries to return to its initial microstructured state. These stresses can create defects in the adhesive that adversely affect its adhesive and optical properties.

A variety of techniques have been used to prepare adhesive articles with microstructured surfaces. Typically the adhesive surface is contacted to a structured tool or release liner to form a structured pattern in the adhesive layer. For example, in US Patent No. 6,315,651 (Mazurek et al.) microstructured pressure sensitive adhesives are formed by molding an adhesive layer against a microstructured tool or a microstructured liner, and in US Patent Publication No. 2006/0188704 (Mikami et al.) fluid egress structures are formed in an adhesive surface by contacting the adhesive to a structured release tool or a structured release liner. Japanese Utility Model Publication 7-29569 (Kawada et al.) describes forming a tack label for a container such as a bottle. The tack label is readily removable from the bottle surface by soaking the bottle in an aqueous solution, because the adhesive contains an uneven shape to form penetration channels permitting fluid entry to the bondline. The labels are formed by contacting an adhesive to a structured release liner, the release liner having been formed by embossing, and then contacting the label material to the exposed adhesive

surface. Additionally, in US Patent Publication No. 2007/0212635 (Sherman et al.), a structured adhesive surface is formed by pressing a microstructured tool or release liner to a crosslinked adhesive surface.

US Patent No. 5,266,228 (Orr), describes a double-sided adhesive-coated foam tape in which the grooves are fine enough that upon bonding the grooves largely or completely disappear. In Japanese Patent Publication 7-138541 (Shimizu), an adhesion process film is prepared with an embossing process to form fine continuous concave grooves.

### Summary

The present disclosure describes structured laminating adhesive articles, and methods for making structured laminating adhesive articles, including microstructured laminating adhesive articles. Methods of forming laminating articles comprise providing a multi-layer article, and providing an embossing tool with a structured surface, and providing a support surface tool that does not have the same structured surface as the embossing tool. The multi-layer article comprises a substrate with a first major surface and a second major surface, an adhesive layer with a first major surface and a second major surface, where the first major surface of the adhesive layer is contacting the second major surface of the substrate, and a liner with a first major surface and a second major surface, where the first major surface of the liner is contacting the second major surface of the adhesive layer. The method further comprises placing the multi-layer article between the structured surface of the embossing tool and the support surface tool to form a construction, such that the first major surface of the substrate is in contact with the support surface tool, applying pressure or a combination of pressure and heat to the construction such that at least some of the structures on the surface of the embossing tool distort the liner and the adhesive layer. The distortion in the liner is retained upon release of the applied pressure. The method can further comprise separation of the liner from the adhesive layer such that the structures on the adhesive layer are unstable, but do not immediately collapse. The adhesive layer can be contacted to an adherend surface to form an adhesive laminate.

### Brief Description of the Drawings

The present application may be more completely understood in consideration of the following detailed description of various embodiments of the disclosure in connection with the accompanying drawings.

Figures 1 shows cross sectional views of a multi-layer adhesive article prior to embossing according to an embodiment of this disclosure.

Figure 2 shows a cross sectional view of a multi-layer adhesive article of Figure 1 contacted to a structured embossing tool and to a support surface tool, according to an  
5 embodiment of this disclosure.

Figure 3 shows a cross sectional view of the multi-layer adhesive article of Figure 2 upon removal of the structured embossing tool and the support surface tool, according to an embodiment of this disclosure.

Figure 4 shows a cross sectional view of a multi-layer adhesive article prior to  
10 embossing according to an embodiment of this disclosure.

Figure 5 shows a cross sectional view of a multi-layer adhesive article of Figure 4 contacted to a structured embossing tool and to a support surface tool, according to an embodiment of this disclosure.

Figure 6 shows a cross sectional view of the multi-layer adhesive article of Figure 5  
15 upon removal of the structured embossing tool and the support surface tool, according to an embodiment of this disclosure.

Figures 7 shows cross sectional views of a multi-layer adhesive article prior to embossing according to an embodiment of this disclosure.

Figure 8 shows a cross sectional view of a multi-layer adhesive article of Figure 7  
20 contacted to a structured embossing tool and to a support surface tool, according to an embodiment of this disclosure.

Figure 9 shows a cross sectional view of the multi-layer adhesive article of Figure 8 upon removal of the structured embossing tool and the support surface tool, according to an embodiment of this disclosure.

Figure 10 shows a cross sectional view of a multi-layer adhesive article of Figure 7  
25 contacted to a structured embossing tool and to a support surface tool, according to an embodiment of this disclosure.

Figure 11 shows a cross sectional view of the multi-layer adhesive article of Figure 10 upon removal of the structured embossing tool and the support surface tool, according to an  
30 embodiment of this disclosure.

In the following description of the illustrated embodiments, reference is made to the accompanying drawings, in which is shown by way of illustration, various embodiments in which the disclosure may be practiced. It is to be understood that the embodiments may be

utilized and structural changes may be made without departing from the scope of the present disclosure. The figures are not necessarily to scale. Like numbers used in the figures refer to like components. However, it will be understood that the use of a number to refer to a component in a given figure is not intended to limit the component in another figure labeled with the same number.

### Detailed Description

The use of adhesive articles with structured surfaces, especially microstructured surfaces is increasing. These structured surfaces may be temporary features, meaning that the structures are designed to eventually disappear, or permanent features, meaning that the structures are not designed to disappear. Permanently structured adhesive surfaces are generally formed to control the adhesive properties of the adhesive layer, such as making the adhesive layer repositionable (as described, for example, in US Patent No. 6,315,651 (Mazurek et al.)) or to control the physical properties of the adhesive layer, such as for example to build in pillows of air to the adhesive layer to make the adhesive layer cushioning (as described, for example, in PCT Publication No. 97/33946 (Hata)).

There are numerous advantages to using adhesive articles with structured surfaces. One such advantage is air egress from the bond line. When an adhesive bond is formed, the adhesive surface is contacted to an adherend surface. When this contact is made, air can become trapped between the adhesive layer and the adherend surface, causing bubbles or other defects to form in the bond line, the line along which the two surfaces are joined together. This is particularly true when dealing with adherends that are rigid and semi-rigid substrates, but is also true when dealing with flexible substrates. This is particularly true with articles that are hand-laminated, as the lamination is subject to variability based upon operator experience and skill. These defects not only affect the adhesion of the adhesive layer to the adherend surface, but also affect the aesthetic appearance of the bond line or of the overall articles in the case of a graphic article, and thus can ruin the formed article. In optical articles in which light travels through the adhesive layer, the presence of air bubbles and similar defects can greatly affect the optical properties such as light transmission, clarity, and haze and can make the bond line unacceptable, and can impact the viewing experience. To prevent these defects, a structured adhesive surface is often used. Generally, these structures are microstructures. During lamination, the microstructured features flatten out, thereby wetting the substrate surface, and forming a bond to the substrate surface. In the

course of lamination, air bleeds out through the microstructured features to minimize or prevent the formation of bonding defects. The air egress feature is particularly important when dealing with lamination to rigid substrates, especially rigid-to-rigid lamination or where the object to be laminated is relatively large. Currently used methods to prevent defects in such laminations include techniques such as coating the adhesive layer with water or a water-detergent solution to prevent bubble formation during lamination. These techniques require removal of the water by evaporation. Bubble formation is particularly unacceptable in optical applications.

A variety of techniques for creating a temporarily or permanently structured adhesive surface have been developed. In some instances the adhesive layer surface is contacted to the surface of a structured tool. This process of pressing a structured tool to an adhesive surface is typically referred to as embossing in the adhesive art. The inverse of the pattern of the tool surface is formed in the adhesive surface. Upon removal of the structured tool a structured adhesive surface is generated. When this technique is used, the adhesive layer is generally contacted to an adherend soon after removal of the structured tool, such as in a continuous in-line process. In a closely related technique, a structured release liner is contacted to the adhesive surface. The structured release liner is similar to a structured tool in that it also has a structured pattern present on its surface. However, unlike a structured tool, the structured release liner generally is designed to remain in contact with the adhesive layer to form a laminate construction. The structured release liner remains in contact with the adhesive layer until it is desired to laminate the adhesive layer to an adherend, at which time the liner is removed to reveal the structured surface. An advantage of this technique is that because the liner remains adhered to the adhesive surface, it protects the structured surface until the adhesive layer is to be used.

Another technique involves coating an adhesive precursor composition to a structured tool or release liner. This adhesive precursor composition may be an adhesive solution, dispersion or a flowable 100% solids composition or it may contain reactive components that form an adhesive upon curing. Curing in this context is meant to merely mean polymerization and may or may not involve crosslinking. Upon coating of the adhesive precursor composition to the structured tool or release liner, the composition is dried, cooled or cured to form an adhesive layer in contact with the structured tool or release liner. Upon removal of the structured tool or release liner, a structured adhesive surface is exposed as described above.

Typically structured release liners are prepared by embossing. This means that the release liner has an embossable surface which is contacted to a structured tool with the application of pressure and/or heat to form an embossed surface. This embossed surface is a structured surface. The structure on the embossed surface is the inverse of structure on the tool surface, that is to say a protrusion on the tool surface will form a depression on the embossed surface, and a depression on the tool surface will form a protrusion on the embossed surface.

In all of these techniques, the structuring agent, whether a structured tool or a structured release liner, is contacted directly to the surface of the adhesive. In this disclosure, methods are described for forming a structured surface on the surface of an adhesive layer by embossing through the adhesive/liner laminate. Rather than a structured liner being contacted to the adhesive layer, a multi-layer construction comprising an adhesive layer and a liner is embossed with a structured tool to impart a structure to the liner and to the adhesive layer. In this way the advantages of having the structures of a structured adhesive layer protected by a structured liner until use is achieved without having to pre-form a structured liner.

In some embodiments, an additional advantage of the techniques described in the present disclosure is that because the adhesive layer is initially present against a flat liner, the initial state for the adhesive layer is flat. The initial state for the adhesive layer is the state to which it wants to return if no stresses are applied to it. The embossing step produces a structured surface in both the liner and the adhesive layer and thus builds stress into the adhesive layer. Upon removal of the liner, the adhesive layer wants to return to its initial state, in other words it wants to return to being flat. This is in contrast to structured adhesive layers that have an initial state that is structured, such as adhesive layers that are coated onto a structured liner and either cured, dried (if solvent or water borne), or allowed to cool (if hot melt processed). Structured adhesive layers that are coated onto a structured liner tend to be stable, meaning the structures do not tend to collapse, upon removal of the liner. In the present disclosure, however, the structures formed in the adhesive layer tend to be unstable upon removal of the liner. By the structures being unstable, it is meant that the adhesive structures spontaneously collapse and wet out a surface to which the adhesive layer is contacted without the need to apply pressure or heat. Typically, the collapse of the structures is slow enough to give the handler time to laminate the adhesive layer to an adherend, but quickly enough so that adhesive strength builds upon lamination without the need for applied

pressure. Typically, complete collapse of the structures is observed, although in all applications complete collapse of structures is not required, especially if the article is not an optical article, and partial collapse of the structures is sufficient. If total collapse occurs, it typically is complete within 30 days, more typically 10 days, or even less. Thus, unlike systems where an adhesive layer is coated to a structured liner making the structured state the unstressed configuration for the adhesive layer, in this instance the unstressed configuration for the adhesive layer is flat, and the structured configuration is the stressed configuration, and this stress built into the adhesive layer is relieved by the collapse of the structures and a return to the flat configuration. This process is related to the techniques and articles described in co-pending patent application Attorney Docket Number 72396US002, titled “METHOD FOR PREPARING STRUCTURED LAMINATING ADHESIVE ARTICLES” filed on the same day as the present application.

In some embodiments, the embossing process described generates two types of structures. One set of structures are temporary and tend to disappear upon removal of the liner in contact with the adhesive layer, as described above. The second set of structures are permanent and do not tend to disappear upon removal of the liner in contact with the adhesive layer, but rather constitute a permanent change in portions of the surface of the adhesive layer. These permanent changes in portions of the surface of the adhesive layer are effected not by changing the composition of the adhesive layer (such as for example by selective crosslinking in those portions, or selective tackification in those portions) or by adding a new composition or particle to those portions (such as, for example, printing a different composition onto the adhesive layer at selected portions to modify the composition at those locations). Rather, the embossing process changes the topological properties of the adhesive. Thus, the embossing process is not only able to prepare an adhesive layer with a structured surface, it produces an adhesive layer with temporary structures that provide air egress channels and also permanent structures which provide locations with a different level of adhesion from the bulk of the adhesive surface. This process is related to the techniques and articles described in co-pending patent application Attorney Docket Number 74022US002, titled “METHOD FOR PREPARING STRUCTURED ADHESIVE ARTICLES” filed on the same day as the present application.

In addition to forming a structured pattern in the adhesive layer, this disclosure also describes methods for simultaneously changing the surface of the exposed substrate surface. A wide variety of changes to the exposed substrate surface can be effected in this way, such



as, for example, imparting surface roughness or a surface pattern to the surface, changing the gloss of the surface, or providing a matte finish, independent of the embossed pattern imparted on the liner and adhesive layers.

Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings disclosed herein. The recitation of numerical ranges by endpoints includes all numbers subsumed within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5) and any range within that range.

As used in this specification and the appended claims, the singular forms "a", "an", and "the" encompass embodiments having plural referents, unless the content clearly dictates otherwise. For example, reference to "a layer" encompasses embodiments having one, two or more layers. As used in this specification and the appended claims, the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

The term "adhesive" as used herein refers to polymeric compositions useful to adhere together two adherends. As used herein, the term "adherend" refers to any surface to which an adhesive layer can be attached, such as the surface of a substrate, a film, etc. Examples of adhesives are pressure sensitive adhesives.

Pressure sensitive adhesive compositions are well known to those of ordinary skill in the art to possess properties including the following: (1) aggressive and permanent tack, (2) adherence with no more than finger pressure, (3) sufficient ability to hold onto an adherend, and (4) sufficient cohesive strength to be cleanly removable from the adherend. Materials that have been found to function well as pressure sensitive adhesives are polymers designed and formulated to exhibit the requisite viscoelastic properties resulting in a desired balance of tack, peel adhesion, and shear holding power. Obtaining the proper balance of properties is not a simple process.

As used herein, the term "release liner", used interchangeably with the term "liner", refers to a thin flexible sheet which after being placed in intimate contact with an adhesive surface may be subsequently removed without damaging the adhesive coating.

As used herein, the term "structured liner" refers to a liner with a structured surface, and the term "microstructured liner" refers to a liner with a microstructured surface.

As used herein, the term "backing" refers to a thin, flexible sheet which, after being placed in intimate contact with an adhesive cannot be subsequently removed without damaging the adhesive coating.

As used herein, the term "microscopic" refers to features of small enough dimension so as to require an optic aid to the naked eye when viewed from any plane of view to determine its shape. One criterion is found in Modern Optic Engineering by W. J. Smith, McGraw-Hill, 1966, pages 104-105 whereby visual acuity, "... is defined and measured in terms of the angular size of the smallest character that can be recognized." Normal visual acuity is considered to be when the smallest recognizable letter subtends an angular height of 5 minutes of arc on the retina. At a typical working distance of 250 mm (10 inches), this yields a lateral dimension of 0.36 mm (0.0145 inch) for this object.

As used herein, the term "microstructure" means the configuration of features wherein at least 2 dimensions of the features are microscopic. The topical and/or cross-sectional view of the features must be microscopic.

The terms "glass transition temperature" and " $T_g$ " are used interchangeably. Typically  $T_g$  values are measure using Differential Scanning Calorimetry (DSC) unless otherwise noted.

The term "room temperature" refers to ambient temperature, generally 20-22°C, unless otherwise noted.

The term "(meth)acrylate" refers to monomeric acrylic or methacrylic esters of alcohols. Acrylate and methacrylate monomers or oligomers are referred to collectively herein as "(meth)acrylates". Polymers described as "(meth)acrylate-based" are polymers or copolymers prepared primarily (greater than 50% by weight) from (meth)acrylate monomers and may include additional ethylenically unsaturated monomers.

Unless otherwise indicated, "optically transparent" refers to an article, film or adhesive composition that has a high light transmittance over at least a portion of the visible light spectrum (about 400 to about 700 nm).

Unless otherwise indicated, "optically clear" refers to an adhesive or article that has a high light transmittance over at least a portion of the visible light spectrum (about 400 to about 700 nm), and that exhibits low haze.

The term "wavelength of visible light" as used herein encompasses the wavelengths of the light spectrum that constitutes visible light (about 400 to about 700 nm).

Unless otherwise indicated, "self wetting" refers to an adhesive which is very soft and conformable and is able to be applied with very low lamination pressure. Such adhesives exhibit spontaneous wet out to surfaces.

Refractive index is defined herein as the absolute refractive index of a material (e.g., a monomer or the polymerized product thereof) which is understood to be the ratio of the speed of electromagnetic radiation in free space to the speed of the radiation in that material, with the radiation being of sodium yellow light at a wavelength of about 583.9 nanometers (nm). The refractive index can be measured using known methods and is generally measured using an Abbe Refractometer.

The term "adjacent" as used herein when referring to two layers means that the two layers are in proximity with one another with no intervening open space between them. They may be in direct contact with one another (e.g. laminated together) or there may be intervening layers.

The term "alkyl" refers to a monovalent group that is a radical of an alkane, which is a saturated hydrocarbon. The alkyl can be linear, branched, cyclic, or combinations thereof and typically has 1 to 20 carbon atoms. In some embodiments, the alkyl group contains 1 to 18, 1 to 12, 1 to 10, 1 to 8, 1 to 6, or 1 to 4 carbon atoms. Examples of alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, cyclohexyl, n-heptyl, n-octyl, and ethylhexyl.

The term "aryl" refers to a monovalent group that is aromatic and carbocyclic. The aryl can have one to five rings that are connected to or fused to the aromatic ring. The other ring structures can be aromatic, non-aromatic, or combinations thereof. Examples of aryl groups include, but are not limited to, phenyl, biphenyl, terphenyl, anthryl, naphthyl, acenaphthyl, anthraquinonyl, phenanthryl, anthracenyl, pyrenyl, perylenyl, and fluorenyl.

The term "alkylene" refers to a divalent group that is a radical of an alkane. The alkylene can be straight-chained, branched, cyclic, or combinations thereof. The alkylene often has 1 to 20 carbon atoms. In some embodiments, the alkylene contains 1 to 18, 1 to 12, 1 to 10, 1 to 8, 1 to 6, or 1 to 4 carbon atoms. The radical centers of the alkylene can be on the same carbon atom (i.e., an alkylidene) or on different carbon atoms.

The term "heteroalkylene" refers to a divalent group that includes at least two alkylene groups connected by a thio, oxy, or -NR- where R is alkyl. The heteroalkylene can be linear, branched, cyclic, substituted with alkyl groups, or combinations thereof. Some heteroalkylenes are poloxyalkylenes where the heteroatom is oxygen such as for example,

-CH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>-.

The term “arylene” refers to a divalent group that is carbocyclic and aromatic. The group has one to five rings that are connected, fused, or combinations thereof. The other rings can be aromatic, non-aromatic, or combinations thereof. In some embodiments, the arylene group has up to 5 rings, up to 4 rings, up to 3 rings, up to 2 rings, or one aromatic ring. For example, the arylene group can be phenylene.

The term “heteroarylene” refers to a divalent group that is carbocyclic and aromatic and contains heteroatoms such as sulfur, oxygen, nitrogen or halogens such as fluorine, chlorine, bromine or iodine.

The term “aralkylene” refers to a divalent group of formula -R<sup>a</sup>-Ar<sup>a</sup>- where R<sup>a</sup> is an alkylene and Ar<sup>a</sup> is an arylene (i.e., an alkylene is bonded to an arylene).

The terms “free radically polymerizable” and “ethylenically unsaturated” are used interchangeably and refer to a reactive group which contains a carbon-carbon double bond which is able to be polymerized via a free radical polymerization mechanism.

As used herein, “temporarily repositionable” refers to the ability to be adhered to and removed from a substrate without substantial loss of adhesion capability. However, over time the adhesive bond strength builds. This is in contrast to adhesives that are “repositionable” which refers to the ability to be repeatedly adhered to and removed from a substrate without substantial loss of adhesion capability and the adhesive does not develop excessive adhesion build-up over time.

Disclosed herein are methods for forming articles. The methods include providing a multi-layer article, providing an embossing tool with a structured surface, and providing a support surface tool such that the support surface tool does not have the same structured surface as the embossing tool. The multi-layer article comprises a substrate with a first major surface and a second major surface, an adhesive layer with a first major surface and a second major surface, where the first major surface of the adhesive layer is contacting the second major surface of the substrate, and a liner with a first major surface and a second major surface, where the first major surface of the liner is contacting the second major surface of the adhesive layer. Examples of suitable materials for each of the components of the multi-layer article are described below.

A wide variety of substrates are suitable in the multi-layer articles of this disclosure, provided they can be processed using the described methods. Particularly suitable substrates

include films, tape backings, graphic articles, plastic articles, wound dressings, protection films or tapes, rigid or semi-rigid plates or sheets, or release liners.

Examples of films include a wide range of polymeric films prepared from a variety of materials and of a wide range of thicknesses. The films may be of a single layer or multi-layer construction. Examples of polymeric films include films comprising one or more polymers such as cellulose acetate butyrate; cellulose acetate propionate; cellulose triacetate; poly(meth)acrylates such as polymethyl methacrylate; polyesters such as polyethylene terephthalate, and polyethylene naphthalate; copolymers or blends based on naphthalene dicarboxylic acids; polyether sulfones; polyurethanes; polycarbonates; polyvinyl chloride; syndiotactic polystyrene; cyclic olefin copolymers; and polyolefins including polyethylene and polypropylene such as cast and biaxially oriented polypropylene. Examples of multi-layer films include, for example, the multi-layer graphic films described in PCT Publication No. WO 2011/091132 (Dennison et al.) and US Patent Publication No. 2011/0316203 (Emslander et al.). The film may be primed or treated to impart some desired property to one or more of its surfaces. Examples of such treatments include corona, flame, plasma and chemical treatments, or coatings to make the surface more receptive to, for example, printing.

Examples of tape backings include a wide range of materials including polymeric films such as those described above, metal films, paper, creped paper, foams and the like. The tape backings may be opaque, optically transparent, or optically clear depending upon the desired use for the tape. The tape backing may be single layer or a multi-layer construction.

Examples of graphic articles include a wide variety of articles that are used for graphic and display purposes. Examples of graphic and display uses include articles that are colored or contain designs, indicia, or logos such as vehicle laminates, decorative films, banners and wall coverings, signs, billboards, decals, bumper stickers, and the like, as well as, articles that may be transparent or partially transparent such as window films or graphics or films for backlit displays. Often graphic articles are multi-layer articles and may contain multiple layers of films, metal or metal oxide layers, adhesives, etc.

Examples of plastic articles include, for example, plastic sheets and plates, such as for example, the relatively thick polycarbonate sheets used as supporting layers for multilayer articles such as screen protectors.

A wide variety of wound dressings are suitable substrates. The wound dressings may include a wide variety of materials including films, elastomeric materials, support materials

such a cloth, fabric, or non-woven webs, absorbent materials such as hydrogels, and antibacterial agents.

Examples of suitable protection films or tapes include film constructions that contain reinforcing layers such as hurricane-resistant window films, and protective films with  
5 conductive elements to protect electronic components by dissipating electrical charges. Other examples of protection films and tapes, include, for example, paint protection films which are applied to vehicles such as automobiles, subways, buses, airplanes and the like to protect the paint from damage from rock chips. Similar protection films are used on wind turbine blades and helicopter blades to protect the surface from damage and reduce the wind  
10 resistance of the surface.

Examples of rigid and semi-rigid plates and sheets include a wide range of optical substrates. As used herein, the term "optical substrate" refers to a substrate that can be used to produce an optical effect. The substrate can be any suitable thickness. The optical  
15 substrates often are at least partially transmissive, reflective, antireflective, polarizing, optically clear, or diffusive with respect to some wavelengths of the electromagnetic spectrum (e.g., wavelengths in the visible, ultraviolet, or infrared regions of the electromagnetic spectrum). Examples of plates include a wide array of optically clear materials. Examples of suitable plates include a variety of glasses or from polymeric materials such as polycarbonate or polymethyl methacrylate. The plates may have a wide  
20 variety of coatings on them such as, for example, tinted coatings, anti-reflection coatings, and anti-glare coatings. Sheets are similar to plates but generally are thinner and less rigid than plates. Examples of sheets include, for example, optically clear semi-rigid substrates of glass or other optically clear materials that are 25-100 micrometers in thickness.

The substrate may also comprise a release liner. Any suitable release liner can be  
25 used. Exemplary release liners include those prepared from paper (e.g., Kraft paper) or polymeric material (e.g., polyolefins such as polyethylene or polypropylene, ethylene vinyl acetate, polyurethanes, polyesters such as polyethylene terephthalate, and the like). At least some release liners are coated with a layer of a release agent such as a silicone-containing material or a fluorocarbon-containing material. Exemplary release liners include, but are not  
30 limited to, liners commercially available from CP Film (Martinsville, Va.) under the trade designation "T-30" and "T-10" that have a silicone release coating on polyethylene terephthalate film. Other exemplary release liners are those described in US Patent Publication No. 2011/0316203 (Emslander et al.). The liner can have a microstructure on its

surface that is imparted to the adhesive to form a microstructure on the surface of the adhesive layer.

Particularly suitable films include films suitable for use in graphic articles such as films prepared from a polyolefin, polyester, vinyl, cellulose ester, polyurethane, or blends or combinations thereof. A blend includes, for example, includes a composition containing more than one polyolefin material, whereas a combination is mixture of two or more types of materials, such as a composition containing a polyolefin and a polyurethane. These films may include coatings or layers that may be continuous or discontinuous, such as for example printed indicia or logos. Additionally, as will be discussed below, coatings or indicia can be applied to the film surface after the simultaneous embossing/substrate surface modification process of this disclosure.

While a wide variety of adhesive types are suitable in the practice of this disclosure, typically the adhesives are pressure sensitive adhesives. A wide variety of pressure sensitive adhesives are suitable. In some embodiments, the adhesive is optically transparent or even optically clear. Examples of each of the suitable classes of adhesives are described below.

Among the pressure sensitive adhesives useful in the articles of this disclosure are those based on natural rubbers, synthetic rubbers, styrene block copolymers, polyvinyl ethers, acrylics, poly- $\alpha$ -olefins, silicones, urethanes or ureas. In many embodiments, the pressure sensitive adhesives are self wetting. Self wetting refers to adhesives which are very soft and conformable and are able to be applied with very low lamination pressure. Such adhesives exhibit spontaneous wet out to surfaces.

Useful natural rubber pressure sensitive adhesives generally contain masticated natural rubber, from 25 parts to 300 parts of one or more tackifying resins to 100 parts of natural rubber, and typically from 0.5 to 2.0 parts of one or more antioxidants. Natural rubber may range in grade from a light pale crepe grade to a darker ribbed smoked sheet and includes such examples as CV-60, a controlled viscosity rubber grade and SMR-5, a ribbed smoked sheet rubber grade. Tackifying resins used with natural rubbers generally include but are not limited to wood rosin and its hydrogenated derivatives; terpene resins of various softening points, and petroleum-based resins, such as, the "SCOREZ 1300" series of C5 aliphatic olefin-derived resins from Exxon, and "PICCOLYTE S" series, polyterpenes from Hercules, Inc. Antioxidants are used to retard the oxidative attack on natural rubber, which can result in loss of the cohesive strength of the natural rubber adhesive.

Another useful class of pressure sensitive adhesives is synthetic rubber-based adhesives. Such adhesives are generally rubbery elastomers, which are either self-tacky or non tacky and require tackifiers. Self-tacky synthetic rubber pressure sensitive adhesives include for example, butyl rubber, a copolymer of isobutylene with less than 3 percent isoprene, polyisobutylene, a homopolymer of isoprene, polybutadiene, such as “TAKTENE 220 BAYER” or styrene/butadiene rubber. Butyl rubber pressure sensitive adhesives often contain an antioxidant such as zinc dibutyl dithiocarbamate. Polyisobutylene pressure sensitive adhesives do not usually contain antioxidants. Synthetic rubber pressure sensitive adhesives, which generally require tackifiers, generally comprise polybutadiene or styrene/butadiene rubber, from 10 parts to 200 parts of a tackifier, and generally from 0.5 to 2.0 parts per 100 parts rubber of an antioxidant such as “IRGANOX 1010”. An example of a synthetic rubber is “AMERIPOL 1011A”, a styrene/butadiene rubber available from BF Goodrich. Tackifiers that are useful include derivatives of rosins such as “FORAL 85”, a stabilized rosin ester from Hercules, Inc., the “SNOWTACK” series of gum rosins from Tenneco, and the “AQUATAC” series of tall oil rosins from Sylvachem; and synthetic hydrocarbon resins such as the “PICCOLYTE A” series, polyterpenes from Hercules, Inc., the “ESCOREZ 1300” series of C<sub>5</sub> aliphatic olefin-derived resins, the “ESCOREZ 2000” Series of C<sub>9</sub> aromatic/aliphatic olefin-derived resins, and polyaromatic C<sub>9</sub> resins, such as the “PICCO 5000” series of aromatic hydrocarbon resins, from Hercules, Inc.

Styrene block copolymer pressure sensitive adhesives generally comprise elastomers of the A-B or A-B-A type, where A represents a thermoplastic polystyrene block and B represents a rubbery block of polyisoprene, polybutadiene, or poly(ethylene/butylene), and resins. Examples of the various block copolymers useful in block copolymer pressure sensitive adhesives include linear, radial, star and tapered styrene-isoprene block copolymers such as “KRATON D1107P”, available from Shell Chemical Co., and “EUOPRENE SOL TE 9110”, available from EniChem Elastomers Americas, Inc.; linear styrene-(ethylene-butylene) block copolymers such as “KRATON G1657”, available from Shell Chemical Co.; linear styrene-(ethylene-propylene) block copolymers such as “KRATON G1750X”, available from Shell Chemical Co.; and linear, radial, and star styrene-butadiene block copolymers such as “KRATON D1118X”, available from Shell Chemical Co., and “EUOPRENE SOL TE 6205”, available from EniChem Elastomers Americas, Inc.

Polyvinyl ether pressure sensitive adhesives are generally blends of homopolymers of vinyl methyl ether, vinyl ethyl ether or vinyl iso-butyl ether, or blends of homopolymers of



vinyl ethers and copolymers of vinyl ethers and acrylates to achieve desired pressure sensitive properties. Depending on the degree of polymerization, homopolymers may be viscous oils, tacky soft resins or rubber-like substances. Polyvinyl ethers used as raw materials in polyvinyl ether adhesives include polymers based on: vinyl methyl ether such as  
5 “LUTANOL M 40”, available from BASF, and “GANTREZ M 574” and “GANTREZ 555”, available from ISP Technologies, Inc.; vinyl ethyl ether such as “LUTANOL A 25”, “LUTANOL A 50” and “LUTANOL A 100”; vinyl isobutyl ether such as “LUTANOL I30”, “LUTANOL I60”, “LUTANOL IC”, “LUTANOL I60D” and “LUTANOL I 65D”; methacrylate/vinyl isobutyl ether/acrylic acid such as “ACRONAL 550 D”, available from  
10 BASF.

Acrylic pressure sensitive adhesives generally have a glass transition temperature of about 20°C or less, more typically 0°C or less and may comprise from 100 to 80 weight percent of a C<sub>3</sub> -C<sub>12</sub> alkyl ester component such as, for example, isooctyl acrylate, 2-ethylhexyl acrylate and n-butyl acrylate and from 0 to 20 weight percent of a polar component  
15 such as, for example, acrylic acid, methacrylic acid, ethylene vinyl acetate, N-vinyl pyrrolidone and styrene macromer. Typically, the acrylic pressure sensitive adhesives comprise from 0 to 20 weight percent of acrylic acid and from 100 to 80 weight percent of isooctyl acrylate. The acrylic pressure sensitive adhesives may be self-tacky or tackified. Useful tackifiers for acrylics are rosin esters such as “FORAL 85”, available from Hercules,  
20 Inc., aromatic resins such as “PICCOTEX LC-55WK”, aliphatic resins such as “PICCOTAC 95”, available from Hercules, Inc., and terpene resins such as  $\alpha$ -pinene and  $\beta$ -pinene, available as “PICCOLYTE A-115” and “ZONAREZ B-100” from Arizona Chemical Co.

Poly- $\alpha$ -olefin pressure sensitive adhesives, also called a poly(1-alkene) pressure sensitive adhesives, generally comprise either a substantially uncrosslinked polymer or a  
25 uncrosslinked polymer that may have radiation activatable functional groups grafted thereon as described in U.S. Pat. No. 5,209,971 (Babu et al.). The poly- $\alpha$ -olefin polymer may be self tacky and/or include one or more tackifying materials. In addition, the polymer generally is predominantly amorphous. Useful poly- $\alpha$ -olefin polymers include, for example, C<sub>3</sub> -C<sub>18</sub> poly(1-alkene) polymers, generally C<sub>5</sub> -C<sub>12</sub>  $\alpha$ -olefins and copolymers of those with C<sub>3</sub> and  
30 more typically C<sub>6</sub> -C<sub>8</sub> and copolymers of those with C<sub>3</sub>. Tackifying materials are typically resins that are miscible in the poly- $\alpha$ -olefin polymer. The total amount of tackifying resin in the poly- $\alpha$ -olefin polymer ranges between 0 to 150 parts by weight per 100 parts of the poly-

$\alpha$ -olefin polymer depending on the specific application. Useful tackifying resins include resins derived by polymerization of C<sub>5</sub> to C<sub>9</sub> unsaturated hydrocarbon monomers, polyterpenes, synthetic polyterpenes and the like. Examples of such commercially available resins based on a C<sub>5</sub> olefin fraction of this type are “WINGTACK 95” and “WINGTACK 15” tackifying resins available from Goodyear Tire and Rubber Co.

Silicone pressure sensitive adhesives comprise two major components, a polymer or gum, and a tackifying resin. The polymer is typically a high molecular weight polydimethylsiloxane or polydimethyldiphenylsiloxane, that contains residual silanol functionality (SiOH) on the ends of the polymer chain, or a block copolymer comprising polydiorganosiloxane soft segments and urea terminated hard segments. The tackifying resin is generally a three-dimensional silicate structure that is endcapped with trimethylsiloxy groups (OSiMe<sub>3</sub>) and also contains some residual silanol functionality. Examples of tackifying resins include SR 545, from General Electric Co., Silicone Resins Division, Waterford, NY, and MQD-32-2 from Shin-Etsu Silicones of America, Inc., Torrance, CA. Manufacture of typical silicone pressure sensitive adhesives is described in U.S. Pat. No. 2,736,721 (Dexter). Manufacture of silicone urea block copolymer pressure sensitive adhesive is described in U.S. Pat. No. 5,214,119 (Leir et al.). One particularly suitable class of silicone pressure sensitive adhesives is the silicone polyoxamide-based pressure sensitive adhesives. These materials are described in, for example, US Patent No. 7,371,464 (Sherman et al.), and US Patent No. 7,705,103 (Sherman et al.).

Polyurethane and polyurea pressure sensitive adhesives useful in the invention include, for example, those disclosed in WO 00/75210 (Kinning et al.) and in U.S. Patent Nos. 3,718,712 (Tushaus); 3,437,622 (Dahl); and 5,591,820 (Kydonieus et al.). Additionally, the urea-based pressure sensitive adhesives described in US Patent Publication No. 2011/0123800 (Sherman et al.) and the urethane-based pressure sensitive adhesives described in US Patent Publication No. 2012/0100326 (Sherman et al.) may be particularly suitable.

In some embodiments, the pressure sensitive adhesive comprises an optically clear pressure sensitive adhesive. Examples of suitable optically clear pressure sensitive adhesives include those based on natural rubbers, synthetic rubbers, styrene block copolymers, polyvinyl ethers, acrylics, poly- $\alpha$ -olefins, silicones, urethanes or ureas. Examples of each of these classes of pressure sensitive adhesives are described above.

One particularly suitable class of pressure sensitive adhesives are (meth)acrylate-based pressure sensitive adhesives. Typically the (meth)acrylate-based pressure sensitive

adhesive is a copolymer that comprises one or more alkyl (meth)acrylate monomers and one or more reinforcing monomer.

To achieve pressure sensitive adhesive characteristics, the corresponding copolymer can be tailored to have a resultant glass transition temperature ( $T_g$ ) of less than about  $20^{\circ}\text{C}$ , more typically less than about  $0^{\circ}\text{C}$ . Such copolymers typically are derived from monomers comprising about 40% by weight to about 98% by weight, often at least 70% by weight, or at least 85% by weight, or even about 90% by weight, of at least one alkyl (meth)acrylate monomer that, as a homopolymer, has a  $T_g$  of less than about  $0^{\circ}\text{C}$ . Examples of such alkyl (meth)acrylate monomers are those in which the alkyl groups comprise from about 4 carbon atoms to about 12 carbon atoms and include, but are not limited to, n-butyl acrylate, 2-ethylhexyl acrylate, isooctyl acrylate, isononyl acrylate, isodecyl acrylate, and mixtures thereof.

Examples of suitable reinforcing monomers include vinyl monomers and alkyl (meth)acrylate monomers which, as homopolymers, have a  $T_g$  greater than  $0^{\circ}\text{C}$ , such as methyl acrylate, methyl methacrylate, isobornyl acrylate, vinyl acetate, styrene, and the like, as well as basic or acidic monomers, such as (meth)acrylamides and (meth)acrylic acids. A mixture of polymers may also be used. In some embodiments, the mixture of polymers include some polymers with acid functional groups and other polymers with base functional groups so that when the polymers are mixed a pseudo-crosslink is formed by an acid-base interaction between the polymers.

In some embodiments, the poly(meth)acrylic pressure sensitive adhesive copolymer is derived from between about 1 and about 20 weight percent of acrylic acid and between about 99 and about 80 weight percent of at least one of isooctyl acrylate, 2-ethylhexyl acrylate or n-butyl acrylate composition. In some embodiments, the pressure sensitive adhesive copolymer is derived from between about 2 and about 10 weight percent acrylic acid and between about 90 and about 98 weight percent of at least one of isooctyl acrylate, 2-ethylhexyl acrylate or n-butyl acrylate composition.

In some embodiments, it may be desirable for the adhesive layer to be a crosslinked pressure sensitive adhesive as taught in US Patent Publication No. 2007/0212535 (Sherman et al.). Embossing the surface of a crosslinked pressure sensitive adhesive to create a microstructured adhesive surface minimizes the formation of stresses within the adhesive after lamination because both the pre-structured and final states of the adhesive are substantially planar. Therefore, the structure is unstable when not in contact with the

microstructured liner or molding tool. This is in contrast to microstructured adhesives produced by coating a flowable adhesive onto a microstructured release liner or a microstructured molding tool, where the initial state of the adhesive to which it tries to return is that of the microstructured configuration, while the final state is substantially planar.

5           The adhesive layer can be any suitable thickness as long as the adhesive layer is thicker than the size of the microstructures embossed into the adhesive layer. In general, the thickness ranges from 10 micrometers (about 0.4 mils) to 1500 micrometers (about 60 mils). More typically the adhesive is generally 25 micrometers (about 1 mil) to 51 micrometers (about 2 mils) thick.

10           The adhesive layer may be continuous or discontinuous. Discontinuous adhesive layers can have a variety of configurations, including random distributions or patterned distributions. Among suitable patterned distributions are stripes (either straight or wavy) and dots (in a variety of shapes and sizes). When the adhesive layer is discontinuous, it is desirable that the adhesive layer be present in those locations where the embossing tool  
15           contacts the release liner to ensure that the embossing tool imparts the structure to the adhesive layer. Additionally, the adhesive layer, whether continuous or discontinuous, can be a segmented adhesive layer. A segmented adhesive layer is one that contains segments which contain different adhesive compositions. A segmented adhesive layer is different from an adhesive blend. In an adhesive blend, a single adhesive composition comprises a mixture  
20           of different adhesive components. In a segmented adhesive layer, different segments of the adhesive layer comprise different compositions. The discontinuous adhesive layer or segmented adhesive layer can be prepared through the use of a variety of different coating techniques, for example, stripe coating, coextrusion, or a variety of different printing techniques.

25           The multi-layer articles of this disclosure also include a liner, often times referred to as a release liner. Any suitable release liner can be used. Exemplary release liners include those prepared from paper (e.g., Kraft paper) or polymeric material (e.g., polyolefins such as polyethylene or polypropylene, ethylene vinyl acetate, polyurethanes, polyesters such as polyethylene terephthalate, and the like, and combinations thereof). At least some release  
30           liners are coated with a layer of a release agent such as a silicone-containing material or a fluorocarbon-containing material. Exemplary release liners include, but are not limited to, liners commercially available from CP Film (Martinsville, Va.) under the trade designation "T-30" and "T-10" that have a silicone release coating on polyethylene terephthalate film.

Typically, the liner has a thickness of from 25 micrometers (1 mil) to 127 micrometers (5 mils), more typically from 25 micrometers (1 mil) to 84 micrometers (3.3 mils).

In some embodiments, the liner is a separately formed article and in other articles the adhesive layer and liner, or even the substrate, adhesive layer, and liner are all generated simultaneously by coextrusion. In this process, separate molten polymeric streams are contacted to form the multilayer article. Particularly suitable are the coextruded release liners described in US Patent Publication No. 2011/0316203 (Emslander et al.). In these liners, the release layer comprises a release agent. The release layer may also comprise other polymers, blended with the release agent. Typically, the release agent comprises copolymers of ethylene and alpha-olefins having from 3 to about 10 carbon atoms and density no greater than 0.91 g/cc. Suitable alpha-olefins include 1-butene, 1-hexene, 1-octene, and combinations thereof. Copolymers of ethylene and octene-1 are particularly suitable for use with acrylate-based pressure sensitive adhesives. The copolymers may be either block copolymers or non-block copolymers. In some embodiments, the copolymer has a density of no greater than 0.91 g/cc, for example, no greater than 0.89 g/cc. Suitable copolymers are commercially available from Dow Chemical Company, Midland, MI, under the tradename "INFUSE" and from ExxonMobil Chemical Company, Houston, TX, under the tradename "EXACT". In some embodiments, the copolymer is polyolefin polymer made using a metallocene catalyst.

As stated above, the release agent may additionally be blended with other polymers to form the release layer. Examples of the polymers useful for blending with the release agent include other polyolefin polymers having a density of no greater than 0.91 g/cc; polyethylene (including low density polyethylene), polydiorganosiloxane polyoxamide copolymers, polypropylene and those polymers sold under the trade names "NUCREL", "BASELL HL 456J", "VISTAMAX", "BYNEL", and combinations thereof.

The structured embossing tool is an implement for imparting a structure to the liner and adhesive layer and which may be continuously reused in the process. Typically, the structured embossing tool is a molding tool. Structured molding tools can be in the form of a planar stamping press, a flexible or inflexible belt, or a roller. Furthermore, molding tools are generally considered to be tools from which the structured pattern is generated in the surface by embossing, coating, casting, or platen pressing and do not become part of the finished article. In many embodiments, the structured tool is a microstructured tool, meaning that the tool has a microstructured pattern on its surface.

A broad range of methods are known to those skilled in this art for generating microstructured molding tools. Examples of these methods include but are not limited to photolithography, etching, discharge machining, ion milling, micromachining, and electroforming. Microstructured molding tools can also be prepared by replicating various microstructured surfaces, including irregular shapes and patterns, with a moldable material such as those selected from the group consisting of crosslinkable liquid silicone rubber, radiation curable urethanes, etc. or replicating various microstructures by electroforming to generate a negative or positive replica intermediate or final embossing tool mold. Also, microstructured molds having random and irregular shapes and patterns can be generated by chemical etching, sandblasting, shot peening or sinking discrete structured particles in a moldable material. Additionally any of the microstructured molding tools can be altered or modified according to the procedure taught in US Patent No. 5,122,902 (Benson ). The tools may be prepared from a wide range of materials including metals such as nickel, copper, steel, or metal alloys, or polymeric materials.

The support surface tool is similar to the embossing tool in that it contains a surface designed to change the surface characteristics of the surface that it contacts. The support surface tool may have a structured surface or it may have a surface that has been rendered smooth, smoother than the normal surface roughness which the support tool would otherwise have. When the support surface tool contains a structured surface, the structured surface of the support surface tool is different from the structured surface of the embossing tool. As part of the structure, the support surface tool can impart on the substrate surface patterns that can include indicia, logos, and the like. Thus, the structural pattern on the support surface tool can change the surface characteristics of the substrate surface, but unlike the embossing pattern on the structured surface of the tool, this pattern is designed to only alter the characteristics of the surface of the substrate and does not affect the other layers. The surface structure of the support surface tool can be generated using the methods described above. For example, the support surface tool may contain a textured surface to impart a matte-type finish to the substrate surface. In other embodiments, for example when it may be desirable to impart a high gloss to the substrate surface, the support surface tool surface is very smooth. In this instance, the support surface tool is one in which the surface has been rendered very smooth, smoother than the normal surface roughness of the support surface, through the use of polishing, coating, or by the placement of a sleeve or shell over the support surface, or other techniques known to decrease surface roughness.

Pressure or a combination of pressure and heat, is applied to the construction comprising the support surface tool, multi-layer article, and structured embossing tool, and is then released. The applied pressure causes at least some of the structures on the surface of the embossing tool to distort the liner and the adhesive layer and may distort the second major surface of the substrate. Simultaneously, the contact of the support surface tool to the first major surface of the substrate, modifies the first major surface of the substrate. As described above, this modification may comprise imparting a structure to the first major surface of the substrate or smoothing of the first major surface of the substrate to increase its gloss. The distortion in the liner is retained upon release of the applied pressure, such that a permanent change is made in the liner. In some embodiments, it may be desirable for a combination of heat and pressure to be applied.

The construction comprising the support surface tool, multi-layer article, and structured embossing tool may be together for a relatively long time or a relatively short time. For example, if a platen press is used to prepare the article the support surface tool may be the support bed of the press or a tool attached to the support bed of the press, and the structured embossing tool may be the platen or the tool may be attached to the platen. In other embodiments, the support surface tool may be support roller, and the embossing tool may be a roller with a structured surface, and the multi-layer article may be passed between the rollers. Thus the process of simultaneously embossing a pattern onto the adhesive layer and the liner and also modifying the outer surface of the substrate, can be done in a batch wise process, a semi-continuous process or a continuous process. In a batch wise process, the multi-layer article is placed in an apparatus such as a platen press, the pressure is applied through the platen that is either a structured tool or has a structured tool attached to it, pressure is released and the embossed multi-layer article is removed. In a semi-continuous process, instead of a discrete multi-layer article, the multi-layer article is a continuous web. The web can then be drawn into the press, pressed, and drawn out of the press. Additionally, a series of presses could be used to press multiple regions of the web at a time. An example of a continuous process is the use of rollers. The multi-layer article can be fed between a pair of rollers, one roller being the support surface tool and the other roller being the structured embossing tool. In this process, the pressure is supplied by passing a web of multi-layer article between the two rollers. A pair of such rollers is often referred to as a nip.

In some embodiments, it is possible to prepare embossed adhesive articles from raw materials in a continuous process. As described above, the multi-layer article comprising a

substrate, adhesive layer and liner can be prepared by coextrusion. In this process, at least two or all three of the layers of the substrate, adhesive and liner materials can be coextruded and contacted to form the multi-layer article. For example the substrate and adhesive layers can be coextruded and the coextrusion output contacted to a moving web of release liner. In other embodiments, the substrate, adhesive and liner layer can be coextruded and contacted to each to form the multi-layer article. The moving multi-layer web can then be passed between a pair of rollers, one comprising the support surface tool and the other comprising the structured embossing tool, to form the embossed article in a single continuous process.

The article formed by this process is a multi-layer article comprising a substrate, an adhesive layer, and a liner as described above. The articles comprise a substrate with a first major surface and a second major surface, an adhesive layer with a first major surface and a second major surface, where the first major surface of the adhesive layer is contacting the second major surface of the substrate, and a liner with a first major surface and a second major surface, where the first major surface of the liner is contacting the second major surface of the adhesive layer. The first major surface of the substrate has been modified by contact with the support surface tool. The second major surface of the liner contains a plurality of concave structures that correspond to a plurality of concave structures in the adhesive layer, produced by contact with the structured embossing tool. Depending upon the nature of the article to be formed, the plurality of concave structures may or may not distort the second major surface of the substrate. Additionally, in some embodiments, the article may also comprise a plurality of convex structures protruding from the adhesive layer surface as described in co-pending patent application Attorney Docket Number 74022US002, titled "METHOD FOR PREPARING STRUCTURED ADHESIVE ARTICLES" filed on the same day as the present application. To form the plurality of convex structures protruding from the adhesive layer surface, typically the support surface is a hard surface, the hard surface being prepared from a hard material such as a metal or other suitable hard material.

Typically, the structures formed in the adhesive layer by the process of embossing the adhesive layer through the liner are unstable as described above, but the structures do not immediately collapse, or do not completely collapse upon removal of the liner from the adhesive layer. If the structures immediately collapsed upon removal of the liner, the advantages of preparing a structured adhesive surface, such as air egress, would be lost. However, because the structures are unstable upon removal of the liner, it is desirable to laminate the adhesive layer to the desired substrate as soon as possible after removal of the



liner. By the structures being unstable, it is meant that upon removal of the liner, the stresses built into the adhesive layer by the embossing process are removed and the adhesive layer begins to return to its original, flat configuration. It is often desirable that the structures do collapse and disappear with time, especially if the adhesive is optically clear and is used in an optical application, but depending upon the use for the formed articles, partial collapse may be sufficient.

A wide variety of structures are possible for the concave structures in the articles of this disclosure. The structures may have a wide variety of shapes and sizes. In some embodiments, the concave structures are concave microstructures, meaning that they are microstructured features with at least 2 dimensions of the structures of microscopic size. The microstructured features may assume a variety of shapes. Representative examples include hemispheres, prisms (such as square prisms, rectangular prisms, cylindrical prisms and other similar polygonal features), pyramids, ellipses, grooves (e.g., V-grooves), channels, and the like. In general, it is desirable to include topographical features that promote air egress at the bonding interface when the adhesive layer is laminated to a substrate. In this regard, V-grooves and channels that extend to the edge of the article are particularly useful. The particular dimensions and patterns characterizing the microstructured features are selected based upon the specific application for which the article is intended.

The substrate surface that has been simultaneously modified by contact with the support surface tool can have a variety of different patterns and topographies. In some embodiments, the surface can be textured to provide a matte type finish, in other embodiments, the surface can be made smoother to provide a higher gloss, in still other embodiments, the surface can have a structured pattern impressed upon it. This pattern can be continuous or discontinuous, and can include logos, indicia, and the like if desired. For example, the pattern could include a company logo or symbol to provide brand recognition. The modification of the surface can be part of a larger process of surface modification, for example, the surface modification may provide a textured surface or a partially textured surface that is more receptive to the application of an additional coating or lamination.

Additionally, as mentioned above, additional modification can be made to the substrate surface after the simultaneous embossing/substrate surface modification process. Examples of such additional modifications include applications of coatings and printing. Examples of coatings include, for example, the application of tinting or coloring coatings, the applications of hardcoats to protect the surface of the substrate, and the like. Examples of

printing include screen printing, inkjet printing, and electrophotographic printing to apply indicia or designs to the film surface. The application of indicia or designs to the film surface may be done in conjunction with the substrate surface modification process described above, for example, selective areas may be surface textured to make the surface more receptive to the application of a coating or printing. Additionally, as mentioned above, the surface modification may make the substrate more receptive to lamination, for example a textured surface may be more receptive to the application of an adhesive laminate.

Depending upon the nature of the elements present in the articles prepared by the simultaneous embossing/substrate surface modification, they can either be used as is, or can be used to form other adhesive articles. For example, if the substrate is an optical film, and the adhesive layer is optically clear, the liner can be removed from the adhesive layer and the adhesive layer, which now contains a structured surface, can be laminated to a wide range of substrate surfaces to form articles. If the substrate is a release liner, the article is sometimes referred to as a “transfer tape” because the adhesive layer is a free-standing film adhered to two liners. When the release liner is removed from the transfer tape, the exposed adhesive surface can be laminated to a wide range of adherend surfaces. Examples of suitable adherend surfaces include a wide range of films and tape backings or a variety of rigid or semi-rigid substrates, such as the exterior surface of an article. The liner that has been embossed can then be removed to expose the structured adhesive surface and the structured adhesive surface can be laminated to the surface of an adherend. This adherend can be the same or different from the other adherend, for example, the transfer tape may be laminated to two films, to a film and a rigid substrate, or to two rigid substrates.

Among the articles that can be prepared using the methods of this disclosure include articles suitable for graphic applications. Examples of graphic applications include applications where the articles are optically clear or optically transparent as well as applications where the outer surface of the article is opaque, tinted, translucent, or contains indicia or designs. Applications where the articles are optically clear or optically transparent include windows, vehicle windshields, displays, solar cells, protection films, over-laminates, and the like. Applications where the articles are opaque, tinted, translucent, or contains indicia or designs include vehicle laminates, banners and wall coverings, billboards, signs, bumper stickers, and the like, as well as electronic displays such as backlit displays. With optically clear articles, useful adhesives are selected such that upon dry lamination to a substrate, the adhesive layer has a haze after lamination, measured according to ASTM D

1003-95, of less than 50%, more typically less than 10%, less than 3%, or even less than 1% of the haze of the adhesive layer before lamination. Such adhesives also generally do not interfere with light transmission over the wavelength region of interest (e.g., the visible region). For example, after dry lamination, the adhesive layer may have a luminous  
5 transmittance of at least 85%, more typically 90%, or even 95% to 99.9%, and a haze of less than 25%, more typically less than 10%, less than 5% or even less than 2%, as measured according to ASTM D 1003-95.

In Figure 1, a cross section of multi-layer article **100** is shown which comprises substrate layer **110**, adhesive layer **120**, and liner **130**. Adhesive layer **120** is shown as a  
10 continuous layer, but as described above this layer can comprise a discontinuous layer, or a stripe coated layer, etc. The interface between the adhesive layer **120** and liner **130** is designated as **135**. The outer surface of substrate layer **110** is designated as **115**, and is shown to have a pattern. Surface **115** can have a regular pattern as shown or it may comprise a roughened surface pattern or it may comprise natural surface roughness which is a random  
15 texture.

Figure 2 shows a cross section of multi-layer article **200**, which is article **100** to which embossing tool **240**, and support surface tool **250** have been simultaneously pressed to substrate layer **210**, adhesive layer **220**, and liner **230**. The structures of embossing tool **240** deform liner **230** and adhesive layer **220** as shown by the liner/adhesive interface **235**, but the  
20 deformation of the tool structures does not deform substrate **210**. Surface **215**, the outer surface of substrate layer **210**, has been made smooth by the pressing of support surface tool **250**. The depth that embossing tool **240** is pressed into the liner **230** and adhesive layer **220** is not necessarily to scale.

Figure 3 shows a cross section of multi-layer article **300**, which is article **200** from  
25 which embossing tool **240** has been removed, support surface tool **250** has been removed, and liner **230** has been removed. Support layer **310** has smoothed surface **315**, and adhesive layer **320** has surfaces **325**, which are the bottom surfaces of the adhesive layer where the embossed structuring has occurred. These structures are retained at least temporarily after the removal of the liner.

30 In Figure 4, a cross section of multi-layer article **400** is shown which comprises substrate layer **410**, adhesive layer **420**, and liner **430**. The substrate layer **410** is a multi-layer film. Adhesive layer **420** is shown as a continuous layer, but as described above this

layer can comprise a discontinuous layer, or a stripe coated layer, etc. The interface between the adhesive layer **420** and liner **430** is designated as **435**.

Figure 5 shows a cross section of multi-layer article **500**, which is article **400** to which embossing tool **540** and support surface tool **550** have been simultaneously pressed to substrate layer **510**, adhesive layer **520**, and liner **530**. In this embodiment, support tool **550** contains a pattern of structures which are impressed into the outer surface of substrate layer **510**. The structures of embossing tool **540** deform liner **530** and adhesive layer **520** as shown by the liner/adhesive interface **535**, but the deformation of the tool structures does not deform substrate **510**. The depth that embossing tool **540** is pressed into the liner **530** and adhesive layer **520** is not necessarily to scale.

Figure 6 shows a cross section of multi-layer article **600**, which is article **500** from which embossing tool **540** has been removed, support surface tool **550** has been removed, and liner **530** has been removed. Support layer **610** has structured outer surface **615**, and adhesive layer **620** has surfaces **635**, which are the bottom surfaces of the adhesive layer where the embossed structuring has occurred. These structures are retained at least temporarily after the removal of the liner.

In Figure 7, a cross section of multi-layer article **700** is shown which comprises substrate layer **710**, adhesive layer **720**, and liner **730**.

Figure 8 shows a cross section of multi-layer article **800**, which is article **700** to which embossing tool **840** and support surface tool **850** have been simultaneously pressed to substrate layer **810**, adhesive layer **820**, and liner **830**. In this embodiment, support tool **850** contains a pattern of structures which are impressed into the outer surface of substrate layer **810**. The structures of embossing tool **840** deform liner **830** and adhesive layer **820** and also deform substrate **810**. In Figure 8, the liner **830** is shown contacting the substrate **810**, but in some embodiments there may be a portion of adhesive layer **820** between the liner **830** and the substrate **810** when the embossing tool **840** is pressed into the multi-layer article. The depth that embossing tool **840** is pressed into the liner **830** and adhesive layer **820** is not necessarily to scale.

Figure 9 shows a cross section of multi-layer article **900**, which is article **800** from which embossing tool **840** has been removed and support surface tool **850** has been removed. Support layer **910** has structured outer surface **915**, and adhesive layer **920** and liner **930** show the embossed structuring. In Figure 9, the liner **930** is shown contacting the substrate

910, but in some embodiments there may be a portion of adhesive layer 920 between the liner 930 and the substrate 910.

Figure 10 shows a cross section of multi-layer article 1000, which is article 700 to which embossing tool 1040 and support surface tool 1050 have been simultaneously pressed to substrate layer 1010, adhesive layer 1020, and liner 1030. In this embodiment, support tool 1050 contains a pattern of structures which are impressed into the outer surface of substrate layer 1010. The structures of embossing tool 1040 deform liner 1030 and adhesive layer 1020 as shown by the liner/adhesive interface 1035, but the deformation of the tool structures does not deform substrate 1010. The depth that embossing tool 1040 is pressed into the liner 1030 and adhesive layer 1020 is not necessarily to scale.

Figure 11 shows a cross section of multi-layer article 1100, which is article 1000 from which embossing tool 1040 has been removed, support surface tool 1050 has been removed, and liner 1030 has been removed. Support layer 1110 has structured outer surface 1115, and adhesive layer 1120 has surfaces 1135, which are the bottom surfaces of the adhesive layer where the embossed structuring has occurred. These structures are retained at least temporarily after the removal of the liner.

### Examples

These examples are merely for illustrative purposes only and are not meant to be limiting on the scope of the appended claims. All parts, percentages, ratios, etc. in the examples and the rest of the specification are by weight, unless noted otherwise. Solvents and other reagents used were obtained from Sigma-Aldrich Chemical Company; Milwaukee, Wisconsin unless otherwise noted. The following abbreviations are used: cm = centimeters; in = inch; psi = pounds per square inch; Pa = Pascals. The terms “weight %”, “% by weight”, and “wt%” are used interchangeably.

### Table of Abbreviations

<u>Abbreviation or Trade Designation</u>	<u>Description</u>
Composite Film-1	A three layer construction of Film-1/Adhesive-1/Liner-1 prepared as described in US Patent Publication No. 2011/0316203 (Emslander et al.) with the components described below.

Film-1	Matte film of 1-2 mil (25 – 51 micrometers) thickness, prepared from Polymer-1 and Pigment-1, 80%/20% mixture.
Adhesive-1	Pressure sensitive adhesive, a 90/10 IOA/AA mixture as a layer of 1.5 mils (38 micrometers).
Liner-1	Release liner, 2 mil (51 micrometer) thick, prepared from low density polyethylene with a density of 0.920 g/cm <sup>3</sup> , commercially available from ExxonMobil, as EXXON 129.24.
Polymer -1	Polymer commercially available as BYNEL 3101 from DuPont Chemical.
Pigment-1	Titanium oxide concentrate containing 70% TiO <sub>2</sub> , commercially available as Standridge 11937.
Engraved Copper Plate	Engraved copper plate with a engraved adjacent linear V-grooves of 25 micrometer depth and a pitch of 300 micrometers.
PET Film	Smooth polyethylene terephthalate film of 25 micrometer thickness.

#### Example 1

A sample of Composite Film-1 was placed in a Wabash press, in the configuration, cardboard/flat chrome plate/PET/Engraved Copper Plate/film composite/PET/flat chrome plate/cardboard, with the Engraved Copper Plate such that the Liner-1 surface contacted the Engraved Copper Plate surface. The sample was processed in the press with 70°C platen temperatures for 3 minutes at 5000 psi (34 MegaPascals) and then for 3 minutes at 15 tons pressure (207 MegaPascals).

After pressing, the topography of the outer face of Liner-1 was determined using a WYKO surface profiler, revealing linear grooves of approximately 13 micrometer depth and a pitch of 294 micrometers. The Liner-1 was removed and the topography of Adhesive-1 was determined to contain linear grooves of 11 micrometer depth. Adhesive-1 was contacted to a glass substrate, was somewhat slideable upon initial contact, and upon application of pressure demonstrated air bleed properties (no air bubbles were present in the bondline). The outer surface of the Film-1 layer appeared unaffected by the embossing process. However, gloss was affected by contact with the support structure tool and had a 60° gloss of 70.5, compared to unprocessed Film-1 which had a 60° gloss of 13.6. Gloss was measured with a BYK-Gardner micro-TRI gloss meter.

## Example 2

A sample of Composite Film-1 was placed in a Wabash press, in the configuration, cardboard/flat chrome plate/PET/Engraved Copper Plate/film composite/PET/flat chrome plate/cardboard, with the Engraved Copper Plate such that the Liner-1 surface contacted the Engraved Copper Plate surface. The sample was processed in the press with 100°C platen temperatures for 3 minutes at 5000 psi (34 MegaPascals) and then for 3 minutes at 15 tons pressure (207 MegaPascals).

After pressing, the topography of the outer face of Liner-1 was determined using a WYKO surface profiler, revealing linear grooves of approximately 23 micrometer depth and a pitch of 294 micrometers. The Liner-1 was removed and the topography of Adhesive-1 was determined to contain linear grooves of 15 micrometer depth. Adhesive-1 was contacted to a glass substrate, was somewhat slideable upon initial contact, and upon application of pressure demonstrated air bleed properties (no air bubbles were present in the bondline). The outer surface of the Film-1 layer appeared unaffected by the embossing process. However, gloss was affected by contact with the support structure tool and had a 60° gloss of 85.9, compared to unprocessed Film-1 which had a 60° gloss of 13.6. Gloss was measured with a BYK-Gardner micro-TRI gloss meter.

What is claimed is:

1. A method of forming an article comprising:

providing a multi-layer article comprising:

a substrate with a first major surface and a second major surface;

an adhesive layer with a first major surface and a second major surface,

wherein the first major surface of the adhesive layer is contacting the second major surface of the substrate; and

a liner with a first major surface and a second major surface, wherein the first major surface of the liner is contacting the second major surface of the

adhesive layer;

providing an embossing tool with a structured surface;

providing a support surface tool such that the support surface tool does not have the same structured surface as the embossing tool;

placing the multi-layer article between the structured surface of the embossing tool

and

the surface of the support surface tool to form a construction, such that the first major surface of the substrate is in contact with the surface of the support surface tool;

applying pressure or a combination of pressure and heat to the construction such that

at

least some of the structures on the surface of the embossing tool distort the liner and the adhesive layer, and simultaneously the support surface tool modifies the surface of the first major surface of the substrate, and wherein the distortion in the liner is retained upon release of the applied pressure.

2. The method of claim 1, wherein the embossing tool comprises a tool with a microstructured surface.

3. The method of claim 2, wherein the embossing tool comprises a roller.

4. The method of claim 1, wherein the support tool modifies the surface of the first major surface of the substrate comprises, a change in surface roughness, a change in surface gloss, or imparting structures to the surface.



5. The method of claim 1, wherein the support tool comprises a roller.

6. The method of claim 1, wherein providing a multi-layer article comprises forming the multi-layer article by coextrusion.

5

7. The method of claim 1, wherein the substrate comprises a film, a tape backing, a graphic article, a plastic article, a wound dressing, a protection film or tape, or a release liner.

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8. The method of claim 1, wherein the substrate comprises a polymeric film comprising polyolefin, polyester, vinyl, cellulose ester, polyurethane, or blends or combinations thereof.

9. The method of claim 1, wherein the liner comprises a polymeric film, a coated polymeric film, or a coated paper sheet.

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10. The method of claim 1, wherein simultaneously applying pressure to the construction comprises passing the multi-layer construction through a nip, the nip comprising the embossing tool and the support surface tool.

20

11. The method of claim 1, further comprising separation of the liner from the adhesive layer such that the structures on the adhesive layer do not immediately collapse.

12. The method of claim 11, further comprising contacting the surface of the adhesive layer to the surface of an adherend to form an adhesive article.

25

13. The method of claim 1, wherein at least some of the structures on the surface of the embossing tool that distort the liner and the adhesive layer, also distort the second major surface of the substrate.

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14. The method of claim 13, wherein the distortion of the second major surface of the substrate also distorts the first major surface of the substrate.

15. The method of claim 1, wherein the structures on the surface of the embossing tool that distort the liner and the adhesive layer, do not distort the second major surface of the substrate.

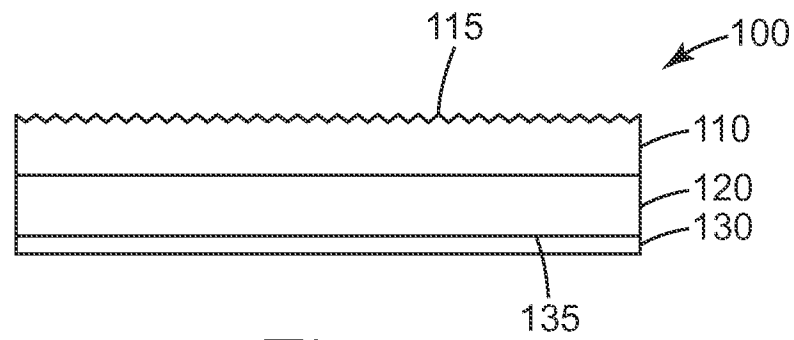
5 16. The method of claim 15, wherein a portion of the adhesive layer is permanently distorted.

10 17. The method of claim 16, wherein the permanent distortion of a portion of the adhesive layer causes the adhesive layer to form two components, a component that is unchanged and a component that has changed topological properties.

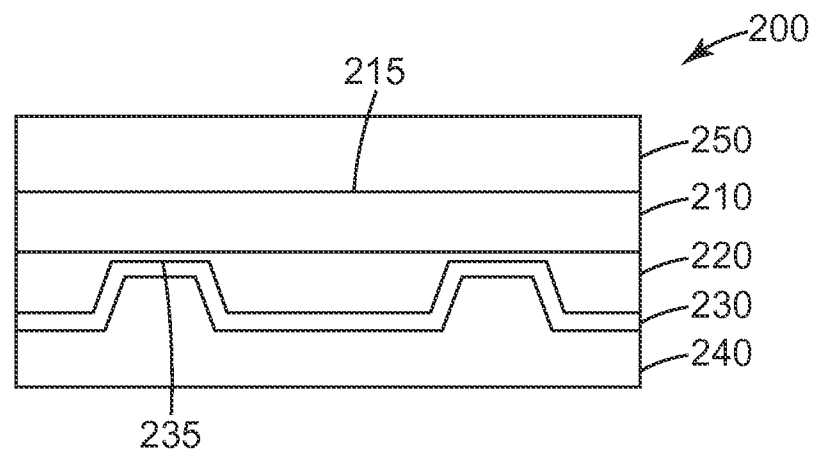
18. The method of claim 17, wherein the change of topological properties causes a change in viscoelastic response, a change in peel adhesion, or a combination thereof.

15 19. The method of claim 16, wherein the portion of the adhesive layer that is permanently distorted comprises a plurality of convex structures adjacent to the concave structures.

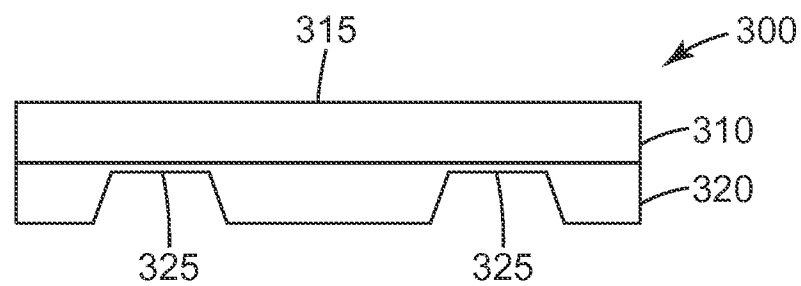
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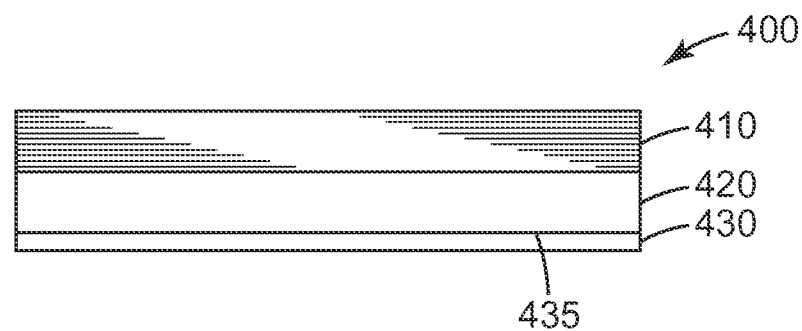
*Fig. 1*



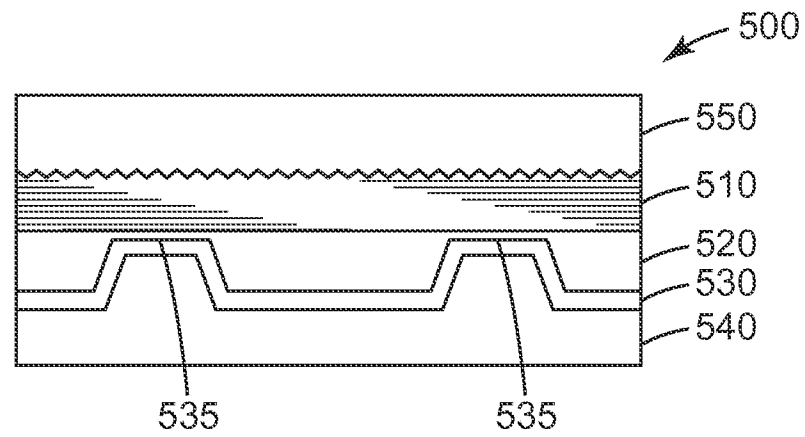
*Fig. 2*



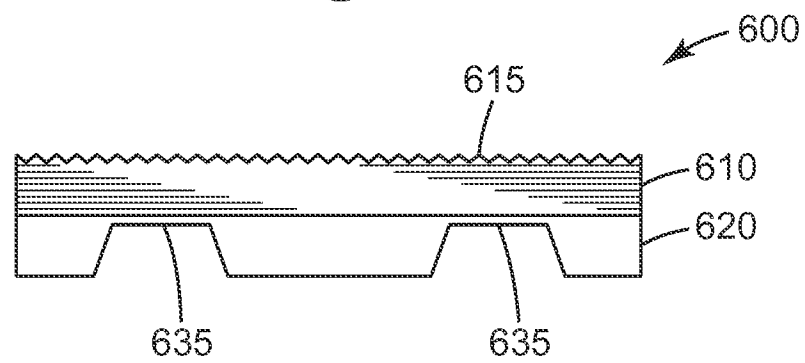
*Fig. 3*



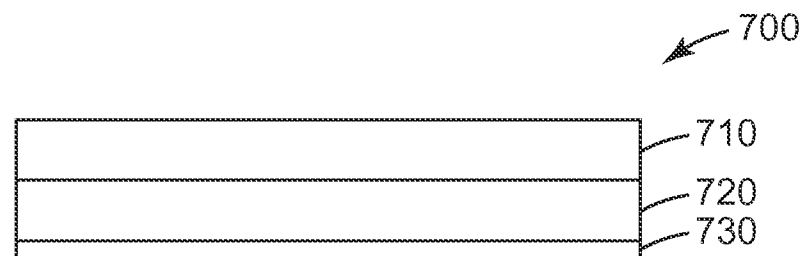
*Fig. 4*



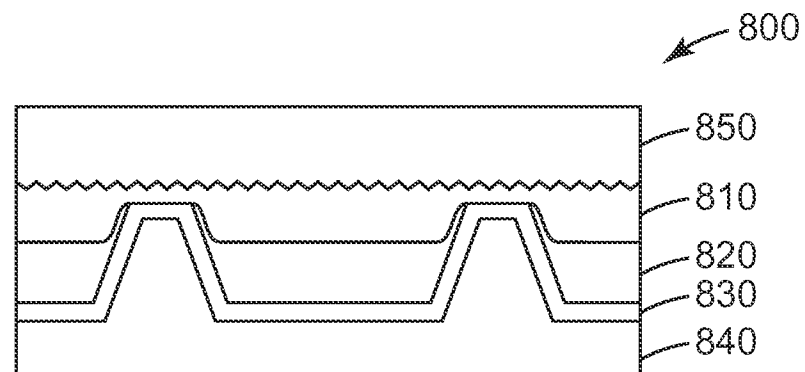
*Fig. 5*



*Fig. 6*

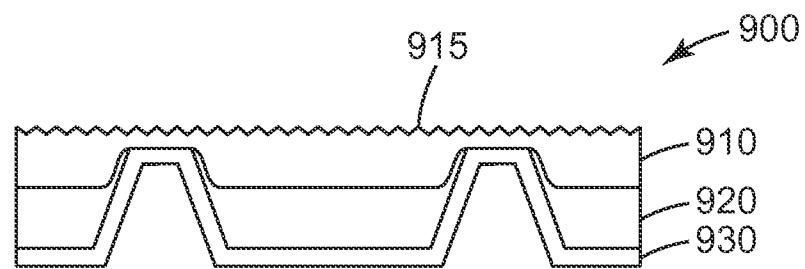
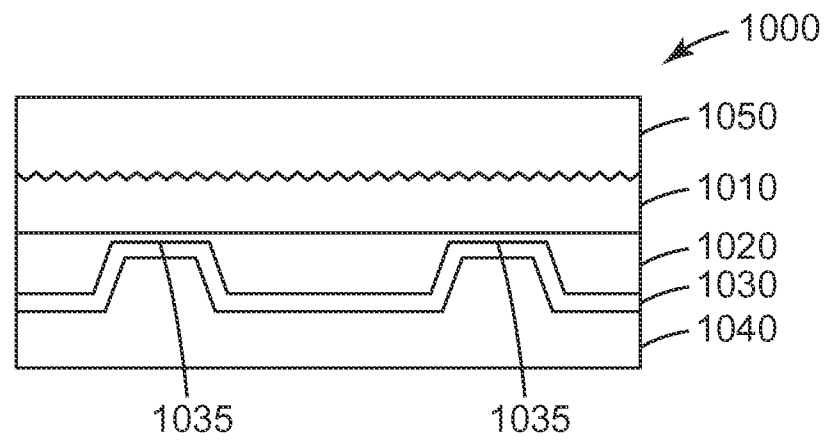
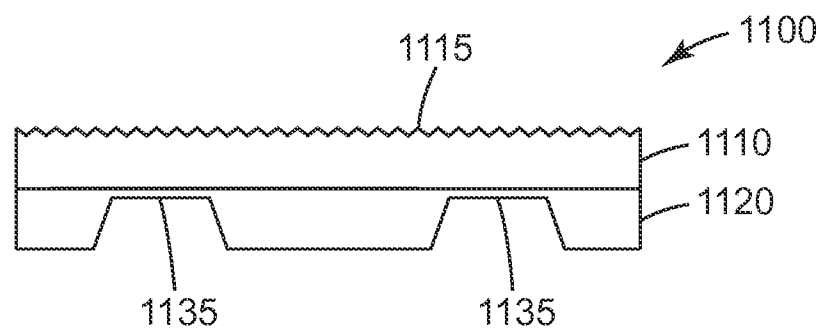


*Fig. 7*



*Fig. 8*

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*Fig. 9**Fig. 10**Fig. 11*

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2014/040513

A. CLASSIFICATION OF SUBJECT MATTER  
INV. B32B3/30 C09J7/02  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
B32B C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 4 315 047 A (SEABOLD THOMAS W ET AL) 9 February 1982 (1982-02-09) abstract	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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Information on patent family members

International application No

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