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(54) **Title**: THIN PROTECTIVE DISPLAY FILM

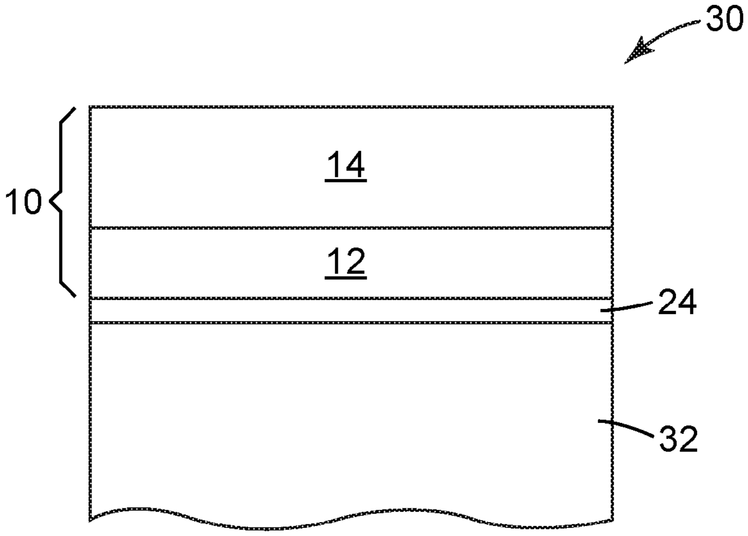

Fig. 3

(57) **Abstract**: A display film includes a transparent polymeric substrate layer having a 0.2% offset yield stress greater than 110 MPa and a transparent aliphatic cross-linked polyurethane layer having a thickness of 100 micrometers or less disposed on the transparent polymeric substrate layer. The transparent aliphatic cross-linked polyurethane layer has a glass transition temperature in a range from 11 to 27 degrees Celsius and a Tan Delta peak value in a range from 0.5 to 2.5. The display film has a haze value of 2% or less.

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THIN PROTECTIVE DISPLAY FILM

BACKGROUND

Displays and electronic devices have evolved to be curved, bent, or folded and provide new user experiences. These device architectures may include flexible organic light emitting diodes (OLEDs), plastic liquid crystal displays (LCDs) and the like, for example.

In order to realize such flexible displays and protect elements in the displays, a flexible cover sheet or flexible window film replaces a conventional glass cover sheet. This flexible cover sheet has a number of design parameters such as; high visible light transmission, low haze, excellent scratch resistance and puncture resistance, in order to protect the elements included in the display devices. In some cases the flexible cover sheet may also need to withstand thousands of folding events around a tight bend radius (about 5 mm or less) without showing visible damage. In other cases, the flexible cover sheet must be able to unfold without leaving a crease after being bent at elevated temperature and humidity.

A variety of hard coated plastic substrates have been explored. More exotic materials like hard coated colorless transparent polyimide films have also been shown to have high hardness and good scratch resistance. However many hard coated films fail to withstand folding events around a tight bend radius without showing visible damage.

SUMMARY

The present disclosure relates to a display film that can protect a display window and survive folding tests intact. The protective display film maintains optical properties of a display film while providing scratch resistance to the display. The protective display film is optically clear and includes a thin polyurethane layer disposed on a high yield substrate.

In one aspect, a display film includes a transparent polymeric substrate layer having a 0.2% offset yield stress greater than 110 MPa and a transparent aliphatic cross-linked polyurethane layer having a thickness of 100 micrometers or less disposed on the transparent polymeric substrate layer. The transparent aliphatic cross-linked polyurethane layer has a glass transition temperature in a range from 11 to 27 degrees Celsius and a Tan Delta peak value in a range from 0.5 to 2.5. The display film has a haze value of 2% or less.

In another aspect, a display film includes a transparent polymeric substrate layer having a 0.2% offset yield stress greater than 110 MPa and a transparent aliphatic cross-linked polyurethane layer having a thickness of 100 micrometers or less disposed on the transparent polymeric substrate layer. The transparent aliphatic cross-linked polyurethane layer has a glass transition temperature in a range from 11 to 28 degrees Celsius and a Tan Delta peak value in a range from 0.5 to 2.5. The display film remains intact after at least 100,000 bending cycles about a 3 mm radius.

In another aspect, an article includes an optical display and a protective film disposed on the optical display. The protective film includes a transparent polymeric substrate layer having a 0.2% offset yield stress greater than 110 MPa and a transparent aliphatic cross-linked polyurethane layer having a thickness of 100 micrometers or less disposed on the transparent polymeric substrate layer. An optical adhesive layer fixes the transparent polymeric substrate layer to the optical display. The transparent aliphatic cross-linked polyurethane layer has a glass transition temperature in a range from 11 to 28 degrees Celsius and a Tan Delta peak value in a range from 0.5 to 2.5 and a cross-link density in a range from 0.34 to 0.65 mol/kg. The display film has a haze value of 2% or less.

These and various other features and advantages will be apparent from a reading of the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

The disclosure may be more completely understood in consideration of the following detailed description of various embodiments of the disclosure in connection with the accompanying drawings, in which:

FIG. 1 is a schematic diagram side elevation view of an illustrative display film;

FIG. 2 is a schematic diagram side elevation view of another illustrative display film;

FIG. 3 is a schematic diagram side elevation view of an illustrative display film on an article; and

FIG. 4 is a schematic diagram perspective view of an illustrative folding article including an illustrative display film.

DETAILED DESCRIPTION

In the following detailed description, reference is made to the accompanying drawings that form a part hereof, and in which are shown by way of illustration several specific embodiments. It is to be understood that other embodiments are contemplated and may be made without departing from the scope or spirit of the present disclosure. The following detailed description, therefore, is not to be taken in a limiting sense.

All scientific and technical terms used herein have meanings commonly used in the art unless otherwise specified. The definitions provided herein are to facilitate understanding of certain terms used frequently herein and are not meant to limit the scope of the present disclosure.

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 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.

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.

As used herein, “have”, “having”, “include”, “including”, “comprise”, “comprising” or the like are used in their open ended sense, and generally mean “including, but not limited to”. It will be understood that “consisting essentially of”, “consisting of”, and the like are subsumed in “comprising,” and the like.

The terms “display film”, “protective film”, and “protective display film” are herein used interchangeably.

“Transparent substrate” or “transparent layer” refers to a substrate or layer that has a high light transmission (typically greater than 90%) over at least a portion of the surface of the substrate over at least a portion of the light spectrum with wavelengths of about 350 to about 1600 nanometers, including the visible light spectrum (wavelengths of about 380 to about 750 nanometers).

"Polyurethane" refers to polymers prepared by the step-growth polymerization of hydroxyl-functional materials (materials containing hydroxyl groups —OH) with isocyanate-functional materials (materials containing isocyanate groups —NCO) and therefore contain urethane linkages (—O(CO)—NH—), where (CO) refers to a carbonyl group (C=O). The term may include "polyurethane-ureas" in which both urethane linkages and urea linkages are present.

The present disclosure relates to a display film that can protect a display window and survive folding tests intact. The protective display film maintains optical properties of a display film while providing scratch resistance to the display. The protective display film is optically clear and includes a thin polyurethane layer disposed on a high yield substrate. The high yield substrate improves the recovery properties of the display film and enables the use of a thinner polyurethane layer as compare to lower yield substrates. For a given polyurethane thickness, the ability to recover from scratches and dents is improved when the polyurethane is disposed on a high yield substrate as compared to a lower yield substrate. The overall thickness of the display film may be less than 250 micrometers, or less than 200 micrometers. The thickness of the polyurethane layer may be less than 100 micrometers. The high yield substrate may have a 0.2% offset yield stress that is greater than 110 MPa or greater than 130 MPa or greater than 150 MPa. The protective display film is formed of an aliphatic cross-linked polyurethane material that is transparent. The protective display film exhibits a haze value of 2% or less or 1.5% or less or 1% or less or 0.5% or less. The protective display film exhibits a visible light transmission of 85% or greater or 90% or greater, or 93% or greater. The protective display film exhibits a clarity of 98% or greater, or 99% or greater. The aliphatic cross-linked polyurethane material may have a glass transition temperature in a range from 11 to 27 degrees Celsius or from 17 to 22 degrees Celsius. The aliphatic cross-linked polyurethane material may have a Tan Delta peak value in a range from 0.5 to 2.5 or from 1 to 2 or from 1.4 to 1.8. The aliphatic cross-linked polyurethane material may have a cross-link density in a range from 0.34 to 0.65 mol/kg. The protective display film exhibits a room temperature scratch resistance or recovery and is able to withstand at least 100,000 folding cycles without failure or visible defects. These protective display film can withstand a bend radius of 3 mm or less, or 4 mm or less, or 3 mm or less, or 2 mm or less, or even 1 mm or less without failure or visible defects, such as delamination, cracking, or haze. While the present disclosure is not so limited, an appreciation of various aspects of the disclosure will be gained through a discussion of the examples provided below.

FIG. 1 is a schematic diagram side elevation view of an illustrative display film **10**. The display film **10** includes a transparent polymeric substrate layer **12** and a transparent aliphatic cross-linked polyurethane layer **14** disposed on the transparent polymeric substrate layer **12**. The display film **10** may be optically transparent, exhibit scratch recovery and is able to withstand at least 100,000 folding cycles without failure or degrading the optical properties of the display film. The display film **10** may not be tacky and exhibit a storage modulus at 0 degree Celsius of 1 GPa or greater.

The display film **10** includes a transparent polymeric substrate layer **12** and a transparent aliphatic cross-linked polyurethane layer **14** disposed on the transparent polymeric substrate layer **12**. The transparent polymeric substrate layer **12** may be referred to as a “high yield” substrate and may have a 0.2% offset yield stress value that is greater than 110 MPa or greater than 130MPa or greater than 150 MPa. The transparent aliphatic cross-linked polyurethane layer **14** may have a thickness of 100 micrometers or less, or 80 micrometers or less, or 60 micrometers or less. The transparent aliphatic cross-linked polyurethane layer **14** may have a thickness in a range from 10 to 100 micrometers, or 30 to 80 micrometers, or 40 to 60 micrometers.

The transparent aliphatic cross-linked polyurethane layer **14** may have a glass transition temperature in a range from 11 to 27 degrees Celsius or from 17 to 22 degrees Celsius. The phrase “glass transition temperature” refers herein to the “on-set” glass transition temperature by DSC and is measured according to ASTM E1256-08 2014.

The transparent aliphatic cross-linked polyurethane layer **14** may have a Tan Delta peak value in a range from 0.5 to 2.5, or from 1 to 2, or from 1.4 to 1.8. Tan Delta peak value and peak temperature is measured according to the DMA analysis described in the Examples.The transparent aliphatic cross-linked polyurethane layer **14** may have a cross-link density in a range from 0.34 to 0.65 mol/kg.

The display film **10** may have a haze value of 2% or less, or 1.5% or less, or 1% or less, or 0.5% or less. In some embodiments the display film **10** may have a haze value of 5% or less. The display film **10** may have a clarity of 98% or greater, or 99% or greater. The display film **10** may have a visible light transmission of 85% or greater, or 90% or greater, or 93% or greater.

The display film **10** may have a yellow index or b* value of 5 or less, or 4 or less, or 3 or less, or 2 or less, or 1 or less. In many embodiments the display film **10** may have a yellow index or b* value of 1 or less.

The display film **10** may maintain a haze value of 2% or less, or 1.5% or less, or 1% or less after at least 100,000 bending or folding cycles about a 3 mm radius. The display film **10** may maintain a stable haze value, or remain intact without cracking or delaminating, after at least 100,000 bending or folding cycles about a 5 mm radius, or about a 4 mm radius, or about a 3 mm radius, or about a 2 mm radius, or about a 1 mm radius. The display film **10** may remain intact after at least 100,000 bending or folding cycles about a 3 mm radius or less.

The display film **10** may have any useful thickness. In many embodiments the display film **10** has a thickness of 250 micrometers or less, or 200 micrometers or less, or 150 micrometers or less, or 125 micrometers or less. The thickness of the display film **10** is a balance between being thick enough to provide the desired display protection and thin enough to provide the folding and reduced thickness design parameters.

The transparent polymeric substrate layer **12** may have any useful thickness. In many embodiments the transparent polymeric substrate layer **12** has a thickness in a range from 10 to 100 micrometers or from 20 to 80 micrometers.

The transparent polymeric substrate layer **12** may be formed of any useful polymeric material that provides the desired mechanical properties (such as dimensional stability) and optical properties (such as light transmission and clarity) to the display film **10**. Examples of materials suitable for use in the polymeric substrate layer **12** include polymethylmethacrylate, polycarbonate, polyamides, polyimides, polyesters (PET, PEN), polycyclic olefin polymers and thermoplastic polyurethanes.

One useful polymeric material for forming the transparent polymeric substrate layer **12** is polyimide. In many embodiments the polyimide substrate layer is colorless. Colorless polyimide can be formed via chemistry or via nanoparticle incorporation. Some exemplary colorless polyimides formed via chemistry are described in WO 2014/092422. Some exemplary colorless polyimides formed via nanoparticle incorporation are described in Journal of Industrial and Engineering Chemistry 28 (2015) 16-27.

The transparent polymeric substrate layer **12** may have any useful tensile modulus or offset yield stress value. The transparent polymeric substrate layer **12** may be referred to as a “high yield” substrate and may have an offset yield stress value that is greater than 110 MPa, or greater than 130 MPa, or greater than 150 MPa, or greater than 180 MPa, or greater than 200 MPa. The phrase "yield stress" or "offset yield stress" refers herein to "0.2% offset yield strength" as defined in ASTM D638-14. ASTM D638 -14 section A2.6 defines the test method for "offset yield strength" and is defined as the stress at which the strain exceeds by a specified amount (the offset) an extension of the initial proportional portion of the stress-strain curve. It is expressed in force per unit area, usually megapascals (poundsforce per square inch).

The transparent aliphatic cross-linked polyurethane layer **14** may have any useful thickness. The transparent aliphatic cross-linked polyurethane layer **14** may have a thickness of 100 micrometers or less, or 80 micrometers or less, or 60 micrometers or less. The transparent aliphatic cross-linked polyurethane layer **14** may have a thickness in a range from 10 to 100 micrometers, or 30 to 80 micrometers, or 40 to 60 micrometers. The thickness of the transparent aliphatic cross-linked polyurethane layer **14** is a balance between being thick enough to provide the desired protection to the display and particularly to the transparent polymeric substrate layer **12** and thin enough to provide the folding and reduced thickness design parameters.

The transparent aliphatic cross-linked polyurethane layer **14** may be coated onto the transparent polymeric substrate layer **12** (that may be primed) and then be cured or cross-linked to form a thermoset polyurethane layer **14**. Polyurethane is a polymer composed of organic units joined by carbamate (urethane) links. The polyurethanes described herein are thermosetting polymers that do not melt when heated. Polyurethane polymers may be formed by reacting a di- or polyisocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain on average two or more functional groups per molecule. The polyurethanes described herein may have a functionality greater than 2.4 or 2.5.

A wide variety of polyols may be used to from the aliphatic cross-linked polyurethane layer. The term polyol includes hydroxyl-functional materials that generally include at least 2 terminal hydroxyl groups. Polyols include diols (materials with 2 terminal hydroxyl groups) and higher polyols such as triols (materials with 3 terminal hydroxyl groups), tetraols (materials with 4 terminal hydroxyl groups), and the like. Typically the reaction mixture contains at least some diol and may also contain higher polyols. Higher polyols are particularly useful for forming crosslinked polyurethane polymers. Diols may be generally described by the structure HO—B—OH, where the B group may be an aliphatic group, an aromatic group, or a group containing a combination of aromatic and aliphatic groups, and may contain a variety of linkages or functional groups, including additional terminal hydroxyl groups.

Polyester polyols are particularly useful. Among the useful polyester polyols useful are linear and non-linear polyester polyols including, for example, polyethylene adipate, polybutylene succinate, polyhexamethylene sebacate, polyhexamethylene dodecanedioate, polyneopentyl adipate, polypropylene adipate, polycyclohexanedimethyl adipate, and poly ε-caprolactone. Particularly useful are aliphatic polyester polyols available from King Industries, Norwalk, Conn., under the trade name “K-FLEX” such as K-FLEX 188 or K-FLEX A308.

A wide variety of polyisocyanates may be used to from the aliphatic cross-linked polyurethane layer. The term polyisocyanate includes isocyanate-functional materials that generally include at least 2 terminal isocyanate groups. Polyisocyanates include diisocyanates (materials with 2 terminal isocyanate groups) and higher polyisocyanates such as triisocyanates (materials with 3 terminal isocyanate groups), tetraisocyanates (materials with 4 terminal isocyanate groups), and the like. Typically the reaction mixture contains at least one higher isocyanate if a difunctional polyol is used. Higher isocyanates are particularly useful for forming crosslinked polyurethane polymers. Diisocyanates may be generally described by the structure OCN—Z—NCO, where the Z group may be an aliphatic group, an aromatic group, or a group containing a combination of aromatic and aliphatic groups.

Higher functional polyisocyanates are particularly useful, such as triisocyanates, to form a crosslinked polyurethane polymer layer. Triisocyanates include, but are not limited to, polyfunctional isocyanates, such as those produced from biurets, isocyanurates, adducts, and the like. Some commercially available polyisocyanates include portions of the DESMODUR and MONDUR series from Bayer Corporation, Pittsburgh, Pa., and the PAPI series from Dow Plastics, a business group of the Dow Chemical Company, Midland, Mich. Particularly useful triisocyanates include those available from Bayer Corporation under the trade designations DESMODUR N3300A and MONDUR 489. One particularly suitable aliphatic polyisocyanate is DESMODUR N3300A.

The reactive mixture used to form the transparent aliphatic cross-linked polyurethane layer **14** also contains a catalyst. The catalyst facilitates the step-growth reaction between the polyol and the polyisocyanate. Conventional catalysts generally recognized for use in the polymerization of urethanes may be suitable for use with the present disclosure. For example, aluminum-based, bismuth-based, tin-based, vanadiumbased, zinc-based, or zirconium-based catalysts may be used. Tin-based catalysts are particularly useful. Tin-based catalysts have been found to significantly reduce the amount of outgassing present in the polyurethane. Most desirable are dibutyltin compounds, such as dibutyltin diacetate, dibutyltin dilaurate, dibutyltin diacetylacetonate, dibutyltin dimercaptide, dibutyltin dioctoate, dibutyltin dimaleate, dibutyltin acetonylacetonate, and dibutyltin oxide. In particular, the dibutyltin dilaurate catalyst DABCO T-12, commercially available from Air Products and Chemicals, Inc., Allentown, Pa. is particularly suitable. The catalyst is generally included at levels of at least 200 ppm or even 300 ppm or greater.

FIG. 2 is a schematic diagram side elevation view of another illustrative display film **20**. The display film **20** may include a removable liner **22** disposed on the transparent polymeric substrate layer **12** or the transparent aliphatic cross-linked polyurethane layer **14**.

The display film **20** may include an optical adhesive layer **24** disposed on the transparent polymeric substrate layer **12** and a removable liner **26** disposed on the optical adhesive layer **24** and a second removable liner **22** disposed on the transparent aliphatic cross-linked polyurethane layer **14**. The optical adhesive layer may include acrylate or silicone based optical adhesives.

The transparent polymeric substrate layer **12** may be primed or treated to impart some desired property to one or more of its surfaces. In particular the transparent polymeric substrate layer **12** can be primed to improve adhesion of the transparent aliphatic cross-linked polyurethane layer **14** with the transparent polymeric substrate layer **12.** Examples of such treatments include corona, flame, plasma and chemical treatments such as, acrylate or silane treatments.

The removable liners **22, 26** may provide transport protection to the underlying display film **10** and optional optical adhesive layer **24.** The removable liners **22, 26** may be layer or film that has a low surface energy to allow clean removal of the liner **22, 26** from the display film **10** and optional optical adhesive layer **24**. The removable liners **22, 26** may be a layer of polyester coated with a silicone, for example.

The removable liner **26** may provide temporary structure to the optional optical adhesive layer **24**. For example, WO2014/197194 and WO2014/197368 describe removable liners that emboss an optical adhesive layer where the optical adhesive losses its structures once the removable liner is stripped away from the optical adhesive layer.

The display film **20** can includes one or more additional layers on or between the transparent polymeric substrate layer **12** and the transparent aliphatic cross-linked polyurethane layer **14**. These optional layers may include a hardcoat layer (thickness of 6 micrometers or less), a transparent barrier layer (thickness from 3 to 200 nanometers), a microstructure layer, an anti-glare layer, anti-reflective layer, or an anti-fingerprint layer.

The hardcoat layer may be disposed on either side of one or both of the transparent polymeric substrate layer **12** and the transparent aliphatic cross-linked polyurethane layer **14**. The hardcoat layer may include a multi-functional acrylate resins with at least 30% wt nanosilica particles. WO2014/011731 describes some exemplary hardcoats.

The transparent barrier layer may be disposed on either side of one or both of the transparent polymeric substrate layer **12** and the transparent aliphatic cross-linked polyurethane layer **14**. The transparent barrier layer can mitigate or slow ingress of oxygen or water through the display film **10**. Transparent barrier layers may include for example, thin alternating layers of silica, alumina or zirconia together with an organic resin. Exemplary transparent barrier layer are described in are described in US7,980,910 and WO2003/094256.

The microstructure layer may be disposed on either side of one or both of the transparent polymeric substrate layer **12** and the transparent aliphatic cross-linked polyurethane layer **14**. The microstructure layer may improve the optical properties of the display film **10**. An exemplary microstructure layer is described in US2016/0016338.

FIG. 3 is a schematic diagram side elevation view of an illustrative display film **10** on an article **30**. **FIG. 4** is a schematic diagram perspective view of an illustrative folding article **40** including an illustrative display film **10**.

The article **30** includes an optical layer **32** and a display film **10** disposed on the optical layer **32**. The display film **10** includes a transparent polymeric substrate layer **12** and a transparent aliphatic cross-linked polyurethane layer **14** disposed on the transparent polymeric substrate layer **12**, as described above. An optical adhesive layer **24** fixes the transparent polymeric substrate layer **12** to the optical layer **32**. In some cases the optical adhesive permanently fixes the display film to the article or optical layer. In other cases the display film and optical adhesive can be removed/debonded/repositioned, relative to the optical layer or article, with the application of heat or mechanical force such that the display film is replaceable or repositionable by the consumer.

The optical layer **32** may form at least a portion of an optical element. The optical element may be display window or element of a display device, such as an optical display

34. The display device **40** can be any useful article such as a phone or smartphone, electronic tablet, electronic notebook, computer, and the like. The optical display may include an organic light emitting diode (OLED) display panel. The optical display may include a liquid crystal display (LCD) panel or a reflective display. Examples of reflective displays include electrophoretic displays, electrofluidic displays (such as an electrowetting display), interferometric displays or electronic paper display panels, and are described in US2015/0330597.

Further examples of optical displays include static display such as commercial graphic signs and billboards.

The display film **10** and the attached optical layer **32** or optical element or optical display **34** may be foldable so that the optical display **34** faces itself and at least a portion of display film **10** contacts another portion of the protective film **10**, as illustrated in **FIG. 4**. The display film **10** and the attached optical layer **32** or optical element or optical display **34** may be flexible or bendable or foldable so that a portion of the display film **10** and the attached optical layer **32** or optical element or optical display **34** can articulate relative to another portion of the display film **10** and the attached optical layer **32** or optical element or optical display **34.** The display film **10** and the attached optical layer **32** or optical element or optical display **34** may be flexible or bendable or foldable so that a portion of the display film **10** and the attached optical layer **32** or optical element or optical display **34** can articulate at least 90 degrees or at least 170 degrees relative to another portion of the display film **10** and the attached optical layer **32** or optical element or optical display **34.**

The display film **10** and the attached optical layer **32** or optical element or optical display **34** may be flexible or bendable or foldable so that a portion of the display film **10** and the attached optical layer **32** or optical element or optical display **34** can articulate relative to another portion of the display film **10** and the attached optical layer **32** or optical element or optical display **34** to form a bend radius of 3 mm or less in the display film **10** at the bend or fold line**.** The display film **10** and the attached optical layer **32** or optical element or optical display **34** may be flexible or bendable or foldable so that a portion of the display film **10** and the attached optical layer **32** or optical element or optical display **34** can articulate relative to another portion of the display film **10** and the attached optical layer **32** or optical element or optical display **34** to form a bend radius such that the display film **10** overlaps itself and is separated from each other by a distance on 10 mm or less, or 6 mm or less or 3 mm or less or contacts each other.

In one embodiment, the display film (having a thickness in a range from 100 to 150 micrometers) includes a transparent polymeric substrate layer (having a thickness in a range from 50 to 75 micrometers) and a transparent aliphatic cross-linked polyurethane layer (having a thickness in a range from 25 to 75 micrometers) disposed on the transparent polymeric substrate layer. The transparent polymeric substrate layer has a 0.2% offset yield stress value that is 150MPa or greater. The transparent aliphatic cross-linked polyurethane layer may have a glass transition temperature in a range from 17 to 22 degrees Celsius, a Tan Delta peak value in a range from 1.4 to 1.8 and a b* value less than 2.5. The display film has a haze value of 1% or less and a visible light transmission of 88% or greater.

Objects and advantages of this disclosure are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this disclosure.

Examples

All parts, percentages, ratios, etc. in the examples are by weight, unless noted otherwise. Solvents and other reagents used were obtained from Sigma-Aldrich Corp., St. Louis, Missouri unless specified differently.

Model Examples

Abaqus finite element modeling software (Dassault Systems, Velizy-Villacodlay, France) was used to study the effect of coating properties and substrate yield stress on the size of the plastic deformation zone as a function on normal load. The scratch implement was modeled as a 1 mm diameter, rigid ball. Mechanical properties of the substrate and thickness of the coating were as shown in Table 1. Both were modeled as elastic-plastic materials. AxiSymmetric modeling technique was used for the analysis. The display film was modeled as lying on top a rigid support with no friction between the substrate and the rigid support. In all cases the coating was modeled as an elastic-plastic material with modulus equal to 900 MPa and yield stress equal to 24 MPa.

The size of the plastic deformation zone for each case was defined as the radius of the zone where the Von Mises stress exceeded the substrate yield stress measured at the depth where the substrate met the rigid support. If the Von Mises stress at this depth was less the yield stress of the polymer substrate, then the plastic deformation zone size was recorded as being equal to zero.

Table 1: Finite Element Analysis Results

Case	Normal Load (N)	Substrate Modulus (GPa)	Substrate Yield Stress (MPa)	Coating Thickness (um)	Plastic Deformation Zone Size (mm)*
1	10	4.7	144	30	0.106
2	10	6.0	170	30	0.073
3	10	7.4	200	30	0.04
4	10	8.2	230	30	0
5	14	4.7	144	50	0.11
6	14	6.0	170	50	0.087
7	14	7.4	200	50	0.042
8	14	8.2	230	50	0

The results in **Table 1** show that as the substrate yield stress increases, the size of the plastic deformation zone associated with a visible dent decreases. The same trend is seen for both 10 N and 14 N normal loads.

Working Examples

A series of aliphatic cross-linked polyurethane were coated on transparent polymer substrates. The scratch resistance, scratch recovery rate, flexibility, and dynamic folding performance were all characterized as described below.

Table 2: Materials

Abbreviation or Trade Designation	**Description**
K-FLEX 188	Aliphatic polyester polyol, commercially available from King Industries, Norwalk, CT under the trade name “K-FLEX 188”
DESMODUR N3300A	Aliphatic polyisocyanate, commercially available from Bayer, Pittsburgh, PA under the trade name “DESMODUR N3300A”.
DABCO T-12	Dibutyltin dilaurate catalyst, commercially available from Air Products and Chemicals, Inc., Allentown, PA, under the trade name “DABCO T-12”.
LmPEN	50 and 75 micron thick low melt polyethylene naphthalate polymer co-polyester made from 90% NDC (dimethyl-2,6-naphthalenedicarboxylate) and 10% terephthalic acid, extruded and bi-axially oriented as described below.
COP	Cyclo-Olefin Polymer (COP) film, trade name ZEONEX from Zeon Corporation, Tokyo Japan.
Upilex 50s	50 um heat treated polyimide film, available from UBE America.

Preparation of Primed LmPEN Film

A 90/10 PEN copolymer was prepared as illustrated in Example Control B of US 8,263,731. This material was melt extruded using a twin screw extruder with vacuum applied for moisture removal. The melt was heated to 525°F and delivered to an extrusion die and quenched on a chilled drum. This quenched film was stretched 3.3-1 at a temperature of 235-250°F in the machine direction and cooled. This machine direction stretched film was fed to a tenter machine which gripped the film edges, heated the film back to 255-300°F and stretched the film 3.7-1 up to 4.1-1 in the transverse direction. The film was then annealed at 450°F for 8 to 30 sec in the same tenter. The film edges were trimmed off and a polyethylene premask applied before the film was wound into roll form.

A primer solution was made by mixing 52.5 grams of VITEL 2200B (Bostik Americas, Wauwatosa, WI) in 2447.5 grams of methyl ethyl ketone (Fisher Scientific) to make a homogeneous solution. The primer solution was applied to 50 micrometer thick corona treated LmPEN films in a roll to roll process where the primer solution was metered through a slot die onto the moving web. Thickness was controlled by the use of a metering pump and a mass flow meter. The volatile components of the coating were then dried in a 3 zone air floatation zone oven (ovens temperatures set all set to 175°F). The dried coating was then wound into a roll and the primer coating had a thickness of approximately 81 nanometer.

Preparation of the Polyurethane Reactive Mixture and Coating Procedure

Preparation of Polyol with Catalyst - In a standard mixer equipped with low shear blade was placed 200 lbs of K-FLEX 188 and 42 grams of DABCO T-12. The components were mixed under vacuum for 4 hours at 70°C and 28 inches of mercury to eliminate dissolved gases in the resin. The resulting resin was placed into 5 gallon pails for later use.

Preparation of DESMODUR N3300 - In a standard mixer equipped with low shear blade was placed 200 lbs of DESMODUR N330. The component was mixed under vacuum for 4 hours at 140°F and 28 inches of mercury to eliminate dissolved gases in the resin. The resulting resin was placed into 5 gallon pails for later use.

Preparation of Examples 1-5

The Polyol with catalyst and DESMODUR N3300 were added to separate pumps carts with mass flow controllers. The Polyol with catalyst was heated to 60°C to lower the viscosity. The two components were delivered in controlled stoichiometry from the pump carts via mass flow control to a Kenics static mixer (355mm long, with 32 elements). The polyurethane reactive mixture was placed between 12" wide T-50 liners and the films were pulled under a notch bar with a gap set to produce a polyurethane coating with the ~ 3 mil thickness in a continuous fashion. The assembly was heated at elevated temperature on hot platens to gel the polyurethane film and was placed into a 70°C oven for 16 hours to cure. Prior to testing, both the liners were removed.

Example 6 - Polyurethane on LmPEN

The Polyol with catalyst and DESMODUR N3300 were added to separate pumps carts with mass flow controllers. The Polyol with catalyst was heated to 60 degrees C to lower the viscosity. The two components were delivered in controlled stoichiometry from the pump carts via mass flow control to a Kenics static mixer (355mm long, with 32 elements). The 2-part polyurethane reactive mixture was coated between a 12" COP liner and the primed LmPEN film described above. The reactive mixture was placed polyurethane coatings of the desired thickness between the films in a continuous fashion. The assembly was heated at elevated temperature on hot platens to gel the polyurethane film and was placed into a 70 degrees C oven for 16 hours to cure. Prior to testing, the COP liner was removed.

The crosslink density of the cured polyurethane coatings was calculated using the method described in *Macromolecules*, Vol. 9, No. 2, pages 206-211 (1976). To implement this model, integral values for chemical functionality are required. DESMODUR N3300 is reported to have an average functionality of 3.5 and an isocyanate equivalent weight of 193 g/equiv. This material was represented in the mathematical model as a mixture of 47.5 wt% HDI trimer (168.2 g/equiv.), 25.0 wt% HDI tetramer (210.2 g/equiv.), and 27.5 wt% of HDI pentamer (235.5 g/equiv.). This mixture yields an average equivalent weight of 193 g/equiv. and an average functionality of 3.5.

Table 3: Coating compositions and theoretical crosslink concentration

Example	Polyol with catalyst pump set rate (g/min)	DESMODUR 3300 pump flow set rate (g/min)	NCO/OH Ratio	Theoretical Gel Content	Theoretical Crosslink Concentration (mol/kg)
1	32.77	20.74	0.8	96.67%	0.34
2	32.77	22.03	0.85	98.31%	0.42
3	32.77	23.33	0.9	99.32%	0.49
4	32.77	24.62	0.95	99.85%	0.57
5	32.77	25.92	1	100%	0.65
6	19.36	15.6	1.025	100%	0.63

Example 7: Polyurethane on Upilex 50 S substrate

In a Max 40 cup (Available from Flaktek, Inc.) at RT (23 °C) were mixed 12 grams of K-FLEX 188 and 1 drop of DABCO T-12 (from micro syringe). To the 12 grams of the above resin mixture was mixed 10 grams of DESMODUR N3300A. The reactive mixture was mixed in a FlackTek, Inc. Speed Mixer at 1500 rpm for 30 seconds and used within 5 minutes of mixing in DESMODUR N3300A. The polyurethane reactive mixture was coated between a 12” wide 4 mil COP and a 50 micron corona treated (Sherman Treaters) Upilex 50S film. The reactive mixture was placed between the two films and the films were pulled under a notch bar with a gap set to produce a 2 mil (100 micron) polyurethane coating between the liners. The film was placed into a 70°C oven for 16 hours to cure. The COP liner was removed prior to testing. The total thickness of the construction was measured as 107 um.

Following the calculation methods as Examples 1-6, the NCO/OH ratio of the Example 7 coating is 1.02, theoretical gel content of the Polyurethane coating is 100%, and the crosslink density is 0.63 mol/kg, all approximately the same as Example 6.

Polyurethane Coating Characterization

Glass Transition Temperature

The glass transition temperature of the polyurethane coatings as a function of cross-link density was characterized using a TA Instruments Model Q2000 Differential Scanning Calorimeter. The scans were taken at 2°C per minute heating rate. For examples 1-5, an empty sample pan was used as a reference. For example 6, a piece of primed LmPEN film was placed in the reference pan. The results are shown in Table 4 below. The onset and mid-point of the glass transition were determined per ASTM E1356-08 (2014).

Dynamic Mechanical Analysis Test Method

Samples from examples 1-5 were cut into strips 6.35 mm wide and about 4 cm long. The thickness of each film was measured. The films were mounted in the tensile grips of a Q800 DMA from TA Instruments with an initial grip separation between 6 mm and 9 mm. The samples were then tested at an oscillation of 0.2% strain and 1 Hz throughout a temperature ramp from -20 °C to 200 °C at a rate of 2 °C per minute. The temperature at which the Tan Delta signal reached a maximum was recorded as the glass transition temperature.

Table 4: Thermal, mechanical, and optical properties of the coatings alone

Example	2nd Scan Glass Transition by DSC		Dynamic Mechanical Analysis		
	Onset °C	Midpoint (I) °C	Storage Modulus @ °0 C (GPa)	Peak Tan Delta	Temp at peak Tan Delta (°C)
1	12.83	19.06	1.47	1.79	39.4
2	17.22	22.47	1.47	1.66	43.9
3	20.67	26.16	1.4	1.68	47.5
4	25.94	29.29	1.43	1.61	49.8
5	26.61	31.16	1.54	1.46	47.5
6	29.10	34.66	NA	NA	NA

Display Film Characterization Methods

Modulus and Yield Stress of the Substrate

Tensile properties were determined on an MTS Insight 5 System. The test specimens were dog bone shape (Type II in ASTM 638-14) cut from the films using a width of 3 mm with the thickness determined using a digital micrometer. Tests were run with a strain rate of 50.8 mm/min and gauge length (grip separation) of 25 mm using a 100N load cell. The 0.2% offset yield stress was determined from the stress strain curves following the procedures defined in section A2.6 of ASTM D638-14 “Standard Test Method for Tensile Properties of Plastics”.

Instrumented Scratch Resistance Test

The scratch resistance of the coated substrates was characterized using a Revetest RST instrumented scratch tester (Anton Paar, USA) fitted with a 1 mm diameter, 100Cr6 stainless steel ball tip. A sample of each construction was clamped against a glass slide and then a series of 8 mm long scratches were made in the samples at constant normal load and a rate of 60 mm/min. The sample was then set aside to recover at 23 ± 2°C and 50 ± 5% relative humidity. The highest normal load dent that was not visible to the naked eye after 24 hrs. recovery was recorded as the critical normal load (N).

Mandrel Bend Test

Bending properties of the coated substrates were tested using a modified version of ASTM Method D522/522M-13 “Mandrel Bend Test of Attached Organic Coatings”, test method B, Cylindrical Mandrel Test. Instead of bending to 90 degrees as specified in the ASTM method, all the samples were wrapped 180 degrees around the mandrel and then evaluated for damage. All samples were tested with the coating(s) on the outside radius (i.e. the coatings are in tension). The minimum cylinder size where no cracking was observed was reported as the minimum bend radius (pass/fail basis).

Transmission, Haze, and Clarity

Optical properties of the prepared examples were measured using a Hazegard instrument. Luminous transmission, clarity, and haze were measured according to ASTM D1003-00 using a Gardner Haze-Guard Plus model 4725 (available from BYK-Gardner Columbia, MD). Each result in Table 6 is the average of three measurements on a given sample.

Results

Table 5: Summary of Experimental Results

Example	Tensile Properties of Polymer Substrate		Overall Thickness including coating (um)	Critical Load for 24 hr. Room Temperature Scratch Recovery (N)	Mandrel Bend Radius (mm)
	Modulus (GPa)	0.2% Offset Yield Stress (MPa)			
6	4.7	84	125	10	2
7	8.0	227	107	12.5	2

Table 6: Optical properties of Example 6

Example	Transmission	Haze (%)	Clarity %)
6	91.0	0.28	100

Table 5 shows that despite being slightly thinner, the Example 7 with the high yield stress substrate showed higher critical normal load than the Example 6. This increase in performance is achieved even though the thickness of the shape memory layer is thinner by ~20 microns. Table 5 illustrates that both films can be bent around a radius of 2 mm without the coating sustaining damage such as cracking or delamination or development of visible haze.

Thus, embodiments of THIN PROTECTIVE DISPLAY FILMS are disclosed.

All references and publications cited herein are expressly incorporated herein by reference in their entirety into this disclosure, except to the extent they may directly contradict this disclosure. Although specific embodiments have been illustrated and described herein, it will be appreciated by those of ordinary skill in the art that a variety of alternate and/or equivalent implementations can be substituted for the specific embodiments shown and described without departing from the scope of the present disclosure. This application is intended to cover any adaptations or variations of the specific embodiments discussed herein. Therefore, it is intended that this disclosure be limited only by the claims and the equivalents thereof. The disclosed embodiments are presented for purposes of illustration and not limitation.

What is claimed is:

1. A display film comprising:

a transparent polymeric substrate layer having an 0.2% offset yield stress greater than 110 MPa; and

a transparent aliphatic cross-linked polyurethane layer having a thickness of 100 micrometers or less disposed on the transparent polymeric substrate layer, the transparent aliphatic cross-linked polyurethane layer having a glass transition temperature in a range from 11 to 27 degrees Celsius and a Tan Delta peak value in a range from 0.5 to 2.5;

the display film having a haze value of 2% or less.

2. The display film according to claim 1, wherein the transparent aliphatic cross-linked polyurethane layer has a cross-link density in a range from 0.34 to 0.65 mol/kg.

3. The display film according to claim 1, wherein the transparent aliphatic cross-linked polyurethane layer has a Tan Delta peak value in a range from 1 to 2.

4. The display film according to claim 1, wherein the display film has a thickness of less than 200 micrometers and the transparent polymeric substrate layer has a 0.2% offset yield stress greater than 130 MPa.

5. The display film according to claim 1, wherein the transparent aliphatic cross-linked polyurethane layer has a glass transition temperature in a range from 17 to 22 degrees Celsius and a Tan Delta peak value in a range from 1.4 to 1.8.

6. The display film according to claim 1, wherein the display film has a haze of 1% or less.

7. The display film according to claim 1, wherein the display film has a visible light transmission of 85% or greater.

8. The display film according to claim 1, further comprising a removable liner disposed on the transparent polymeric substrate layer or the transparent aliphatic cross-linked polyurethane layer.

9. The display film according to claim 1, further comprising an optical adhesive layer disposed on the transparent polymeric substrate layer and a removable liner disposed on the optical adhesive layer and a second removable liner disposed on the transparent aliphatic cross-linked polyurethane layer.

10. The display film according to claim 1, wherein the transparent polymeric substrate comprises polyimide.

11. A display film comprising:

a transparent polymeric substrate layer having an 0.2% offset yield stress greater than 110 MPa; and

a transparent aliphatic cross-linked polyurethane layer having a thickness of 100 micrometers or less disposed on the transparent polymeric substrate layer, the transparent aliphatic cross-linked polyurethane layer having a glass transition temperature in a range from 11 to 28 degrees Celsius and a Tan Delta peak value in a range from 0.5 to 2.5;

the display film remains intact after at least 100,000 bending cycles about a 3 mm radius.

12. The display film according to claim 11, wherein the transparent aliphatic cross-linked polyurethane layer has a cross-link density in a range from 0.34 to 0.65 mol/kg.

13. The display film according to claim 11, wherein the transparent aliphatic cross-linked polyurethane layer has a Tan Delta peak value in a range from 1 to 2.

14. The display film according to claim 11, wherein the display film has a thickness of less than 200 micrometers and the transparent polymeric substrate layer has a 0.2% offset yield stress greater than 130 MPa.

15. The display film according to claim 11, wherein the transparent aliphatic cross-linked polyurethane layer has a glass transition temperature in a range from 17 to 22 degrees Celsius and a Tan Delta peak value in a range from 1.4 to 1.8.

16. The display film according to claim 11, wherein the display film has a haze of 1% or less and a visible light transmission of 85% or greater

17. The display film according to claim 11, wherein the transparent polymeric substrate comprises polyimide.

18. An article, comprising:
an optical display;
a protective film disposed on the optical display, the protective film comprising:
    a transparent polymeric substrate layer having a 0.2% offset yield stress greater than 110 MPa;
    a transparent aliphatic cross-linked polyurethane layer having a thickness of 100 micrometers or less disposed on the transparent polymeric substrate layer, the transparent aliphatic cross-linked polyurethane layer having a glass transition temperature in a range from 11 to 28 degrees Celsius and a Tan Delta peak value in a range from 0.5 to 2.5 and a cross-link density in a range from 0.34 to 0.65 mol/kg;
    the display film having a haze value of 2% or less;
an optical adhesive layer fixing the transparent polymeric substrate layer to the optical display.

19. The article according to claim 18, wherein the optical display comprises an OLED display panel.

20. The article according to claim 18, wherein the optical display and protective film is foldable so that the optical display faces itself and at least a portion of protective film overlaps another portion of the protective film.

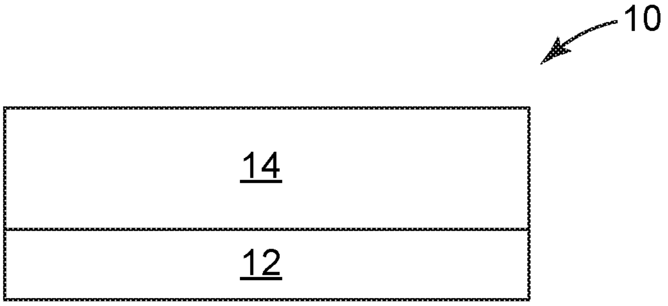

Fig. 1

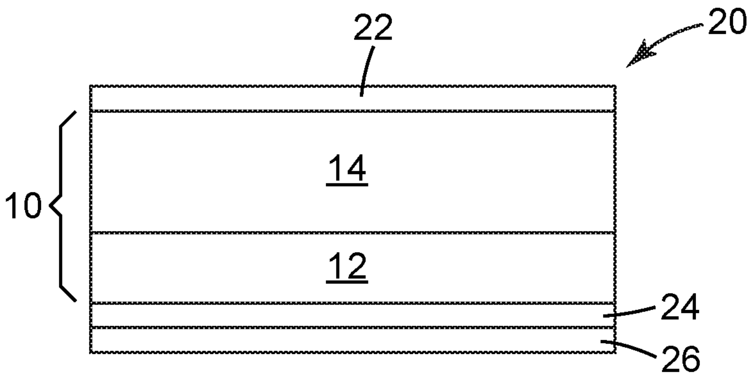

Fig. 2

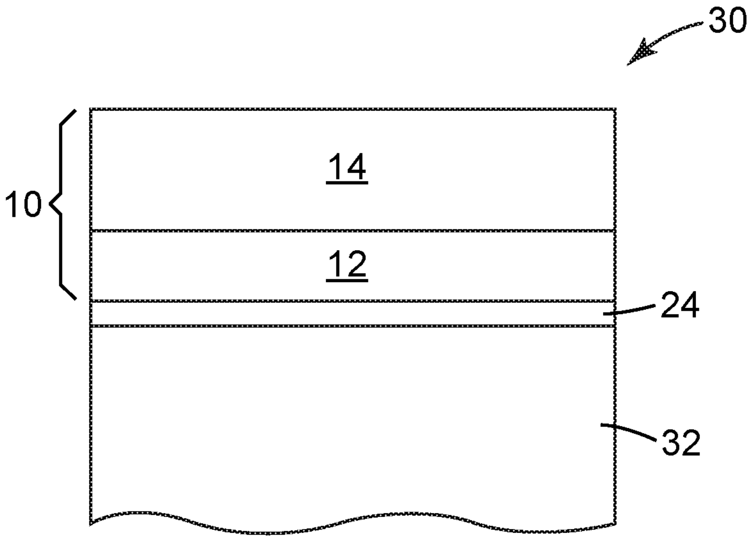

Fig. 3

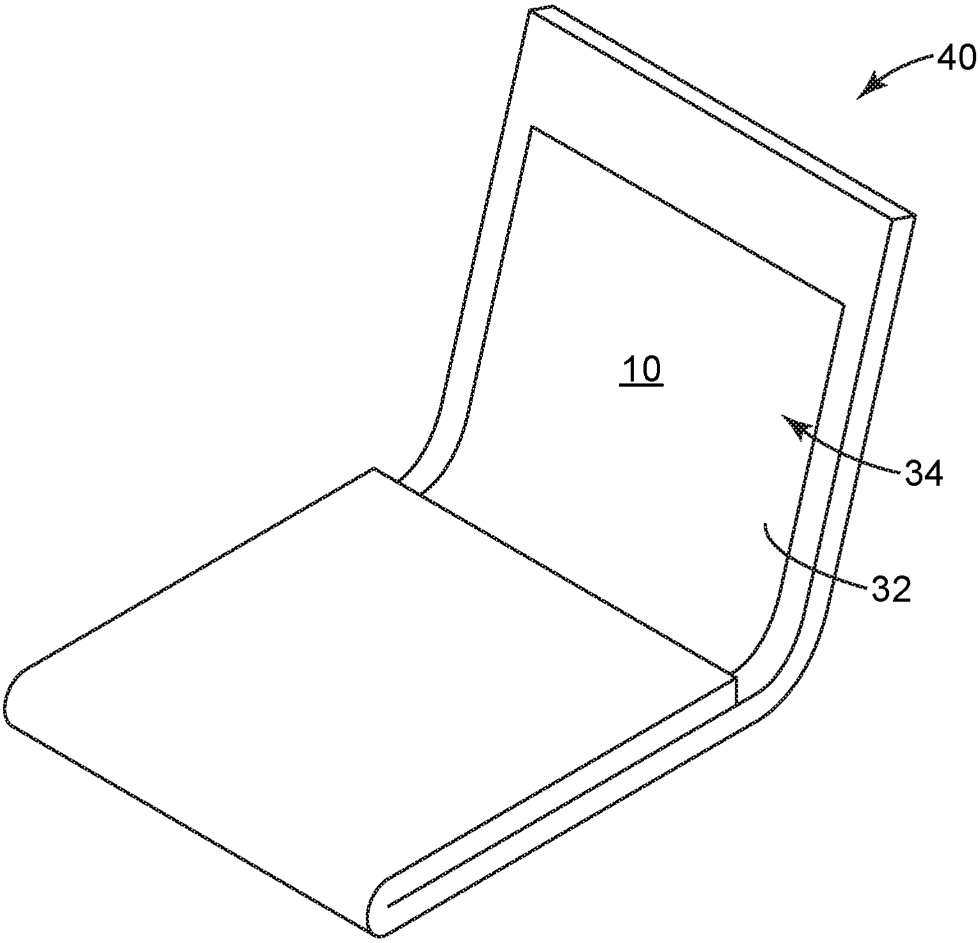

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/065043

A. CLASSIFICATION OF SUBJECT MATTER

B32B 27/08(2006.01)i, B32B 27/40(2006.01)i, B32B 7/02(2006.01)i, B32B 7/12(2006.01)i, B32B 27/28(2006.01)i

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 27/08; B29C 65/54; B32B 27/40; B32B 23/20; C08G 18/18; B32B 7/06; B32B 38/00; B32B 7/02; B32B 7/12; B32B 27/28

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: display, film, layer, transparent, aliphatic cross-linked polyurethane,Tan delta peak, haze, glass transition, offset yield stress, thickness, bending

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011-0045306 A1 (JOHNSON, M. A. et al.) 24 February 2011 See paragraphs [0099], [0108], [0134], [0217], [0304]; claim 39; and figure 1.	1-20
A	US 2013-0035466 A1 (VANLANDSCHOOT, K. et al.) 07 February 2013 See paragraph [0025]; and claims 1, 14.	1-20
A	US 2010-0032082 A1 (HO, C. C. et al.) 11 February 2010 See paragraph [0040]; claim 33; and figure 1.	1-20
A	US 2012-0021209 A1 (MONCUR, M. et al.) 26 January 2012 See paragraph [0029]; claims 1, 7; and figure 1.	1-20
A	WO 2015-148772 A1 (BAYER MATERIALSCIENCE LLC) 01 October 2015 See claims 1, 10, 14.	1-20

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 07 April 2017 (07.04.2017)	Date of mailing of the international search report **07 April 2017 (07.04.2017)**
Name and mailing address of the ISA/KR International Application Division Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea Facsimile No. +82-42-481-8578	Authorized officer LEE, Ki Cheul Telephone No. +82-42-481-3353

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2016/065043

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International application No.

PCT/US2016/065043

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