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(54) Title: LAMINATE WITH SUPERIOR BARRIER PERFORMANCE AND PREPARATION METHOD THEREOF

(57) Abstract: A laminate, an article comprising the laminate and a method for preparing the laminate are provided. The present disclosure relates to a laminate, comprising a first substrate comprising a metalized polyethylene-based (PE based) film; a second substrate comprising a polyethylene terephthalate-based film or a polypropylene-based film; and, an adhesive layer adhering the first substrate to the second substrate, wherein the adhesive layer is derived from a two-component solvent-based polyurethane adhesive composition; wherein the concentration of fatty acids or fatty acid derivatives in the metalized PE-based film is less than 300ppm, based on the total weight of the metalized PE-based film, wherein the two-component solvent-based polyurethane adhesive composition comprises a polyester polyol component and a polyisocyanate component, wherein the polyester polyol component has about 40wt%-60 wt %of aromatic rings in the backbone, based on the total weight of the polyester polyol and a molecular weight (Mw) between 5,000 and 50,000; and wherein the weight ratio of the polyester polyol component to the polyisocyanate component is from 100: 5 to 100: 30.



LAMINATE WITH SUPERIOR BARRIER PERFORMANCE AND PREPARATION METHOD THEREOF

FIELD OF THE INVENTION

The present disclosure relates to a laminate, an article comprising the laminate and a method for preparing the laminate. The laminate exhibits superior barrier performance.

BACKGROUND TECHNOLOGY

Nowadays, market trends such as consumerism, food safety and e-commerce has placed increasing demands on packaging functionalities, which require more sophisticated packaging structures with extended shelf life and/or enhanced packaging integrity. Therefore, these changes are leading to a fast growing market of high barrier films, which provide crucial protection to the contents from exterior circumstance to ensure longer shelf life.

In the flexible packaging industry, polyethylene terephthalate (PET), polyethylene (PE) and polypropylene (PP) are typical materials of substrate films to offer desired mechanical and barrier properties. PET or PP film, which has high stiffness, good optics and heat resistance, is widely used in the skin layer of laminate films as printing substrate. Meanwhile, PE film, which normally has better toughness and heat seal properties than PET or PP, is very popular as inner heat seal layer of lamination film. However, based on polymer properties, PET, PP and PE films typically cannot provide desired high oxygen barrier that is critical to protection of sensitive content like some meat, candy, snacks or cookies. Therefore, in the industry, there are various approaches to acquire the barrier performance, e.g. incorporating polymeric barrier resin through co-extrusion, vacuum metallization on a film substrate, or coating barrier materials on a film surface, etc. However, it is still a challenge in packaging industry to achieve high barrier performance of a laminate in terms of oxygen transmission rate (OTR).

For the above reasons, there is still a need in the packaging industry to develop a package with superior barrier performance.

SUMMARY

The present disclosure provides a unique laminate exhibiting superior barrier performance, an article comprising the laminate and a method for preparing the laminate.

In a first aspect, the present disclosure provides a laminate, comprising
a first substrate comprising a metalized polyethylene-based (PE based) film;
a second substrate comprising a polyethylene terephthalate-based (PET-based) film or a polypropylene-based (PP-based) film; and,

an adhesive layer adhering the first substrate to the second substrate, wherein the adhesive layer is derived from a two-component solvent-based polyurethane adhesive composition;

wherein the concentration of fatty acids or fatty acid derivatives in the metalized PE-based film is less than 300ppm, based on the total weight of the metalized PE-based film,

wherein the two-component solvent-based polyurethane adhesive composition comprises a polyester polyol component and a polyisocyanate component,

wherein the polyester polyol component has about 40wt%-60 wt % of aromatic rings in the backbone, based on the total weight of the polyester polyol and a molecular weight (Mw) between 5,000 and 50,000; and

wherein the weight ratio of the polyester polyol component to the polyisocyanate component is from 100:5 to 100:30.

In a second aspect, the present disclosure provides an article comprising the laminate of the present disclosure.

In a third aspect, the present disclosure provides a method for preparing the laminate of the present disclosure, comprising

1) providing a first substrate comprising a metalized PE-based film and a second substrate comprising a PET-based film or a PP-based film.

2) adhering the first substrate to the second substrate using a two-component solvent-based polyurethane adhesive composition;

wherein the concentration of fatty acids or fatty acid derivatives in the metalized PE-based film is less than 300 ppm, based on the total weight of the metalized PE-based film,

wherein the two-component solvent-based polyurethane adhesive composition

comprises a polyester polyol component and a polyisocyanate component,

wherein the polyester polyol component has 40wt%-60 wt % of aromatic rings in the backbone, based on the total weight of the polyester polyol and a Mw between 5,000 and 50,000; and

wherein the weight ratio of the polyester polyol component to the polyisocyanate component is from 100:5 to 100:30.

DETAILED DESCRIPTION

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention belongs. Also, all publications, patent applications, patents, and other references mentioned herein are incorporated by reference.

As disclosed herein, all ranges include endpoints unless otherwise indicated.

According to an embodiment of the present disclosure, the adhesive composition is a "two-component" or "two-part" composition comprising a polyester polyol component and a polyisocyanate component. According to another embodiment, the polyester polyol component and the polyisocyanate component are packaged, transported and stored separately, combined shortly or immediately before being used for the manufacture of the laminate.

"Polyethylene polymer", "polyethylene-based polymer", "PE-based polymer", "polyethylene", or "ethylene-based polymer" shall mean polymers comprising a majority amount (>50 mol %, or >60 mol %, or >70 mol % or >80 mol %, or >90 mol %, or >95 mol % or >97 mol %) of units which have been derived from ethylene monomer. This includes polyethylene homopolymers or copolymers (meaning units derived from two or more comonomers). Common forms of polyethylene known in the art include Low Density Polyethylene (LDPE); Linear Low Density Polyethylene (LLDPE); Ultra Low Density Polyethylene (ULDPE); Very Low Density Polyethylene (VLDPE); single-site catalyzed Linear Low Density Polyethylene, including both linear and substantially linear low density resins (m-LLDPE); Medium Density Polyethylene (MDPE); and High Density Polyethylene (HDPE). These polyethylene materials are generally known in the art; however, the following descriptions may be helpful in understanding the differences between some of these different polyethylene resins.

The term “LDPE” may also be referred to as “high pressure ethylene polymer” or “highly branched polyethylene” and is defined to mean that the polymer is partly or entirely homo-polymerized or copolymerized in autoclave or tubular reactors at pressures above 14,500 psi (100 MPa) with the use of free-radical initiators, such as peroxides (see for example US 4,599,392, which is hereby incorporated by reference). LDPE resins typically have a density in the range of 0.916 to 0.935 g/cm³.

The term “LLDPE”, includes both resin made using the traditional Ziegler-Natta catalyst systems and chromium-based catalyst systems as well as single-site catalysts, including, but not limited to, bis-metallocene catalysts (sometimes referred to as “m-LLDPE”) and constrained geometry catalysts, and includes linear, substantially linear or heterogeneous polyethylene copolymers or homopolymers. LLDPEs contain less long chain branching than LDPEs and includes the substantially linear ethylene polymers which are further defined in U.S. Patent 5,272,236, U.S. Patent 5,278,272, U.S. Patent 5,582,923 and US Patent 5,733,155; the homogeneously branched linear ethylene polymer compositions such as those in U.S. Patent No. 3,645,992; the heterogeneously branched ethylene polymers such as those prepared according to the process disclosed in U.S. Patent No. 4,076,698; and/or blends thereof (such as those disclosed in US 3,914,342 or US 5,854,045). The LLDPEs can be made via gas-phase, solution- phase or slurry polymerization or any combination thereof, using any type of reactor or reactor configuration known in the art.

The term “MDPE” refers to polyethylenes having densities from 0.926 to 0.935 g/cm³. “MDPE” is typically made using chromium or Ziegler-Natta catalysts or using single-site catalysts including, but not limited to, bis-metallocene catalysts and constrained geometry catalysts, and typically have a molecular weight distribution (“MWD”) greater than 2.5.

The term “HDPE” refers to polyethylenes having densities greater than about 0.935 g/cm³ and up to about 0.970 g/cm³, which are generally prepared with Ziegler-Natta catalysts, chrome catalysts or single-site catalysts including, but not limited to, bis-metallocene catalysts and constrained geometry catalysts.

The term “ULDPE” refers to polyethylenes having densities of 0.880 to 0.912 g/cm³, which are generally prepared with Ziegler-Natta catalysts, chrome catalysts, or single-site catalysts including, but not limited to, bis-metallocene catalysts and constrained geometry catalysts.

“polypropylene-based polymer”, “PP-based polymer” or “propylene-based polymer” shall mean polymers comprising a majority amount (>50 mol %, or >60 mol %, or >70 mol % or >80 mol %, or >90 mol %, or >95 mol %) of units which have been derived from propylene monomer.

“polyethylene terephthalate-based polymer”, or “PET-based polymer” shall mean polymers comprising a majority amount (>50wt %, or >60 wt %, or >70 wt % or >80 wt%, or >90 wt %, or >95 wt %) of ethylene terephthalate.

“Polyolefin plastomer” can be a polyethylene plastomer or a polypropylene plastomer. Polyolefin plastomers include, for example, polymers made using single-site catalysts such as metallocenes and constrained geometry catalysts. Polyolefin plastomers have a density of 0.885 to 0.915 g/cm³. All individual values and subranges from 0.885 g/cm³ to 0.915 g/cm³ are included herein and disclosed herein; for example, the density of the polyolefin plastomer can be from a lower limit of 0.895, 0.900, or 0.905 g/cm³ to an upper limit of 0.905, 0.910, or 0.915 g/cm³. In some embodiments, the polyolefin plastomer has a density from 0.890 to 0.910 g/cm³.

“Polyolefin elastomer” can be a polyethylene elastomer or a polypropylene elastomer. The polyolefin elastomers have a density of 0.857 to 0.885 g/cm³. All individual values and subranges from 0.857 g/cm³ to 0.885 g/cm³ are included herein and disclosed herein; for example, the density of the polyolefin elastomer can be from a lower limit of 0.857, 0.860, 0.865, 0.870, or 0.875 g/cm³ to an upper limit of 0.870, 0.875, 0.880, or 0.885 g/cm³. In some embodiments, the polyolefin elastomer has a density from 0.860 to 0.880 g/cm³.

“polyethylene-based film” or “PE-based film” refers to a film that comprises at least 90 weight percent of polyethylene, at least 95 weight percent of polyethylene, at least 97 weight percent of polyethylene based on the total weight of the film.

“polypropylene -based film” or “PP-based film” refers to a film that comprises at least 90 weight percent of polypropylene, at least 95 weight percent of polypropylene, at least 97 weight percent of polypropylene based on the total weight of the film.

“polyethylene terephthalate-based film” or “PET-based film” refers to a film that comprises at least 90 weight percent of polyethylene terephthalate, at least 95 weight percent of polyethylene terephthalate, at least 97 weight percent of polyethylene terephthalate based on the total weight of the film.

The first substrate

The first substrate comprises a metalized PE-based film. The metalized PE-based film comprises a PE-based film and a metal layer.

The PE-based film in the metalized PE-based film has at least one layer comprising polyethylene. There can be one layer comprising polyethylene. Alternatively, there can be two or more layers comprising polyethylene. These two or more layers can be extruded together to form a PE-based film. There can be three (or three or more) layers comprising polyethylene. When there are three (or three or more) layers comprising polyethylene, the layer adjacent the metal layer is called herein a skin layer, the layer opposite the metal layer on the outside of the PE-based film is called a sealant layer, and a layer or layers between the skin and sealant layers is a core layer or core layers. When there is only one layer comprising polyethylene, any of the polyethylene compositions discussed herein as skin, core or sealant layers can be used. When there are only two layers comprising polyethylene, any combinations of skin layer and core layer, skin layer and sealant layer, or core layer and sealant layer can be used. When there are two or more polyethylene-comprising layers, each polyethylene-comprising layer can be immediately adjacent to at least one other polyethylene-comprising layer, or an adhesive layer or other intermediary layer can be used between the two or more polyethylene-comprising layers. In an embodiment, the PE-based film in the metalized PE-based film comprises a sealant layer. In an embodiment, the PE-based film in the metalized PE-based film comprises a skin layer, a core layer and a sealant layer.

The PE-based film in the metalized PE-based film can comprise a linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), a low density polyethylene (LDPE) as well as combinations of two or more of the foregoing. Preferably, the PE-based film in the metalized PE-based film can comprise a Ziegler-Natta catalyzed, single site catalyzed (including, without limitation, metallocene), or Chromium catalyzed linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), an autoclave produced or tubular produced low density polyethylene (LDPE) as well as combinations of two or more of the foregoing.

The PE-based film in the metalized PE-based film can further comprise at least one of an ultra-low density polyethylene, a polyolefin plastomer, a polyolefin elastomer, an ethylene vinyl acetate copolymer, an ethylene ethyl acrylate copolymer,

an ethylene vinyl alcohol, and any polymer comprising at least 50% ethylene monomer, and combinations thereof.

A skin layer can comprise a linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), a low density polyethylene (LDPE) as well as combinations of two or more of the foregoing; preferably can comprise a linear low density polyethylene (LLDPE), a low density polyethylene (LDPE) or combinations thereof. This LLDPE can be a single site catalyzed polyethylene (such as, and without limitation, m-LLDPE). The skin layer can further comprise additives, such as, for example, antioxidants, ultraviolet light stabilizers, thermal stabilizers, slip agents, antiblock, pigments or colorants, processing aids, crosslinking catalysts, flame retardants, fillers and foaming agents. When used in combination with a core layer or sealant layer, the skin layer is the layer that is metalized and in that instance is advantageously free of slip agents but may include anti-block agents (e.g. talc, silicon dioxide, etc.), anti-oxidants, and processing aids. In an embodiment, the additives such as slip agents and anti-block agents typically will not be used in the skin layer.

A core layer can comprise a linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), a low density polyethylene (LDPE) as well as combinations of two or more of the foregoing. The core layer can preferably comprise a middle density polyethylene (MDPE), a high density polyethylene (HDPE) or combinations thereof. The core layer can also comprise additives as mentioned for the skin layer. Preferably, additives such as slip agents and anti-block agents typically will not be used in the core layer. This layer can be adjacent the skin layer on an opposite side of the skin layer from the metal layer.

A sealant layer can comprise a linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), a low density polyethylene (LDPE), polyolefin elastomers or plastomers, as well as combinations of two or more of the foregoing. Preferably, the sealant layer can comprise a Ziegler-Natta catalyzed, single site catalyzed (including metallocene), or Chromium catalyzed linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), an autoclave produced or tubular produced low density polyethylene (LDPE) as well as combinations of two or more of the foregoing, preferably comprise a linear low density polyethylene (LLDPE), a low density polyethylene (LDPE) or combinations thereof. The LLDPE

can be a single site catalyzed polyethylene (e.g. mLLDPE). This can be an outer layer of the film. The sealant layer may advantageously include an anti-blocking agent. For example, an anti-block agent may be present in the sealant layer at an amount of at least about 200ppm, at least about 1000ppm or at least about 1500 ppm, preferably not greater than about 6000 ppm, or not greater than about 5000 ppm. In addition, slip agents (e.g. erucamide) may be helpful. For example, slip agents may be present in the sealant layer at an amount of less than 500ppm, or less than 300ppm, or less than 200ppm, less than 100ppm, preferably less than 50 ppm, or equal to 0 ppm, based on total weight of the sealant layer.

The PE-based film of the metalized PE-based film can be a blown film, a cast film, a machine direction oriented film or a biaxially oriented film. The PE-based film of the metalized PE-based film layer can be fabricated through blown, casting, water quenching, double bubble, or other techniques known to those of ordinary skill in the art such as those described in *Film Processing Advances*, Toshitaka Kanai and Gregory A. Campbell (editors), Chapter 7 (Biaxial Oriented Film Technology), pp. 194-229. In some embodiments, after fabrication, the film may be subjected to machine direction orientation (MDO) or biaxial orientation process to provide a machine direction oriented film or a biaxially oriented film, respectively.

The PE-based film of the metalized PE-based film layer can be metallized by any known method for metallizing polyethylene films. For example, the metal layer can be applied using vacuum metallization. This can include providing a metal source and evaporating it in a vacuum environment causing it to condense on the surface of the film. The metal is deposited on the skin layer of the PE-based film.

Suitable metals include Al, Zn, Au, Ag, Cu, Ni, Cr, Ge, Se, Ti, Sn, or oxides thereof. The metal layer can be formed from aluminum or aluminum oxide (Al_2O_3) in some embodiments.

After metallization, the metallized PE-based film can conveniently be stored in rolls. In this process, the metallized surface layer is in contact with a polyethylene layer on the opposite side of the film.

The overall thickness of the metalized film can be at least 10, at least 20, or at least 30 microns. The overall thickness of the metallized film according to certain embodiments is no more than 200, no more than 150, no more than 120, no more than 100, no more than 80, no more than 70, or no more than 60 microns.

The metallized PE-based film can have an optical density (OD) at least 1.5, or at least 1.8 and no more than 4.0, no more than 3.5, or no more than 3.0. In some embodiments, the OD is 2.0. The optical density of a metallized PE-based film (e.g., a multilayer structure comprising a polyethylene film with a metal layer deposited on it) can be measured using an optical density meter (Model No. LS177 from Shenzhen Linshang Technology).

The metallized PE-based film can retain a surface energy of the metallized surface of at least 34 dyne/cm, at least 38 dyne/cm, at least 40 dyne/cm, or at least 42 dyne/cm, or at least 46 dyne/cm for at least one or at least two weeks from the metallization.

The metallized PE-based film can be characterized by the absence (0 ppm) or substantial absence of fatty acids or its derivatives. Such fatty acids or its derivatives that are absent or substantially absent include saturated fatty acid with an even number of carbon atoms, from 4 to 28, such as stearic acid (18 carbon atoms) and palmitic acid (16 carbon atoms), etc., and the metal salts of the respective fatty acid, such as calcium stearate, zinc stearate, calcium palmitate, etc. Specifically, the concentration of fatty acids or its derivatives in the metallized PE-based film can be no more than 300 ppm, no more than 250 ppm, no more than 200 ppm, no more than 100 ppm, or no more than 50 ppm, or equal to 0 ppm, based on total weight of the metallized PE-based film.

The concentration of anti-oxidants in the metallized PE-based film layer is less than 3000 ppm, or less than 2000 ppm, or less than 1500ppm, or less than 1300ppm, based on the total weight of the metallized PE-based film.

Additives

An anti-oxidant is a compound included in polymeric films to stabilize the polymer(s) or prevent oxidative degradation of the polymer(s). Anti-oxidants are well known to persons of ordinary skill in the art.

An antiblock agent is a compound that minimizes, or prevents, blocking (i.e., adhesion) between two adjacent layers of film. Blocking can cause issues, for example, during unwinding of a film roll. The use of antiblock agents is well known to persons of ordinary skill in the art. Examples of common antiblock agents include, without limitation, silica, talc, calcium carbonate, and combinations thereof.

A slip agent is a compound added to a film to reduce friction between films and/or between films and equipment. Typical slip agents include migratory and non-migratory slip agents and are well to persons of ordinary skill in the art.

The adhesive layer

The adhesive layer is derived from a two-component solvent-based polyurethane adhesive composition, wherein the two-component solvent-based polyurethane adhesive composition comprises a polyester polyol component and a polyisocyanate component.

A. The polyester polyol component

The polyester polyol is typically obtained by reacting polyfunctional alcohols having from 2 to 12 carbon atoms, preferably from 2 to 10 carbon atoms, with polyfunctional carboxylic acids having from 2 to 12 carbon atoms, preferably 2 to 10 carbon atoms, or anhydrides/esters thereof. Typical polyfunctional alcohols for preparing the polyester polyol are preferably diols, triols, tetraols, and may include ethylene glycol, butylene glycol, diethylene glycol, triethylene glycol, polyalkylene glycols, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, trimethylolpropane, glycerol, erythritol, pentaerythritol, trimethylolbenzene, and any combinations thereof. Typical polyfunctional carboxylic acids for preparing the polyester polyol can be aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic and may be substituted, for example with halogen atoms, and/or may be saturated or unsaturated. Preferably, the polyfunctional carboxylic acids are selected from the group consisting of adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, glutaric acid, tetrachlorophthalic acid, maleic acid, fumaric acid, itaconic acid, malonic acid, 2-methyl succinic acid, 3,3-diethyl glutaric acid, 2,2-dimethyl succinic acid, trimellitic acid, the anhydrides thereof, and any combinations thereof. Preference is given to adipic acid or a mixture of adipic acid and isophthalic acid. In another embodiment, the polyester polyol has an OH number of 2 to 30 mg KOH/g, preferably from 5 to 25 mg KOH/g, and more preferably from 8 to 20 mg KOH/g.

According to an embodiment of the present disclosure, the polyester polyol has a hydroxyl functionality of at least 1.8, or at least 1.9, or at least 2.0, or at least 2.1, or at least 2.2, or up to 2.3, or up to 2.4, or up to 2.5, or up to 2.6, or up to 2.7, or up to 2.8, or up to 2.9, or up to 3.0, or within a numerical range obtained by combining any

two of the above indicated end points. The polyester polyol may have a molecular weight from 5000 to 50,000 g/mol, or from 5500 to 30,000 g/mol, or from 6,000 to 25,000 g/mol, or from 10,000 to 15,000 g/mol, or within a numerical range obtained by combining any two of the above indicated end points. The above introduction about the origin, preparation process, category, molecular structure and various parameters of polyester polyol also apply to this second polyester polyol.

According to an embodiment of the present disclosure, the polyester polyol has an aromatic ring content of from about 40 wt% to about 60wt% or from about 45wt% to about 55wt% or from about 47 wt% to about 55 wt%, based on the dry weight of the polyester polyol.

For example, as one illustrative embodiment, the content of the polyester polyol can be from 40 wt% to 85 wt%, or from 50 wt% to 80 wt%, or from 60 wt% to 77 wt%, or from 65 wt% to 75 wt%, based on the total weight of the polyurethane adhesive composition.

The solid content of polyester polyol component can be 40-85wt%, preferably 50-80wt%, more preferably 55-75%, and the solvent used for the polyester polyol could be ethyl acetate or MEK, or combination, preferably ethyl acetate.

B. The polyisocyanate component

The polyisocyanate may include any molecules having 2 or more isocyanate groups, and mixtures thereof. Such polyisocyanates can be aliphatic, alicyclic, aromatic, araliphatic or mixtures thereof. The polyisocyanates may have an average functionality of >2 or from 2.5 to 10. Examples of suitable polyisocyanates include C₂-C₁₂ aliphatic diisocyanates, as well as dimers and trimers thereof, such as, for example, C₂-C₈ alkylene diisocyanates, such as tetramethylene diisocyanate and hexamethylene diisocyanate (HDI), 1,12-dodecane diisocyanate, 2,2,4-trimethyl-hexamethylene diisocyanate, 2,4,4-trimethyl-hexamethylene diisocyanate, 2-methyl-1,5-pentamethylene diisocyanate; C₆-C₁₅ alicyclic diisocyanates, as well as dimers and trimers thereof, such as, for example, isophorone diisocyanate (IPDI) and dicyclohexyl methane diisocyanate (HMDI), 1,4-cyclohexane diisocyanate, and 1,3-bis-(isocyanatomethyl)cyclohexane; C₆-C₁₂ aromatic diisocyanates, as well as dimers and trimers thereof, such as, for example, toluene diisocyanate (TDI), and diphenyl methane diisocyanate (MDI); C₇-C₁₅ araliphatic diisocyanates as well as dimers and trimers thereof, such as, for example,

Preferably, the polyisocyanate comprises aliphatic or aromatic polyisocyanates. More preferably, the polyisocyanates are hexamethylene diisocyanate homopolymers, hexamethylene diisocyanate adducts, isophorone diisocyanate homopolymers, isophorone diisocyanate adducts, toluene diisocyanate (TDI), toluene diisocyanate (TDI) adducts, diphenyl methane diisocyanate (MDI), diphenyl methane diisocyanate (MDI) adducts, or mixtures thereof. The trimers (or isocyanurates) in the polyisocyanate may be prepared by methods known in the art, for example, as disclosed in U.S. Patent Publication No. 2006/0155095A1, to Daussin et al., by trimerizing an alicyclic diisocyanate (e.g. isophorone diisocyanate) in the presence of one or more trimerization catalyst, such as, for example, a tertiary amine or phosphine or a heterogeneous catalyst, and, if desired, in the presence of solvents and/or assistants, such as co-catalysts, expediently at elevated temperature, until the desired isocyanate (NCO) content has been reached, and then deactivating the catalyst using inorganic and organic acids, the corresponding acid-halides and alkylating agents and, preferably, heating. Isocyanurate compositions containing isocyanurates from aliphatic diisocyanates may likewise be formed by cyclizing aliphatic diisocyanates in the presence of one or more trimerization catalyst and then deactivating the catalyst. Any of the isocyanurates can be further modified by conventional methods to contain urethane, urea, imino-s-triazine, uretonimine or carbodiimide moieties. Preferably, the polyisocyanate useful in the present invention is selected from the group consisting of an aromatic diisocyanate, dimers and trimers thereof, or mixtures thereof.

The polyisocyanate useful in the present invention may include one or more polyisocyanate prepolymers, which may be formed by reaction of a diisocyanate with a monol, diol, diamine, or monoamine, which is then modified by the reaction of additional isocyanate to form allophanate or biuret modified prepolymers. Such prepolymers may further comprise a polyalkoxy or polyether chain. Alternatively, such prepolymers can then be mixed with a trimerization catalyst giving an allophanate or biuret modified polyisocyanate compositions. Preparation of such allophanate or biuret prepolymers, followed by trimerization, is known in the art, see for example, U.S. Patent No.s 5,663,272 and 6,028,158. Still further, suitable polyisocyanates may be modified by an ionic compound such as aminosulfonic acid.

Commercially available polyisocyanates may include, for example, Desmodur L75, N3300, N3600, and N3900 polyisocyanates and Bayhydur XP 2655, 401-60 and 401-70 polyisocyanates (Covestro); Tolonate HDT, HDT-LV and HDT-LV2, and

Easaqua L 600 polyisocyanates (Vencorex Chemicals); DURANATE TLA-100 and TMA-100 polyisocyanates (AsahiKASEI); and Aquolin 268, 269 and 270 polyisocyanates (Wanhua Chemicals).

The polyisocyanate useful in the present invention can be used alone or diluted with one or more solvents to form a polyisocyanate solution, prior to mixing with the polyol component. Such solvents (also as “diluting solvents”) can reduce the viscosity of the polyisocyanate and have no reactivity with the polyisocyanate. The solvent may be used in an amount of from 5% to 150%, from 15% to 130%, from 20% to 120%, or from 30% to 100%, by weight based on the weight of the polyisocyanate. Suitable diluting solvents may include, for example, ethyl acetate, butyl acetate, MEK, or mixtures thereof. The solid content of the polyisocyanate component can be 40-100wt%, preferably 50-90wt%, more preferably 55-80%. The polyurethane adhesive composition of the present invention may have equivalent ratios of the total number of isocyanate group equivalents in the polyisocyanates, which may contain several different polyisocyanates, to the total number of hydroxyl group equivalents in the polyester polyol component, in the range of, for example, from 1:1 to 2.0:1, or from 1:1 to 1.8:1, or from 1:1 to 1.5:1 or 1:1 to 1.2:1. According to a preferable embodiment of the present disclosure, the amount of the polyisocyanate compound is properly selected so that the isocyanate group is present at a stoichiometric molar amount relative to the total molar amount of the hydroxyl groups included in the polyester polyol component.

The polyurethane adhesive composition of the present invention may further comprise conventional additives such as, for example, catalysts to enhance curing, pigments, light stabilizers, ultraviolet (UV) absorbing compounds, leveling agents, wetting agents, dispersants, neutralizers, defoamers, or rheology modifiers, or mixtures thereof. These additives may be present in an amount of from zero to 20%, from 1 to 10%, by weight based on the weight of the polyurethane composition.

According to an embodiment of the present disclosure, the weight ratio of the polyester polyol component to the polyisocyanate component is from about 100:5 to about 100:30, preferably from about 100:8 to about 100:25, more preferably from about 100:10 to about 100:20.

The polyurethane adhesive can be prepared by mixing polyester polyol component and polyisocyanate component together to mix them homogeneously and adding a certain amount of solvent to achieve a desired solid content.

The second substrate

The second substrate comprises a polyethylene terephthalate-based (PET-based) film or a polypropylene-based (PP-based) film.

There are three general types of PP polymer: homopolymer, random copolymer, and block copolymer. The comonomer is typically used with ethylene or butylene. Suitable suppliers/products for PP may include Sinopec Chemicals.

The PP-based film may comprise from 50% to 100%, by weight of the PP-based film of a PP component. Preferably the PP-based film comprises from 70% to 99%, preferably 80% to 95%, alternatively from 90% to 98%, by weight of the PP-based film, of the PP component. The PP component has at least one PP polymer, optionally two or more PP polymers (i.e., different grades of PP).

Preferably the PP-based film comprises from 50% to 100% by weight of the PP component, of a homo-polymer PP or random copolymer PP or combination thereof. Preferably the PP-based film comprises 100% by weight of the PP component of either a homo-polymer PP or a PP random copolymer.

One example of a PP grade is a homopolymer PP. Preferably the homopolymer PP comprises a Melt Flow Rate (230° C/2.16Kg) ("MFR") from 2.6 to 3.0 g/10 min, preferably 2.7 to 2.9 g/10 min, more preferably about 2.8 g/10 min. Preferably the homopolymer PP comprises a Tensile Strength at Yield of 26 to 36 MPa, preferably 28 to 35 MPa, more preferably at or greater than about 30 MPa. Preferably the homopolymer PP comprises an Isotactic Index at or greater than 93%, more preferably at or greater than 94%, yet more preferably at or greater than 95%, alternatively at or less than 98%.

One example of a PP grade is a random copolymer PP (RCPP). Preferably the RCPP comprises a Melt Flow Rate (230° C/2.16Kg)("MFR") from 2.6 to 3.0 g/10 min, preferably 2.7 to 2.9 g/10 min, more preferably 2.8 g/10 min. Preferably the random copolymer PP comprises a Tensile Strength at Yield of 27 to 37 MPa, preferably 29 to 36 MPa, more preferably at or greater than 31 MPa. Preferably the random copolymer PP comprises an Isotactic Index at or greater than 96%, more preferably at or greater than 97%, yet more preferably at or greater than 98%.

The PP-based film in the second substrate can be a blown film, a cast film, a machine direction oriented film or a biaxially oriented film. The PP-based film in the second substrate can be fabricated through blown, casting, water quenching, double

bubble, or other techniques known to those of ordinary skill in the art such as those described in *Film Processing Advances*, Toshitaka Kanai and Gregory A. Campbell (editors), Chapter 7 (Biaxial Oriented Film Technology), pp. 194-229. In some embodiments, after fabrication, the film may be subjected to machine direction orientation (MDO) or biaxial orientation process to provide a machine direction oriented film or a biaxially oriented film, respectively.

PET refers to polyethylene terephthalate. Polyethylene terephthalate can be obtained by a conventionally known method of polycondensation of the diol component (i.e. ethylene glycol) and dicarboxylic acid component (i.e. terephthalic acid) known in the art. Specifically, it can be produced by a general melt polymerization method in which polycondensation is performed under reduced pressure after esterification and/or transesterification of the diol component and the dicarboxylic acid component, or a known solution heating dehydration condensation using an organic solvent.

The fabrication process of PET may include a machine direction oriented film or a biaxially oriented film.

An amount of the diol component used in producing the PET is substantially equivalent molar amount to 100 moles of dicarboxylic acid or a derivative thereof, but is, in general, excessive by 0.1% by mole or more and 20% by mole or less because of distillation occurring in esterification and/or transesterification and/or polycondensation.

Besides, polycondensation is preferably performed in the presence of a polymerization catalyst. Timing of adding the polymerization catalyst is not especially limited as long as it is before the polycondensation, and the catalyst may be added in charging raw materials, or in starting pressure reduction.

The PET-based film or PP-based film in the second substrate can comprises 1-10 layers, or 1-8 layers or 1-5 layers.

The laminate

The laminate can be prepared by a method comprising the following steps:

- 1) providing a first substrate comprising a metalized PE-based film (as described above) and a second substrate comprising a polyethylene terephthalate-based film or a polypropylene-based film (as described above),

2) adhering the first substrate to the second substrate using a two-component solvent-based polyurethane adhesive composition;

wherein the concentration of fatty acids or fatty acid derivatives in the metalized PE-based film is less than 300 ppm, based on the total weight of the metalized PE-based film,

wherein the two-component solvent-based polyurethane adhesive composition comprises a polyester polyol component and a polyisocyanate component,

wherein the polyester polyol component has 40wt%-60 wt % of aromatic rings in the backbone, based on the total weight of the polyester polyol and a Mw between 5,000 and 50,000; and

wherein the weight ratio of the polyester polyol component to the polyisocyanate component is from 100:5 to 100:30.

The laminate of the present disclosure has an OTR of lower than $2.3 \text{ cc/m}^2 \cdot 24$ hours measured under the condition of 23°C and 0% relative humidity when measured using the Test Method described herein, or less than $2.0 \text{ cc/m}^2 \cdot 24$ hours or less than $1.9 \text{ cc/m}^2 \cdot 24$ hours or not greater than $1.8 \text{ cc/m}^2 \cdot 24$ hours when measured using the Test Method described herein.

The laminate can be used to form articles such as packages. Examples of packages that can be formed from the laminate of the present invention can include flexible packages, pouches, stand-up pouches, and pre-made packages or pouches. The laminate of the present invention can be used for food packages. Examples of food that can be included in such packages include meats, cheeses, cereal, nuts, juices, sauces, and others. Such packages can be formed using techniques known to those of skill in the art based on the teachings herein and based on the particular use for the package (e.g., type of food, amount of food, etc.).

EXAMPLES

Some embodiments of the invention will now be described in the following Examples. However, the scope of the present disclosure is not, of course, limited to the formulations set forth in these examples. Rather, the Examples are merely inventive of the disclosure.

The information of the raw materials used in the examples is listed in the following Table 1:

Table 1. Raw materials used in the examples

	Code	Composition	Remark	Supplier
Adhesive	ADCOTE™ 516A	NCO prepolymer, 70%, solid content	Solvent-based (SB) adhesive	The Dow Chemical Company
	ADCOTE™ 516B	Polyol coreactant, 70%, solid content		The Dow Chemical Company
	IE-PES-1(47% IPA/16% AdA/7%EG/30%DEG)*	Polyester polyol, aromatic ring=47% Mw=14288, 66%, solid content		Prepared in the Example Section
	IE-PES-2(47%IPA/15% AdA/8% EG/31% DEG)*	Polyester polyol, 47% aromatic ring, Mw=22578 60%, solid content		Prepared in the Example Section
	IE-PES-3 (55%IPA/10%AdA/8%E G/27%DEG/1%TMP)*	Polyester polyol, aromatic ring=55% Mw=6231 80%, solid content		Prepared in the Example Section
	CE-PES-1(54% IPA/15%SA/12% EG/19%DEG)*	Polyester polyol, aromatic ring=54%, Mw=60916, 51%, solid content		Prepared in the Example Section
	CE-PES-2 (29%IPA/29%SA/2%EG/ 34%NPG)*	Polyester polyol, aromatic ring=29%, Mw=13280 66%, solid content		Prepared in the Example Section
	Coreactant F	Polyisocyanate crosslinker based on TDI, 75%, solid content		The Dow Chemical Company
	ROBOND™ L168D	Polyacrylic emulsion	Water base adhesive	The Dow Chemical Company

	CR3A	Polyisocyanate	Crosslinker for WB adhesive	The Dow Chemical Company
PE products	ELITE™ AT6410	MI=0.85, Density=0.912	LLDPE	The Dow Chemical Company
	ELITE™ AT6900	MI=1.2, Density=0.969	HDPE	The Dow Chemical Company
	UNIVAL™ DMDA6400	MI=0.8, Density=0.961	HDPE	The Dow Chemical Company
	DOW™ LDPE 450E	MI=2.0, Density=0.923	LDPE	The Dow Chemical Company
Anti-block agent	AB20 masterbatch	MI=1.9, Density 0.925		BEIJING YALUNZ HILIAN SCIENCE & TECHNOLOGY CO.,LTD
PET film	PET flat film	NA Thickness=12μm		Anhui Guofeng Plastic Industry Co.,Ltd.
BOPP film	PP	product type: PP Thickness=18μm		Guangdong Weifu Packaging Material Co., Ltd

*IPA represents isophthalic acid; PA represents phthalic acid; AdA represents adipic acid, EG represents ethylene glycol, DEG represents diethylene glycol, SA represents sebacic acid, NPG represents neopentyl glycol.

All the PE-based films were fabricated through blown process. Formulations are listed in Table 2. Film-1 and Film-2 had a thickness of 50 μ m. The vacuum metallization was conducted on an industrial metallization machine (Machine type K5 EXPERT, BOBST Company) with OD=2.0. MET-1 and MET-2 is the symbol indicating the metallized Film-1 and Film-2, respectively. Before adhesive lamination, the vacuum-metallized Films fabricated were stored in manner of film rolls for 2 weeks under an environment of 23 °C and 50% humidity. The surface energy of metal layer of Metalized film-1 (MET-1) declined to <34 Dyne and the surface energy of metal layer of Metalized film-2 (MET-2) is still >46 Dyne/cm. Thereafter, the adhesive lamination was conducted on Labo-Combi 400 machine from Nordmeccanica.

Table 2. Formulation of PE-based films for vacuum metallization

PE-based film name	Skin Layer	Core Layer	Sealant Layer	Sample name of metallized PE-based films
Layer ratio by thickness	1	2	1	
Film-1	90% ELITE™ AT6410+10%LDPE 450E	ELITE™ AT6900	88% ELITE™ AT6410+10%LDPE +2% AB20L	MET-1
Additive concentrations (ppm)	-	-	Anti-block in the sealant layer: 4000 slip agent in the sealant layer: 0	

	overall anti-oxidant in the film: 2000; overall fatty acid or its derivatives in the film: 350			
Film-2	90% ELITE™ AT6410+10%LDPE 450E	UNIVAL™ DMDA6400	88% ELITE™ AT6410+10%LDPE +2% AB20L	MET-2
Additive concentrations (ppm)	-	-	Anti-block in the sealant layer: 4000 slip agent in the sealant layer: 0	
	overall anti-oxidant in the film: 1200; overall fatty acid or its derivatives in the film: 0			

Before adhesive lamination, the fabricated VMPE films were stored in manner of film rolls for 2 weeks under an environment of 23 °C and 50% humidity. The surface energy of metal layer of MET-1 declined to <34 Dyne and the surface energy of metal layer of MET-2 is still >46 Dyne/cm. Thereafter, all the VMPE films were laminated with PET film (Thickness=12μm, product type: PET flat film, Anhui Guofeng Plastic Industry Co.,Ltd.) or BOPP film (Thickness=18μm, product type: PP, Guangdong Weifu Packaging Material Co., Ltd) using adhesive listed in Table 3 and 4. In addition, 3-ply laminate structure comprising VMPET (Thickness=12μm, product type: P11, Jiaying Pengxiang Packaging Materials CO. Ltd) were prepared as shown in Table.3 for comparison.

As shown in Table 3 and 4, all the inventive samples have lower OTR than comparative samples. The results demonstrated that, in terms of boosting oxygen barrier of laminate structures, there is a good synergy between adhesive with inventive chemistry compositions and inventive VMPE film with good surface energy of the metal layer.

Example 1

Table 3. Sample details of Example 1

Sample Name	Laminate structure	Adhesive formulation	PE film composition	OTR
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Inventive Example (IEx) 1-1	PET//VMPE	IE-PES-1/F =100:11	MET-2	1.4
Inventive Example 1-2	PET//VMPE	IE-PES-1/F =100:20	MET-2	0.9
Inventive Example 1-3	PET//VMPE	IE-PES-3/F =100:14	MET-2	1.4
Inventive Example 1-4	PET//VMPE	IE-PES-2/F =100:10	MET-2	1.6
Comparative Example (CEx) 1-1	PET//VMPE	CE-PES-1/ F=100:6.5	MET-2	2.2
Comparative Example 1-2	PET//VMPE	CE-PES-1/ F=100:12	MET-2	2.1
Comparative Example 1-3	PET//VMPE	Adcote™ 516A/B=10 0:35	MET-2	3.3
Comparative Example 1-4	PET//VMPE	CE-PES-2/ F=100:12	MET-2	2.7
Comparative Example 1-5	PET			115.9
Comparative Example 1-6	VMPE(MET -2)			47.3
Comparative Example 1-7	PE (Film-2)			>1000

All coating weight is 3.0 gsm

IEx.1-1, IEx.1-2, IEx.1-3, and IEx.1-4 used inventive two component SB (solvent-based) PU adhesive and inventive metalized PE-based film (MET-2), and they showed good OTR results.

CEx.1-1, CEx.1-2 and CEx.1-4 used the same inventive metalized PE-based film (MET-2) and a two component SB PU adhesive, which was polyester polyol based but had either lower aromatic ring backbone or too high Mw, which were out of the scope of the present invention, and they showed poor OTR vs the inventive examples;

CEx.1-3 used the same inventive metalized PE-based film (MET-2) but a two component SB PU adhesive which used a polyether polyol backbone, rather than a polyester polyol backbone, and its OTR was not as good as the inventive examples;

CEx1-5 was PET film, without lamination by an adhesive, showed quite high OTR results vs the inventive examples, which indicated that both metallization and adhesive are crucial to achieve good OTR.

CEx1-6 was pure metalized PE film, without lamination by an adhesive, showed quite high OTR results vs the inventive examples, which indicated that the adhesive is crucial to achieve good OTR.

CEx1-7 was PE film, without lamination by an adhesive, showed extremely high OTR results vs the inventive examples, which indicated that both metallization and adhesive are crucial to achieve good OTR.

Example 2

Table 4. Sample details of Example 2

Sample Name	Laminate structure	Adhesive formulation	PE film composition	OTR
Inventive Example (IEx) 2-1	PET//VMPE	IE-PES-1/F=100 :11	MET-2	1.22
Inventive Example 2-2	OPP//VMPE	IE-PES-1/F=100 :11	MET-2	1.89
Comparative Example (CEx) 2-1	PET//VMPE	IE-PES-1/F=100 :11	MET-1	3.09
Comparative Example 2-2	BOPP//VMPE	IE-PES-1/F=100 :11	MET-1	6.23

Comparative Example 2-3	BOPP//VMPE	Adcote™ 516A/B=100:35	MET-2	8.20
Comparative Example 2-4	BOPP//VMPE	Robond L168D/CR3A=1 00:2	MET-2	23.23
Comparative Example 2-5	BOPP//VMPE T//PE	Robond L168D/CR3A=1 00:2	Film-2	3.8
Comparative Example 2-6	PET//VMPET //PE	Robond L168D/CR3A=1 00:2	Film-2	3.1
Comparative Example 2-7	PET			115.9
Comparative Example 2-8	BOPP			>1000
Comparative Example 2-9	VMPE (MET-1)			41.3
Comparative Example 2-10	VMPE (MET-2)			47.3
Comparative Example 2-11	PE (Film-2)			>1000

All coating weight is 3.0gsm

IEx.2-1 and IEx.2-2 used inventive two component SB (solvent-based) PU adhesive and inventive metalized PE-based film (MET-2), and they showed good OTR results.

CEx 2-1 and CEx 2-2 used the inventive adhesive, but different metalized PE film (MET-1), and showed poor OTR results.

CEx. 2-3 used the same inventive metalized PE-based film (MET-2) but a two component SB PU adhesive which used a polyether polyol backbone, rather than a polyester polyol backbone, and its OTR was not as good as the inventive examples.

CEx.2-4 used the same inventive metalized PE-based film (MET-2) but a polyacrylic based WB adhesive, not the inventive adhesive, and they showed poor OTR results.

CEx.2-5 used OPP//VMPET//PE and a polyacrylic based WB adhesive and they showed poor OTR results.

CEx.2-6 used PET//VMPET//PE and a polyacrylic based WB adhesive and they showed poor OTR results.

CEx.2-7 was PET film, without lamination by an adhesive, showed quite high OTR results vs the inventive examples.

CEx.2-8 was OPP film, without lamination by an adhesive, showed quite high OTR results vs the inventive examples.

CEx.2-9 was pure metalized PE film (MET-1), without lamination by an adhesive, showed quite high OTR results vs the inventive examples.

CEx.2-10 was pure metalized PE film (MET-2), without lamination by an adhesive, showed quite high OTR results vs the inventive examples.

CEx.2-11 was PE film, without lamination by an adhesive, showed quite high OTR results vs the inventive examples.

Standard process to prepare Inventive Example Polyesters (IE-PES) and Comparative Example Polyesters (CE-PES):

Charge all raw materials(such as IPA, AdA, EG and DEG) into reactor and heat to 100 °C, and hold at this temperature for 30 minutes, then heat to 175 °C and hold for another 45 minutes, then increase temperature to 225°C and hold until acid value below 25mg KOH/g. Then apply vacuum (ca 500mmHg) and hold for 15-30 minutes. Then maintain temperature and decrease vacuum to ca.200mmHg gradually. When acid value is below 10 KOH/g, decrease vacuum to ca 50mmHg, when acid value is below 2 KOH/g, then decrease vacuum to ca 10mmHg, then start to cool to 160 °C and break vacuum with N₂, when temperature is below 160 °C, then start to add ethyl acetate to achieve desired solid content, continue to cool to 70 °C and pack out.

Preparation of the polyurethane adhesive composition

The solvent-borne (SB) adhesive was prepared according to below procedure: weigh a certain amount of polyester polyol and coreactant F and mix them together according to the designed mixing ratio, then start to agitate and add calculated amount of ethyl acetate to achieve 30% solid content, and continue to agitate to make sure adhesive is homogeneous. The prepared SB adhesive was conducted lamination process on Labo-Combi 400 machine from Nordmeccanica and make sure the dry coating weight was between 3.0-3.5 gsm.

Solventless (SL) adhesive: weigh a certain amount of NCO prepolymer and polyol coreactant and mix them together to get a homogenous adhesive, then pour the adhesive into coating roller on Labo-Combi 400 machine from Nordmeccanica to conduct lamination and make sure dry coating weight is 1.8-2.0 gsm coating weight.

Water-borne (WB) adhesive: WB adhesive was conducted lamination directly on Labo-Combi 400 machine from Nordmeccanica to make sure dry coating weight was between 2.0-2.5 gsm.

Test Method

Oxygen Transmission Rate (OTR)

The oxygen transmission rate was measured in accordance with ASTM D-3985 using a MOCON OX-TRAN Model 2/21 measurement device at a temperature of 23°C at a relative humidity of 0% using purified oxygen. When the barrier data of sample was over 200 cc/m²-day, mask was applied for reducing the testing area from 50 cm² to 5 cm² to acquire data in larger testing range.

Optical Density (OD) Test

OD testing was done with a spectrophotometer (Type LS117, Shenzhen Linshang Technology Co.,Ltd). The metallized film was positioned between the optical emitter and receptor, with metallized surface facing the emitter. OD was read and recorded.

Surface energy test

The test was based on the usage of ACCU DYNE TEST™ marker pens, which was based on a valve tip applicator. The principle was to keep the testing part of the pen away from the fluid storage part of the pen.

The dyne level testing procedure using the pens was as below:

Place a piece of metallized film sample on flat glass plate;

Record ambient temperature and relative humidity. If sample temperature differs from ambient, allow it to stabilize.

Test at least three points across the sample; 1/4, 1/2, and 3/4 across the film section

Determination of Wetting

1. Choose a marker pen of a dyne level you believe is slightly lower than that of the test sample.

2. Press applicator tip firmly down on subject material until the tip is saturated with ink.

3. Use a light touch to draw the pen across the test sample in two or three parallel passes. Disregard the first pass(es); to flush any contamination from the tip, and to ensure that the test fluid layer is thin enough for accurate measurement, evaluate only the last pass.

4. If the last ink swath remains wetted out on the test sample for three seconds or more, repeat steps 2 and 3 with the next higher dyne level marker. If the last ink swath beads up, tears apart, or shrinks into a thin line within one second or less, repeat steps 2 and 3 with the next lower dyne level marker.

5. If the ink swath holds for one to three seconds before losing its integrity, the dyne level of the marker closely matches that of the sample. And the value of corresponding pen is recorded.

Determination of the fatty acid content

The fatty acid content was analyzed by extracting the additive from films using CH_2Cl_2 , followed by filtration and analyzing with LC-MS (Liquid chromatography-mass spectrometry). Standard solutions were made in appropriate concentration range of fatty acid.

Determination of the anti-block agent content

The anti-block agent was analyzed by thermal gravimetric (TGA) analysis. TGA was conducted on a TA Q500 instrument. Film samples were tested under a N_2 environment. The test protocol was:

- Heat from 25 to 800 °C at 10 °C/min
- Isothermal at 800 °C for 3 min

The residue weight was recorded as the anti-block additive amount.

Determination of the slip agent content and anti-oxidant content

The slip agent and anti-oxidant content was analyzed by total dissolution method. The film sample was dissolved by 0.075% triethyl phosphite in o-xylene at 130 °C. The solution is let cooled and methanol added followed by stirring. After the solid settled, the solution was injected into liquid chromatography (LC) autosampler for antioxidant analysis and gas chromatography (GC) for slip additive analysis.

CLAIMS:

1. A laminate, comprising
a first substrate comprising a metalized polyethylene -based (PE based) film;
a second substrate comprising a polyethylene terephthalate-based film or a polypropylene-based film; and,
an adhesive layer adhering the first substrate to the second substrate, wherein the adhesive layer is derived from a two-component solvent-based polyurethane adhesive composition;
wherein the concentration of fatty acids or fatty acid derivatives in the metalized PE-based film is less than 300ppm, based on the total weight of the metalized PE-based film,
wherein the two-component solvent-based polyurethane adhesive composition comprises a polyester polyol component and a polyisocyanate component,
wherein the polyester polyol component has about 40wt%-60 wt % of aromatic rings in the backbone, based on the total weight of the polyester polyol and a molecular weight (Mw) between 5,000 and 50,000; and
wherein the weight ratio of the polyester polyol component to the polyisocyanate component is from 100:5 to 100:30.
2. The laminate of claim 1, wherein the weight ratio of the polyester polyol component to the polyisocyanate component is from 100:10 to 100:20.
3. The laminate of claim 1, the metalized PE-based film comprises a PE-based film and a metal layer.
4. The laminate of claim 1, wherein the PE-based film in the metalized PE-based film comprises a skin layer, a core layer and a sealant layer.
5. The laminate of claim 4, wherein anti-block agents are present in the sealant layer at an amount of at least 200ppm, based on total weight of the sealant layer.
6. The laminate of claim 4, wherein slip agents are present in the sealant layer at an amount of less than 500ppm, based on total weight of the sealant layer.
7. The laminate of claim 1, wherein the metallized PE-based film has an optical density (OD) of at least 1.5 and no more than 4.0.

8. The laminate of claim 1, wherein the concentration of anti-oxidants in the metalized PE-based film layer is less than 3000 ppm, based on the total weight of the metallized PE-based film.

9. The laminate of claim 1, wherein the PE-based film of the metalized PE-based film layer is a blown film, a cast film, a machine direction oriented film, or a biaxially oriented film.

10. The laminate of claim 3, the metal layer includes Al, Zn, Au, Ag, Cu, Ni, Cr, Ge, Se, Ti, Sn, or oxides thereof

11. The laminate of claim 1, wherein the PP-based film comprises from 50% to 100%, by weight of the PP-based film of a PP component.

12. An article comprising the laminate of any one of claims 1-11.

13. A method for preparing the laminate of any one of claims 1-11, comprising

1) providing a first substrate comprising a metalized PE-based film and a second substrate comprising a PET-based film or a PP-based film.

2) adhering the first substrate to the second substrate using a two-component solvent-based polyurethane adhesive composition;

wherein the concentration of fatty acids or fatty acid derivatives in the metalized PE-based film is less than 300 ppm, based on the total weight of the metalized PE-based film,

wherein the two-component solvent-based polyurethane adhesive composition comprises a polyester polyol component and a polyisocyanate component,

wherein the polyester polyol component has 40wt%-60 wt % of aromatic rings in the backbone, based on the total weight of the polyester polyol and a Mw between 5,000 and 50,000; and

wherein the weight ratio of the polyester polyol component to the polyisocyanate component is from 100:5 to 100:30.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2021/129194

A. CLASSIFICATION OF SUBJECT MATTER

B32B 27/12(2006.01)i; B32B 27/40(2006.01)i; C08G 18/10(2006.01)i; C08G 18/46(2006.01)i; C09J 175/04(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; C08G; 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)

CNKI,CNXT,DWPI,VEN:laminate, polyester, polyol, pe,pet,pp, polyisocyanate, adhesive, dow, polyethylene, metalized, polyethylene terephthalate, polyurethane, molecular weight

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2021133475 A1 (DOW GLOBAL TECHNOLOGIES LLC) 01 July 2021 (2021-07-01) claims 1-4, description from [0005] to [0070]	1-13
A	WO 2018140116 A1 (DOW GLOBAL TECHNOLOGIES LLC) 02 August 2018 (2018-08-02) the whole documents	1-13
A	WO 2015125160 A1 (CHATURVEDI ASHOK) 27 August 2015 (2015-08-27) the whole document	1-13
A	WO 2019190622 A1 (DOW GLOBAL TECHNOLOGIES LLC) 03 October 2019 (2019-10-03) the whole documents	1-13



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

11 July 2022

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2021/129194

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