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(71) Applicant: DOW GLOBAL TECHNOLOGIES LLC

[US/US]; 2211 H.H. Dow Way, Midland, Michigan 48674 (US).

(72) Inventors: WU, Jie; 230 Abner Jackson Parkway, Lake Jackson, Texas 77566 (US). GUO, Yinzhong; 230 Abner Jackson Parkway, Lake Jackson, Texas 77566 (US).

(74) Agent: BARTHEL, Ted J.; Boyle Fredrickson SC, 840 N. Plankinton Avenue, Milwaukee, Wisconsin 53203 (US).

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(54) Title: HIGH PERFORMANCE LAMINATING ADHESIVES WITH LOW FREE MONOMER

(57) Abstract: A solvent based adhesive composition comprising at least one isocyanate component comprising an aromatic-based isocyanate wherein the weight of the free monomeric isocyanate is less than 1 wt.% based on the weight of the isocyanate component, and at least one isocyanate reactive component comprising at least one phosphaste ester polyol is disclosed. A procedure for making the adhesive as well as a laminate partially made from the adhesive and a procedure for making the laminate are also disclosed.



WO 2023/224904 A1

HIGH PERFORMANCE LAMINATING ADHESIVES WITH LOW FREE MONOMER

FIELD

The present disclosure relates to adhesive compositions. More particularly, the disclosure relates to solvent-based, two-component adhesive compositions for use with laminate films, the adhesive composition exhibiting excellent adhesion performance, heat and chemical resistance, along with a very low level of migrated aromatic species.

BACKGROUND

Adhesive compositions are useful for a wide variety of purposes. For instance, some adhesives are used to adhere two or more film layers of substrates together thereby forming composite films, i.e., laminates comprising the two or more film layers. Example of substrates typically include polyethylenes, polypropylenes, polyesters, polyamides, metals, papers, or cellophane and the like. The use of adhesives in different laminating end-use applications is generally known. For example, adhesives, are generally applied between laminating films, can be used in the manufacture of film/film and film/foil laminates used in the flexible packaging industry for packaging of foodstuffs, pharmaceuticals, and industrial consumables, especially for food packaging. Laminating adhesives can be classified generally into three categories: (1) solvent-based laminating adhesives, (2) solventless laminating adhesives, and (3) water-based laminating adhesives. The performance of an adhesive varies by category and by the application in which the adhesive is applied. Within the solvent-based category of laminating adhesives, solvent-based polyurethane has been widely used to achieve relatively good heat, moisture, and chemical resistance.

Within the category of solvent-based laminating adhesives, there are many varieties; and one particular variety includes multi-component polyurethane-based laminating adhesives; and more specifically a two-component adhesive. Typically, a two-component polyurethane-based laminating adhesive includes a first component comprising an isocyanate and/or a polyurethane prepolymer and a second component comprising one or more polyols. A polyurethane prepolymer can be obtained by the reaction of a polyisocyanate with a polyether polyol and/or polyester polyol. The second component comprises polyether polyols and/or polyester polyols. Each component can optionally include one or more additives. Common solvents used in such systems include methyl ethyl ketone, ethyl acetate, toluene, and the like, all of which must be moisture-free to prevent premature reaction of the isocyanate groups of the polyurethane.

The two components (i.e., the isocyanate and polyol components) of the adhesive composition are combined in a predetermined ratio, thereby forming an adhesive composition. The adhesive composition, carried in a solvent, is then applied on a film/ or foil substrate. The solvent is evaporated from the applied adhesive composition. Another film/or foil substrate is then brought into contact with the other substrate, forming a curable laminate structure. The laminate structure is cured to bond the two substrates together.

Solvent-based adhesive compositions can be used in high-performance laminate applications (e.g., hot-fill, boil-in-bag, freeze condition etc.). The known adhesives are typically based on aromatic isocyanate, which exhibit excellent adhesion and fast curing characteristics. However, the free monomeric isocyanate in isocyanate component is typically high, with the level of often more than 10 wt. %, which could compromise the operation safety and food safety. Thus, a need exists for a high performing solvent-based adhesive with excellent adhesion performance, fast curing, and meet strict regulatory standards.

DETAILED DESCRIPTION

The numerical ranges disclosed herein include all values from, and including, the lower and upper value. For ranges containing explicit values (e.g., a range from 1, or 2, or 3 to 5, or 6, or 7), any subrange between any two explicit values is included (e.g., the range 1 to 7 above includes subranges 1 to 2; 2 to 6; 5 to 7; 3 to 7; 5 to 6; etc.).

The term "composition" refers to a mixture of materials which comprise the composition, as well as reaction products and decomposition products formed from the materials of the composition.

The terms "comprising," "including," "having," and their derivatives, are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is specifically disclosed. In order to avoid any doubt, all compositions claimed through use of the term "comprising" may include any additional additive, adjuvant, or compound, whether polymeric or otherwise, unless stated to the contrary. In contrast, the term "consisting essentially of" excludes from the scope of any succeeding recitation any other component, step, or procedure, excepting those that are not essential to operability. The term "consisting of" excludes any component, step, or procedure not specifically delineated or listed. The term "or," unless stated otherwise, refers to the listed members individually as well as in any combination. Use of the singular includes use of the plural and vice versa.

An "isocyanate" is a chemical that contains at least one isocyanate group in its structure. An isocyanate group is represented by the formula: —N=C=O or abbreviated as "NCO". An isocyanate that contains more than one, or at least two, isocyanate groups is a "polyisocyanate."

An isocyanate that has two isocyanate groups is a diisocyanate and an isocyanate that has three isocyanate groups is a triisocyanate, etc.

A "polyisocyanate" is a molecule that contains at least two isocyanate groups.

5 A "polyether" is a compound containing two or more ether linkages in the same linear chain of atoms.

A "polyester" is a compound containing two or more ester linkages in the same linear chain of atoms.

A "polyol" is an organic compound containing multiple hydroxyl (OH) groups. In other words, a polyol contains at least two OH groups. Nonlimiting examples of suitable polyols include diols having two OH groups, triols having three OH groups, and tetraols having four
10 OH groups.

A "polyester polyol" is a compound that contains a polyester and a polyol in the backbone structure of the compound.

15 A "polyether polyol" is a compound that contains a polyether and a polyol in the backbone structure of the compound.

A "film," including when referring to a "film layer" in a thicker article, unless expressly having the thickness specified, includes any thin, flat extruded or cast thermoplastic article having a generally consistent and uniform thickness of about 0.5 millimeters (mm) (20 mils) or less in one dimension.

20 A "polymer film" is a film that is made of a polymer or a mixture of polymers. The composition of a polymer film is typically, 80 percent by weight (wt %) of one or more polymers.

A "polymer" is a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term
25 "homopolymer" (employed to refer to polymers prepared from only one type of monomer, with the understanding that trace amounts of impurities can be incorporated into the polymer structure), and the term "interpolymer," which includes copolymers (employed to refer to polymers prepared from two different types of monomers), terpolymers (employed to refer to polymers prepared from three different types of monomers), and polymers prepared from more
30 than three different types of monomers. Trace amounts of impurities, for example, catalyst residues, may be incorporated into and/or within the polymer. It also embraces all forms of copolymer, e.g., random, block, etc. It is noted that although a polymer is often referred to as being "made of" one or more specified monomers, "based on" a specified monomer or monomer type, "containing" a specified monomer content, or the like, in this context the term

"monomer" is understood to be referring to the polymerized remnant of the specified monomer and not to the unpolymerized species. In general, polymers herein are referred to as being based on "units" that are the polymerized form of a corresponding monomer.

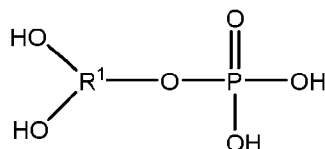
A solvent based adhesive is disclosed comprising at least one isocyanate component and at least one isocyanate reactive component. The isocyanate component contains less than 1 wt. % of an aromatic-based isocyanate based on the weight of the isocyanate component. The isocyanate reactive component comprises at least one phosphate ester polyol and at least one polyester polyol. A process for producing a laminate product using the above adhesive is also disclosed.

The aromatic-based isocyanate in the isocyanate component can be, for example, an isocyanate monomer, a polyisocyanate (e.g. dimers, trimers, etc.) an isocyanate prepolymer, and mixtures of two or more of the preceding. A "polyisocyanate" is any compound that contains two or more isocyanate groups.

The aromatic-based isocyanates useful in the present disclosure can include, for example, one or more polyisocyanate compounds including, but are not limited to, for example 1,3- and 1,4-phenylene diisocyanate; 1,5-naphthylene diisocyanate; 2,4'-diphenylmethane diisocyanate (2,4'-MDI); 4,4'-diphenylmethane diisocyanate (4,4'-MDI); 3,3'-dimethyl-4,4'-biphenyldiisocyanate (TODI) and isomers thereof; polymeric isocyanates; and mixtures of two or more thereof.

Exemplary of some of the commercial aromatic-based components useful in the present disclosure can include, for example, ISONATE™ 125 M, ADCOTTE™ L76-204, COREACTANT CT™, , available from The Dow Chemical Company; DESMODUR™ E 2200/76, available from The Covestro Company; and mixtures thereof.

The phosphate ester in the isocyanate reactive component can be selected, for example, from a phosphate ester compound having the following chemical structure:

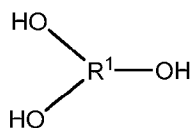


Structure (I)

where R¹ is any organic group. In addition to the pendant groups shown in Structure (I), R¹ may or may not have one or more additional pendant -OH groups, and R¹ may or may not have one or more additional pendant groups of Structure (I). Any two or more of the -OH groups

and the group(s) of Structure (I) may or may not be attached to the same atom of R¹. Each -OH group and each group of Structure (I) can be attached to a separate atom of R¹.

A convenient way to characterize R¹ is to describe the compound having the following Structure (II):



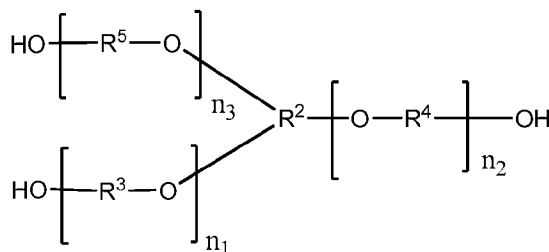
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Structure (II)

where R¹ is the same as in Structure (I). The compound having Structure (II) is referred to herein as a "precursor polyol."

Suitable precursor polyols can have number average Mw of 90 g/mol or higher, 200 g/mol or higher, or 400 g/mol or higher. Suitable precursor polyols can have number average Mw of 4,000 g/mol or lower, 2,000 g/mol or lower, 1,200 g/mol or lower, 900 g/mol or lower, or 500 g/mol or lower. Suitable precursor polyols can have number average Mw from 200 g/mol to 4,000 g/mole, from 400 g/mol to 2,000 g/mol, from 400 g/mol to 1,200 g/mol, or from 400 g/mol to 900 g/mol.

15 Suitable precursor polyols can be alkyl higher polyols, monosaccharides, disaccharides, and compounds having the following Structure (III):



Structure (III)

where each of R², R³, R⁴, and R⁵ is, independent of the other, any organic group; each of n₁, n₂, and n₃ is, independent of the other, an integer from 0 to 10. In addition to the pendant groups shown in Structure (III), R² may or may not have one or more additional pendant groups. It is further understood that any two or more of the pendant groups may or may not be attached to the same atom of R². In some embodiments, a mixture of compounds having Structure (III) is present, where the compounds of Structure (III) differ from each other in the value of one or more of n₁, n₂, and n₃. Such mixtures are described herein by stating a non-integer value for the parameter n₁, n₂, or n₃, where the non-integer value represents the number average of that

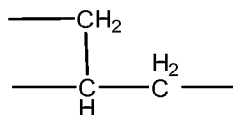
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parameter. When it is desired to assess the molecular weight of such a mixture, the number-average molecular weight is used.

Among precursor polyols having Structure (III), each pendant group can be attached to a separate atom of R^2 . Among precursor polyols having Structure (III), one or more of R^3 , R^4 , and R^5 can be a hydrocarbon group having 1 C to 4 Cs, 2 Cs to 3 Cs or 3 Cs. Among precursor polyols having Structure (III), one or more of R^3 , R^4 , or R^5 can be an alkyl group, which may be linear or cyclic or branched or a combination thereof; one or more of R^3 , R^4 , or R^5 can be a linear or branched alkyl group; and one or more of R^3 , R^4 , or R^5 can be a branched alkyl group. R^3 , R^4 , or R^5 can be identical to each other.

Among precursor polyols having Structure (III), one or more of n_1 , n_2 , and n_3 can be from 0 to 8. Among precursor polyols having Structure (III), one or more of n_1 , n_2 , and n_3 can be 1 or more. Among precursor polyols having Structure (III), one or more of n_1 , n_2 , and n_3 can be 6 or less. Among precursor polyols having Structure (III), n_1 , n_2 , and n_3 can be the same.

The group of precursor polyols having Structure (III) can be compounds in which each of R^2 , R^3 , R^4 , and R^5 is an alkyl group; such precursor polyols are known herein as alkoxyated alkyl triols. In a triol, when at least one of n_1 , n_2 , and n_3 is 1 or more and R^2 has the following Structure (IV):



Structure (IV)

then the triol is known herein as an alkoxyated glycerol. In alkoxyated triols, when each of R^3 , R^4 , and R^5 is a branched alkyl group with exactly 3 C, the alkoxyated triol is known herein as a propoxyated triol. A propoxyated triol in which R^2 has Structure (IV) is known herein as propoxyated glycerol.

Among precursor polyols that are alkyl higher polyols, can be compounds with 10 C or fewer carbon atoms; compounds with 6 C or fewer carbon atoms; compounds with 3 or fewer carbon atoms; or glycerol.

Precursor polyols can be alkyl higher polyols and compounds having Structure (III). It is noted that, if n_1 is equal to (=) $n_2 = n_3 = 0$ and if R^2 is either an alkyl group or an alkyl group having hydroxyl groups, then the compound having Structure (IV) is an alkyl higher polyol.

The group of precursor polyols can be alkyl triols and alkoxyated alkyl triols. Among these compounds, are glycerol and alkoxyated glycerols. Among alkoxyated glycerols, are propoxyated glycerols.

Another class of suitable phosphate ester compounds useful in the present disclosure includes compounds that contain urethane linkages. Phosphate ester compounds containing urethane linkages are made by reacting one or more suitable phosphate-functional polyol with one or more polyisocyanate, one or more diisocyanates can also be included. The amount of polyisocyanate can be kept low enough so that some or all of the reaction products are phosphate-functional polyols. Alternatively, the polyol may be first reacted with the polyisocyanate to make an -OH terminated prepolymer which is then reacted with polyphosphoric acid. Phosphate ester compounds with urethane linkages include those compounds having a number average Mw in the range of 1,000 g/mol to 6,000 g/mol, in the range of 1,200 g/mol to 4,000 g/mol, and in the range of 1,400 g/mol to 3,000 g/mol.

The phosphate ester compound can be the reaction product of reactants including a precursor polyol and a phosphoric-type acid, where the resulting phosphate ester compound has the chemical structure of Structure (I).

The amounts of phosphoric-type acid and precursor polyol are chosen to determine the ratio of $M_p:M_x$ as follows: M_{Hy} = the number of hydroxyl groups per molecule of the precursor polyol; $N_x = M_{Hy} - 2$; $M_x = (\text{the moles of precursor polyol}) \times (N_x)$; and M_p = the moles of phosphorous atoms contained in the phosphoric-type acid.

In general, the ratio of $M_p:M_x$ is 0.1:1 or higher, 0.2:1 or higher, 0.5:1 or higher, or 0.75:1 or higher. The ratio of $M_p:M_x$ can be 1.1:1 or lower.

Generally, the weight ratio of phosphoric-type acid to precursor polyol is 0.005:1 or higher, 0.01:1 or higher, or 0.02:1 or higher. The weight ratio of phosphoric-type acid to precursor polyol can be 0.3:1 or lower, or 0.2:1 or lower, or 0.12:1 or lower.

The phosphoric-type acid can contain polyphosphoric acid. And, in general, the amount of polyphosphoric acid in the phosphoric-type acid is, by weight based on the weight of the phosphoric-type acid, 75 wt % or more, 80 wt % or more, or 90 wt % or more. Polyphosphoric acid is available in various grades; each grade is characterized by a percentage. To determine the grade, it is first recognized that pure monomeric orthophosphoric acid, the content of phosphorous pentoxide is considered to be 72.4 %. Any grade of polyphosphoric acid can also be analyzed, to consider that one mole of polyphosphoric acid (formula weight labeled "Fppa") contains the number of moles of phosphorous pentoxide labeled "Nppo," and the phosphorous pentoxide percentage ("PCppo") is given by $PCppo = (Nppo \times 142)/Fppa$, expressed as a

percentage. Then, the grade of that polyphosphoric acid is the ratio, expressed as a percentage:
Grade = PCppo/72.4.

The polyphosphoric acid used can have a grade of 100 % or higher, or 110 % or higher.
The polyphosphoric acid used can have a grade of 150 % or lower, or 125 % or lower.

5 Further information about suitable phosphate esters and the preparation of such suitable phosphate esters can be found, for example, in PCT Publication No. WO/2015/168670.

The amount of the phosphate ester polyol used in the isocyanate reactive component can be from 0.1 wt. % to 1 wt. %, 1 wt. % to 5 wt. %, 5 wt. % to 10 wt. %, 10 wt. % to 15 wt. %, or 15 wt. % to 20 wt. % based on the dry weight of the isocyanate reactive component.

10 The disclosed solvent-based adhesive compositions can contain one or more phosphorous-free polyols in addition to the one or more phosphate-functional polyols. The isocyanate reactive component can include one or more polyester polyols. The polyester polyol, can have a molecular weight of >2000g/mol.

Suitable polyester polyols useful in the present disclosure include, but are not limited to, for example, aliphatic polyester polyols; aromatic polyester polyols; copolymers of aliphatic and aromatic polyester polyols; polycarbonate polyols; polycaprolactone polyols; and mixtures thereof. These polyester polyols: are the reaction products of polybasic acids and polyhydric alcohols; or are the reaction of phosgene or a carbonate monomer with a polyhydric alcohol; or are produced via ring opening polymerization of cyclic ester compounds.

20 Exemplary of suitable polybasic acids useful in the present disclosure include succinic acid, adipic acid, azelaic acid, sebacic acid, dodecanedicarboxylic acid, maleic anhydride, fumaric acid, 1,3-cyclopentane-dicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, terephthalic acid, isophthalic acid, phthalic acid, 1,4-naphthalenedicarboxylic acid, 2, 5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, naphthalic acid, biphenyldicarboxylic acid, 1,2-bis(phenoxy)ethane-p,p'-dicarboxylic acid, and anhydrides or ester-forming derivatives of these dicarboxylic acids; and p-hydroxybenzoic acid, p-(2-hydroxyethoxy)benzoic acid, and ester-forming derivatives or dimer acids of these dihydroxycarboxylic acids; and mixtures thereof. These polybasic acids may be used alone or in a combination of two or more polybasic acids.

30 Any known polyhydric alcohol can be used according to this disclosure. Non-limiting examples of suitable polyhydric alcohols useful in the present disclosure include: glycols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, neopentylglycol, methylpentanediol, dimethylbutanediol, butylethylpropanediol, diethylene glycol, triethylene glycol, tetraethylene

glycol, dipropylene glycol, tripropylene glycol, bishydroxyethoxybenzene, 1,4-cyclohexanediol, 1,4-cyclohexane-dimethanol, triethylene glycol, polycaprolactone diol, dimer diol, bisphenol A, and hydrogenated bisphenol A; polyesters produced through ring opening polymerization of cyclic ester compounds such as propiolactone, butyrolactone, ϵ -caprolactone, 8-valerolactone, and β -methyl- δ -valerolactone; and polyethers produced from addition polymerization of one or more monomers including ethylene oxide, propylene oxide, butylene oxide, styrene oxide, epichlorohydrin, tetrahydrofuran, and cyclohexylene in the usual manner with the aid of one or more compounds containing two active hydrogen atoms as an initiator, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, trimethylene glycol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, and neopentyl glycol; and mixtures thereof. These polyhydric alcohols may be used alone or in a combination of two or more polyhydric alcohols.

The amount of the polyester polyol used in the isocyanate reactive component can be over 10 wt. %, over 20 wt. %, over 30 wt. %, over 40 wt. %, over 50 wt. %, over 60 wt. %, or over 70 wt. % based on the dry weight of the polyol component.

Furthermore, the polyol component may contain polyether polyols. Suitable polyether polyols include but not limited to polypropylene glycols, polytetramethylene ether glycols, polybutylene oxide based polyols, or mixtures and copolymers of them. Suitable polypropylene glycols include polyols based on propylene oxide, ethylene oxide, or mixture of them with initiators selected from propylene glycol, dipropylene glycol, sorbitol, sucrose, glycerin, and/or mixtures of them, available from the Dow Chemical Company under the trade name of VORANOL™, the BASF Company under the trade name of PLURACOL™, Lonza under trade name POLY-G™, POLY-L™, and POLY-Q™, and Covestro under the trade name ACCLAIM™. In particular, polypropylene glycols with functionality between 2 to 6 and molecular weight from 250 to 1500 are preferred. Suitable polytetramethylene ether glycols include but not limited to POLYTHF™ from the BASF Company, TERTHANE™ from Invista, PTMG™ from Mitsubishi, and PTG™ from Dairen. Suitable polybutylene oxide based polyols include but not limited to polybutylene oxide homopolymer polyols, polybutylene oxide-polypropylene oxide copolymer polyols, and polybutylene oxide-polyethylene oxide copolymer polyols.

In addition, low molecular weight glycols, including but not limited to ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, trimethylene glycol, 1,3-butanediol,

1,4-butanediol, 1,6-hexanediol, trimethylolpropane, triisopropanolamine, and neopentylglycol can be incorporated in the polyol component.

The adhesive composition of the present disclosure generally includes at least one solvent. Suitable solvents can include but are not limited to, ethyl acetate, propyl acetate, methyl ether ketone, methyl butyl ketone, acetone, toluene, and mixtures thereof.

The amount of the solvent, used in the present disclosure process can be, for example, from 20 wt % to 90 wt %, from 30 wt % to 80 wt %, or from 40 wt % to 70 wt % based on the total amount of the components in the adhesive composition.

The adhesive composition of the present disclosure can include one or more additional optional conventional ingredients or additives including but not limited to, catalysts, tackifiers, adhesion promoters, antioxidants, fillers, colorants, pigments, surfactants, solvents, polymers (including, for example, thermoplastic resins other than those discussed herein above), dehydrating agents (including, for example, silanes), benzoyl chloride, other polyols (including, for example, fatty polyols), ultraviolet indicators, and combinations of two or more of these.

The adhesive composition may include, for example, an adhesion promoter. Non-limiting examples of suitable adhesion promoters include coupling agents such as a silane coupling agent, a titanate coupling agent, and an aluminate coupling agent; epoxy resin, phosphoric acid, polyphosphoric acid, and phosphate esters.

Examples of the silane coupling agent useful in the present disclosure include, but are not limited to, aminosilanes such as γ -aminopropyltriethoxysilane, γ -aminopropyltrimethoxysilane, N- β (aminoethyl)- γ -aminopropyltrimethoxysilane, N- β (aminoethyl)- γ -aminopropyltrimethyl dimethoxysilane, and N-phenyl- γ -aminopropyltrimethoxysilane; epoxysilanes such as β -(3,4-epoxycyclohexyl)-ethyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane, and γ -glycidoxypropyltriethoxysilane; vinylsilanes such as vinyl tris(β -methoxyethoxy)silane, vinyltriethoxysilane, vinyltrimethoxysilane, and γ -methacryloxypropyltrimethoxysilane; hexamethyldisilazane; γ -mercaptopropyltrimethoxysilane; and mixtures thereof.

Examples of the titanate coupling agent useful in the present disclosure include, but are not limited to, tetraisopropoxy titanium, tetra-n-butoxy titanium, butyl titanate dimer, tetrasteryl titanate, titanium acetylacetonate, titanium lactate, tetraoctyleneglycol titanate, titanium lactate, tetra stearoxy titanium; and mixtures thereof.

Examples of the epoxy resin useful in the present disclosure include, but are not limited to, a variety of readily available epoxy resins such as bisphenol A-epichlorohydrin (epi-bis) type epoxy resin, novolak type epoxy resin, β -methylepichlorohydrin type epoxy resin, cyclic oxirane type epoxy resin, glycidyl ether type epoxy resin, glycidyl ester type epoxy resin, polyglycol ether type epoxy resin, glycol ether type epoxy resin, epoxidation fatty acid ester type epoxy resin, polycarboxylic acid ester type epoxy resin, aminoglycidyl type epoxy resin, resorcin type epoxy resin; and mixtures thereof.

The adhesion promoter can be a phosphate ester compound or an epoxy silane ((3-glycidyoxypropyl)-trimethoxysilane). Phosphoric acid can be incorporated in the polyol component while epoxy silane can be incorporated in the isocyanate component. Both epoxy silane and phosphoric acid can be incorporated in the polyol component.

The average functionality of the adhesive composition (i.e., the isocyanate component together with the polyol component), excluding non-reactive components such as solvents, can be from 2 to 3.

The amount of optional components when used can be from 0 wt % to 15 wt %, from 0.01 wt % to 10 wt % or from 0.1 wt % to 5 wt % based on the total amount of components in the adhesive composition.

It is contemplated that two components, an isocyanate component and a polyol component, are employed in the present disclosure. It is also contemplated that the isocyanate component and the polyol component of the disclosed adhesive composition can be made separately and, if desired, stored until it is desired to use the adhesive composition. The process of producing the adhesive composition includes mixing the isocyanate and polyol components described above to form a curable adhesive composition. In some embodiments, both the isocyanate component and the polyol component are each liquid at 25 °C. When it is desired to use the adhesive composition, the isocyanate component and the polyol component are brought into contact with each other and mixed together, typically at a stoichiometric ratio (NCO/OH) between 1 and 2.5. It is contemplated that when these two components are brought into contact, a curing reaction begins in which the isocyanate groups react with the hydroxyl groups to form urethane links. The adhesive composition formed by bringing the two components into contact can be referred to as a "curable mixture."

To form the adhesive composition, mixing of the two components may take place at any suitable time in the process of forming the adhesive composition and applying the adhesive to a substrate, such as before, during, or as a result of the application process. All of the present steps may be carried out under ambient, room temperature conditions. As desired, heating or

cooling may be employed. The mixing can be carried out using a suitable conventional mixer, such as using an electrically, pneumatically, or an otherwise powered mechanical mixer.

The process for preparing the solvent-based adhesive composition of the present disclosure includes, for example, the steps of (1) providing the isocyanate component; (2) providing the polyol component; (3) mixing the two components to form a resin mixture; (4) diluting the resin mixture in a solvent to form a diluted resin mixture having an application solid content of from 25 wt % to 55 wt %, from 30 wt % to 45 wt %, or from 35 wt % to 40 wt % based on the total weight of the diluted resin mixture; and (5) removing the solvent from the composition to form the adhesive composition after the composition is applied to a substrate and before the composition is cured.

Some of the advantageous properties exhibited by the solvent-based adhesive composition of the present disclosure include, for example, (1) good adhesion performance; (2) fast curing; and (3) a low level of migrated undesirable aromatic amines such as MDA and TDA into food packed in packages using the adhesive.

For example, the bond of the adhesive after 1 hr of thermal testing at 100 and above °C can be greater than 2 N/15 mm. The bond can be dependent on the type of film substrate used and in some embodiments the films can be bonded where after testing the substrates failure mode occurs before the bond.

The curing time of the adhesive can be from 1 day to 8 days, from 1 day to 7 days, or from 2 days to 7 days.

A process of forming a laminate using the adhesive composition of the present disclosure is also disclosed herein. The adhesive composition, such as the adhesive composition discussed above, can be in a liquid state at 25 °C. Even if the composition is solid at 25 °C, it is acceptable to heat the composition as necessary to transform the composition into a liquid state. Solvent is added to the mixed adhesive composition until the desired solids content is reached. A solids content of 25 % or greater can be used.

The adhesive composition of the present disclosure is useful for bonding substrates together; and the adhesive composition can be used on a wide variety of a single suitable substrate or a plurality of suitable substrates. The substrates may be similar materials or dissimilar materials. For example, the substrate may be selected from high, low or medium density plastics (e.g., of a type selected from polystyrene, polyethylene, ABS, polyurethane, polyethylene terephthalate, polybutylene terephthalate, polypropylene, polyphenylene, polycarbonate, polyacrylate, polyvinyl chloride, polysulfone, and mixtures thereof), paper, wood and reconstituted wood products, polymer coated substrates, wax coated paperboard,

cardboard, particle board, textiles, leather, and metal (e.g., aluminum, ferrous as well as other non-ferrous), metallized plastics (e.g., metallized plastic film) or the like.

Wet and dry bond lamination of a plurality of substrate layers is possible. The adhesive composition can be applied to desired substrates using conventional application techniques such as rotogravure printing, flexographic printing, conventional or airless spray, roll coating, 5 brush coating, wire wound rod coating, knife coating, or coating processes such as curtain-, flood-, bell-, disc-, and dip-coating processes. Coating a substrate with the adhesive composition may be done over the entire surface of the substrate or to a portion of the substrate's surface, such as along an edge, or at intermittent locations. Once applied to the 10 substrate, the adhesive composition is dried, such as by application of heat and air flow, or some other suitable conventional approach for removing substantially all remaining solvent present in the adhesive composition.

A laminate comprising the solvent-based adhesive composition of the present disclosure can be formed by applying the adhesive to at least one of two different substrates 15 and combining the substrates together such that the adhesive is disposed between the surfaces of the two substrates; and then curing the adhesive to form a bond between the two substrates. The substrates can include, for example, two separate films; and each of the films can be made of a different material or of the same material. Generally, a layer of the adhesive composition is applied to a surface of a film. The thickness of the layer of the curable adhesive composition 20 mixture applied to a surface of a film is from 1 micron (μm) to 5 μm . As used herein, a "film" is any structure that is 0.5 mm or less in one dimension of the structure; and is 1 centimeter (cm) or more in both of the other two dimensions of the structure.

A surface of another film is brought into contact with the layer of the curable mixture to form an uncured laminate. The curable mixture is then cured or allowed to cure. The 25 uncured laminate may be subjected to pressure, for example by passing through nip rollers, which may or may not be heated. The uncured laminate may be heated to speed the cure reaction.

Suitable substrates used to form the laminate structure include films such as paper, woven and nonwoven fabric, polymer films, metal foil, metal-coated (metallized) polymer 30 films, and combinations thereof. The substrates are layered to form a laminate structure, with an adhesive composition according to the present disclosure adhering one or more of the substrates together. Films can optionally have a surface on which an image is printed with ink. The ink may be in contact with the adhesive composition. The films can be polymer films, metal-coated polymer films, or polymer films. A "polymer film" is a film that is made of a

polymer or mixture of polymers. The composition of a polymer film is, typically, 80 wt % or more of one or more polymers.

The adhesive composition is particularly attractive for packaging and sealing applications. For example, a plastic film, metal film, or metallized plastic film can be laminated (e.g., over all of its surface or at least a portion of its surface, such as along its edges, or at intermittent locations) with the adhesive composition of the present disclosure to form a laminate. The laminate can be used, to form a pouch made of at least two layers of film with the adhesive bonded in-between the two film layers. Food may be packaged for boil-in-bag preparation, or the resulting laminate might be used for sealing or packaging some other article.

EXAMPLES

The following examples are presented to further illustrate the present disclosure in detail but are not to be construed as limiting the scope of the claims. Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percentages are based on weight and all test methods are current as of the filing date of this disclosure.

Various raw materials or ingredients used in the Inventive Examples (Inv. Ex.) and the Comparative Examples (Comp. Ex.) are explained in Table I as follows:

Table 1- Raw Materials

Ingredient	Brief Description	Supplier
ADCOTETM 545E	POLYESTER POLYOL WITH AN OHN OF ABOUT 10 KOH/MG	DOW
ADCOTETM 548	65% SOLIDS AND AN OHN OF ABOUT 3.0 KOH/MG	DOW
ADCOTETM 88X102	POLYESTER POLYOL AN OHN OF ABOUT 54KOH/MG	DOW
ADCOTETM 536A	AN NCO-TERMINATED ISOCYANATE BASED ON MDI ISOCYANATE WITH FREE MONOMERIC MDI OF OVER 1 WT. %	DOW
ADCOTETM 522	AN NCO-TERMINATED ISOCYANATE BASED ON MDI ISOCYANATE WITH FREE MONOMERIC MDI OF OVER 1 WT. %	DOW
PREPOLYMER 1	AN NCO-TERMINATED ISOCYANATE BASED ON MDI ISOCYANATE WITH FREE MONOMERIC MDI OF 0.1WT. %	DOW
ADCOTETM 536B	SOLVENT BASED POLYOL	DOW
POLYPHOSPHORIC ACID	115 % POLYPHOSPHORIC ACID	SIGMA ALDRICH

Ingredient	Brief Description	Supplier
ISONATE™ 125M MDI	METHYLENE DIPHENYL DIISOCYANATE	DOW
VORANOL PUP 2025 POLYOL	POLYPROPYLENE GLYCOL	DOW
VORANOL™ CP 450	POLYETHER POLYOL WITH AVERAGE MOLECULAR WEIGHT OF ABOUT 450 AND A FUNCTIONALITY OF 3	DOW

Table 2 Adhesive formulation (parts)

Ingredient	Inventive Sample 1	Inventive Sample 2	Inventive Sample 3	Comparative Sample 1	Comparative Sample 2
Isocyanate Reactive Component					
ADCOTE™ 545E	98			98	
ADCOTE™ 88x102		98			
Phosphate Ester Compound	2	2	2	2	
ADCOTE™ 548			98		
ADCOTE™ 536B					11
Isocyanate Component					
Prepolymer 1	56	140	56		
ADCOTE™ 522				115	
ADCOTE™ 536A					100
Solvent					
Ethyl Acctate	230	420	230	210	116

Preparation of Prepolymer 1 – the Isocyanate Component

5 673g of ISONATE™ 125M MDI are melted in a 40°C oven and added to a 3L round bottom flask pre-heated to 60°C under N₂ atmosphere. 1327g of VORANOL PUP 2025 polyol are pre-heated to 50°C and added to the ISONATE™ 125M MDI. The mixture is stirred continuously as all exothermic phenomena are completed and then while stirring is continued heated to between 80-85°C. The mixture is then stirred continuously for 1.5 hours while the

10 temperature is maintained at 80°C. Residual %NCO is checked via titration until the measured value is 8.4 close to the theoretical value 8.5. The solution is then cooled to between 40-50°C and transferred to metallic cans. The cans are filled with nitrogen to prevent reaction with moisture and stored in the freezer until distilled.

The evaporator temperature, condenser temperature, pressure, feed rate, and wiper speed of a laboratory-scale UIC KDL 5 distillation device is set to 175°C, 45°C, 0.04 mbar, 0.6 to 1.2 kg/hour, and 360U/minute respectively. In the laboratory a single pass is used, but it is likely that upon scale up two or more passes may be needed. The NCO% of the final prepolymer should be 2.82, viscosity should be 15560mPas, and the residual free MDI monomer should be 0.1%.

Residual MDI is reported as weight % based on the weight of the prepolymer. Viscosity is measured at 25°C with a Brookfield viscometer model DVIII, following ASTM method D2196, using the spindle 4 and 20 rpm.

10 General Preparation of Phosphate Ester Compounds

A 1 liter (L) multi-neck round bottom flask is dried in an oven, flushed with dry nitrogen (N₂) for 30 min, then charged with 150 grams (g) of VORANOL™ CP 450 polyether polyol and placed under an N₂ sweep of 70 milliliters per minute (mL/min). A syringe is loaded with 4 g of 115 % Polyphosphoric 20 acid (PPA). The PPA is added dropwise to the polyether polyol with strong agitation. A minimal temperature increase should be observed. The reactor contents are heated to 100 °C for 1 hr then cooled to 45 °C. Then, 40 g of ethyl acetate are added to the reactor, followed by a slow addition of 50 g of ISONATE™ 125M diisocyanate. A significant exotherm is controlled with the application of an ice batch to keep the reaction pot below 75 °C and development of a yellow to amber color should be observed. The reactor is then maintained at 65 °C for 1 hr, at which point the contents are cooled and packaged. The product should have the following properties: 76.0 % solids, a hydroxyl number (OHN) of 112 mg KOH/g, acid value (AV) of 19.0 mg KOH/g, and a viscosity at 25 °C of 1,665 millipascals-seconds (mPa·s).

General Procedure for Preparing the Isocyanate – Reactive Component

25 The polyester polyol, and the phosphate ester polyol are charged into a glass reactor. The reactor is heated to about 40°C and the resulting mixture is stirred for about 30 min at 40°C. The resulting mixture is then packaged and stored.

General Procedure for Preparing the Adhesive Formulation

The pertinent ingredients for preparing the adhesive formulations including the isocyanate-reactive component, the isocyanate component and solvent are described in Table 2.

Using the adhesive of Inventive Example 1 as a typical example for an adhesive formulation sample preparation, about 750 g of isocyanate-reactive component (Part A), about 420 g of

isocyanate component (Part B) and about 1,725 g of ethyl acetate are loaded into a plastic container. The materials are mixed using a mechanical mixer at room temperature (about 25 °C) for 30 min to obtain the formulated adhesive of Inventive Example.

General Procedure for Preparing Laminates

5 The laminates based on the solvent-based adhesives were produced via a Nordmeccania LABO COMBI™ 400 pilot coater at room temperature (about 25°C) at a nip temperature of 180°F and a two-minute drying temperature of 176°F. Polymer films were corona treated before lamination and an aluminum (Al) foil was used without corona treatment. The coat weight of each laminate was maintained at about 2.5 lbs/ream. The prepared laminates were
10 subsequently cured in a controlled environment (e.g., at 25°C and 50% relative humidity.)

The Examples are prepared using films including a “Prelam” which is a 12 µm (48 gauge) polyester (“PET”) film laminated to a 0.00035 mil Al foil with ADCOTE™/Coreactant F at 3.26 g/m² (2.00 lbs/ream), commercially available from The Dow Chemical Company, and a cast polypropylene (“CPP”) film with a thickness of 65 µm,
15 commercially available from Bipack Company. GF-19, Polyethylene sealant film containing high amount of slip additive with thickness of 1.5 mil is commercially available from Berry Plastics.

Bond Strength Measurement

Laminate samples are cut to 15mm wide strips and pulled on a THWING ALBERT™
20 QC-3A peel tester equipped with a 50N loading cell at a rate of 4 inch/min. When the two films in the laminate separate, the average of the force during the pull is recorded. If one of the films stretches or breaks the maximum force or force at break is recorded. The values are the average of three separate sample strips. The initial or green bonds are tested as soon as possible after the laminate is made. Additional T-peel tests are conducted at the time intervals
25 indicated below.

General Procedure for Preparing Pouches

Performance Testing

Boil-in-Bag Test Procedure

Laminates are made from the Prelam Al and GF-19. One of the 9” x 12” (23 cm x 30.5
30 cm) sheets of laminate is folded over to give a double layer about 9” x 6” (23 cm x 15.25 cm) such that the PE film of one layer is in contact with the PE film of the other layer. The edges are trimmed on a paper cutter to give a folded piece about 5” x 7” (12.7 cm x 17.8 cm). Two long sides and one short side are heat sealed at the edges to give a finished pouch with an

interior size of 4" x 6" (10.2 cm x 15.2 cm). The heat sealing is done at 177°C (350°F) for 1 second at a hydraulic pressure of 276 kpa (40 PSI). Two or three pouches are made for each test.

Pouches are filled through an open edge with 100±5 ml of 1:1:1 sauce (blend of equal parts by weight of ketchup, vinegar and vegetable oil). Splashing the filling onto the heat seal area is avoided as this could cause the heat seal to fail during the test. After filling, the top of the pouch is sealed in a manner that minimizes air entrapment inside of the pouch.

The seal integrity is inspected on all four sides of pouches to ensure that there are no flaws in the sealing that would cause the pouch to leak during the test. Any suspect pouches are discarded and replaced. In some cases, flaws in the laminate are marked to identify whether new additional flaws are generated during the testing.

A pot is filled two-thirds full of water and brought to a rolling boil. The boiling pot is covered with a lid to minimize water and steam loss. The pot is observed during the test to ensure that there is enough water present to maintain boiling. The pouch(es) are placed in the boiling water and kept there for 30 minutes. The pouches are removed and the extent of tunneling, blistering, de-lamination, or leakage is compared with any of the marked preexisting flaws. The observations are recorded. The pouches are cut open, emptied, and rinsed with soap and water. One or more 15 mm strips are cut from the pouches and the laminate bond strength is measured at 4 inch/min according to the standard bond strength test described earlier. This is done as soon as possible after removing the pouch contents. The interior of the pouches are examined and any other visual defects are recorded.

121 C Test Procedure

Laminates are made from the Prelam//CPP as described above. One of the 9 inches x 12 inches (23 cm x 30.5 cm) sheets of laminate are folded over to give a double layer of about 9 inches x 6 inches (23 cm x 15.3 cm) such that the CPP film of one layer is in contact with the CPP film of the other layer. The edges of the folded laminate are trimmed on a paper cutter to give a folded piece of about 5 inches x 7 inches (12.7 cm x 17.8 cm). Two long sides and one short side of the folded piece are heat sealed at the edges to give a finished pouch with an interior size of 4 inches x 6 inches (10.2 cm x 15.2 cm). The heat sealing was done at 400 °F (204 °C) for 1 second (s) at a hydraulic pressure of 40 pounds per square inch (psi) (276 kilopascals [kPa]). Two or three pouches were made for each test.

The pouches prepared as described above are filled through the open edge with 100 milliliters (mL) ± 5 mL of distilled water (DI water) or 1:1:1 sauce (blend of equal parts by weight of ketchup, vinegar, and vegetable oil). Splashing the filling onto the heat seal area

should be avoided as this could cause the heat seal to fail during the test. After filling, the top of the pouch is sealed in a manner that minimizes air entrapment inside of the pouch. The seal integrity is inspected on all four sides of the pouches to ensure that there are no flaws in the sealing that would cause the pouch to leak during the test. Any defected pouches are discarded and replaced. In some cases, flaws in the laminate are marked to identify whether new additional flaws are generated during the testing.

The pouches, containing 1:1:1 sauce, are then placed in a STERIS autoclave set at 121 °C for 1 hr. The pouches are removed after testing and the extent of tunneling, blistering, de-lamination, or leakage is compared with any of the marked pre-existing flaws. The observations are recorded. The pouches are cut open, emptied, and rinsed with soap and water. One or more 15 mm strips are cut from the pouches and the laminate bond strength is measured according to the standard bond strength test described above. This was done as soon as possible after removing the pouch contents. The interior of the pouches are examined visually and any visual defects are recorded.

15 Migration Sample Preparation

The pouches consisting of 30.8 square inches (in²) (198.7 square centimeters (cm²)) of laminate each are filled with 100 mL 3 % acetic acid per sample. The pouches are then transferred to the chamber where they are stored for 2 hr at 121 °C. After testing and upon cooling to ambient temperature, the acetic acid is transferred to polyethylene bottles.

20 The acetic acid samples are extracted and prepared for analysis within days of preparation and analyzed via UV-Vis Spectroscopy within 24 hr of preparation.

Table 4 – Performance of Inventive and comparative samples under 121 C testing condition

	Inventive Example 1	Inventive Example 2	Inventive Example 3	Comparative Example 1	Comparative Example 2
Description	Foil/Inventive Sample 1/ CPP	Foil/Inventive Sample 2/ CPP	Foil/Inventive Sample 3/ CPP	Foil/Comparative Sample 1/ CPP	Foil/Comparative Sample 2/ CPP
Bond strength before retort testing (N/15 mm)	5.1, AT	4.5, AT	4.1, AT	16.1, AT	7.7, AT
Bond after 121 C, water for 1 hr Testing (N/15 mm)	4.9, AT	7.2, AT	4.0, AT	5.5, AT	0.2, DL
Bond after 121 C, 1:1:1 sauce for 1 hr Testing (N/15 mm)	3.9, AT	7.4, AT	4.3, AT	3.2, AT	0.1, DL
PAA level after 121 C, 2 hr Testing (ppb)	5.1	5.8	5.5	11.7	10.9
Curing Time	2 days at 25°C	2 days at 25°C	2 days at 25°C	2 days at 25°C	2 days at 25°C

DL: Delaminated, the secondary film separated from the primary film

AT: Adhesive transfer (adhesive fails to adhere to the primary film and is transferred to the secondary film).

Table 5 – Performance of Inventive and comparative samples under boil-in-bag testing condition

	Inventive Example 4	Comparative Example 3
Description	Foil/Inventive Sample 1/PE (GF-19)	Foil/Comparative Sample 2/PE (GF-19)
Bond strength before boil-in-bag testing (N/15 mm)	2.5, AT	5.4, AT
Bond after boil-in-bag, 1:1:1 sauce for 1 hr Testing (N/15 mm)	2.0, AT	0, DL

5

DL: Delaminated, the secondary film separated from the primary film

AT: Adhesive transfer (adhesive fails to adhere to the primary film and is transferred to the secondary film).

WHAT IS CLAIMED IS:

1. A solvent-based adhesive composition comprising:
 - a. at least one isocyanate component comprising an aromatic-based isocyanate wherein the weight of the free monomeric isocyanate is less than 1 wt. % based on the weight of the isocyanate component, and
 - b. at least one isocyanate reactive component comprising at least one phosphate ester polyol.
2. The adhesive of claim 1, wherein the at least one aromatic-based isocyanate prepolymer comprising a reaction product of: at least one isocyanate compound and at least one polyol compound.
3. The adhesive of any of the preceding claims wherein the weight % of the at least one phosphate ester polyol is at least 0.1 based on the weight of the isocyanate reactive component.
4. The adhesive of any of the preceding claims wherein the NCO reactive component further comprises a polyester polyol, or a blend of polyester polyol and polyether polyol.
5. The adhesive of any of the preceding claims wherein the molecular weight of at least one polyester polyol is above 2000 g/mol and less than 15,000 g/mol.
6. The adhesive of any of the preceding claims wherein the weight % of the at least one polyester polyol is at least 10 based on the weight of the isocyanate reactive component.
7. The adhesive of any of the preceding claims wherein the weight % of the at least one phosphate ester polyol is less than 20 based on the weight of the isocyanate reactive component.
8. The composition of any of the preceding claims, further comprising a solvent selected from the group consisting of ethyl acetate, methyl ether ketone, acetone, toluene, and other appropriate solvents, mixture of two or more thereof.

9. A process for producing a solvent-based polyurethane adhesive composition for producing laminates comprising admixing:
- a. at least one isocyanate component comprising an aromatic-based isocyanate wherein the weight of the free monomeric isocyanate is less than 1 wt. % based on the weight of the isocyanate component, and
 - b. at least one isocyanate reactive component comprising at least one phosphate ester polyol.
10. A multi-layer laminate product comprising:
- (a) at least a first layer;
 - (b) at least a second layer; and
 - (c) the adhesive of claim 1 disposed in-between the first layer and the second layer; wherein the adhesive is cured to bond the first layer to the second layer.
11. A process for producing a laminate product comprising the steps of:
- a. applying the adhesive of claim 1 to at least a portion of the surface of the first layer and/or the second layer;
 - b. contacting the first layer and the second layer such that the adhesive is disposed in-between the first layer and the second layer; and
 - c. curing the adhesive to form a laminate comprising the first layer bonded to the second layer via the cured adhesive.
12. An article for flexible packaging comprising the laminate of claim 11.

25

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/022227

A. CLASSIFICATION OF SUBJECT MATTER
INV. **B32B27/40** **B65D81/24** **C08G18/10** **C08G18/32** **C08G18/38**
 C08G18/48 **C08G18/50** **C08G18/76** **C09J175/04** **C09J175/12**
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
B65D 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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 2022/026082 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; ROHM & HAAS [US]) 3 February 2022 (2022-02-03) table II</p> <p style="text-align: center;">-----</p>	1-12

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
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- "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
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- "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

25 August 2023

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Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Bergmeier, Martin

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2023/022227

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2022026082 A1	03-02-2022	AR 123025 A1	26-10-2022
		BR 112023001661 A2	23-02-2023
		CN 116134065 A	16-05-2023
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		TW 202204465 A	01-02-2022
		US 2023250324 A1	10-08-2023
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