

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

17 September 2020 (17.09.2020)



(10) International Publication Number

WO 2020/185554 A1

(51) International Patent Classification:

C09J 163/00 (2006.01)

B32B 27/08 (2006.01)

C08G 59/50 (2006.01)

B32B 37/12 (2006.01)

B32B 7/12 (2006.01)

Published:

— with international search report (Art. 21(3))

(21) International Application Number:

PCT/US2020/021379

(22) International Filing Date:

06 March 2020 (06.03.2020)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/815,534

08 March 2019 (08.03.2019)

US

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(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,

CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO,

DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,

HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,

KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME,

MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,

OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,

SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR,

TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH,

GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,

UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,

TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,

MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,

KM, ML, MR, NE, SN, TD, TG).

(54) Title: NON-ISOCYANATE SOLVENT-FREE LAMINATING ADHESIVE COMPOSITION

(57) Abstract: Disclosed are two component laminating adhesive comprising a separate Component A and Component B. Component A comprises an amine curing agent. Component B comprises an epoxy composition. Components A and B react when mixed to form a cured adhesive material. The two components are combined and the resulting adhesive can be used to form a flexible packaging material.



Non-Isocyanate Solvent-Free Laminating Adhesive Composition

Field:

[0001] Disclosed are two component laminating adhesive comprising Component A and Component B. Component A comprises an amine curing agent. Component B comprises an epoxy composition. Components A and B are stored separately and mixed before use to react and form a cured adhesive material. The two components are combined to provide an adhesive that can be used to form a flexible packaging material.

Background:

[0002] Product packaging has been changing from sealed metal cans and glass bottles to sealed flexible packages such as pouches. As one example tuna fish is now available in both traditional metal cans and flexible pouches. The flexible package when filled with a food or other product and closed or sealed can be readily changed in shape. The flexible package is typically prepared from two layers of flexible packaging material that are overlaid and sealed around most of their periphery to form a cavity inside. Typically the two layers of flexible packaging material are heat sealed by applying heat and pressure to fuse the layers together around a thin portion of the package periphery. Food or other product is placed in the cavity through an opening and the opening is closed by heat sealing the layers together. The sealed package and enclosed product can be heated for preservation purposes. In some demanding applications the sealed package and enclosed product can be boiled in water at 100 °C.

[0003] Flexible packaging material is prepared by laminating two or more layers of film. Each film is chosen for specific properties. For example, a flexible packaging material can be a lamination of three layers. The inner layer will contact the packaged product. Polypropylene has desirable product contact properties as well as heat sealability and can be used as an inner layer. an optional middle layer will provide a barrier to moisture, oxygen and/or light. Metal films or foils have desirable barrier properties and metal films such as aluminum foil can be used as a middle layer. The outer layer will provide protection for the package and also provides a surface for printing information

such as contents, packaging date, warnings, etc. Polyester films are tough, can receive printing ink and can be used as an outer layer. Flexible packaging material can range in thickness from about 13 to about 75 micrometers (0.0005 inches to 0.003 inches).

[0004] Each layer of the flexible packaging material is bonded to the adjacent layer by an adhesive. Adhesive can be applied to the layer from a solution in a suitable solvent using gravure or smooth roll coating cylinders or from a solvent-free state using special application machinery and that layer is laminated to another layer. The laminated packaging material is dried if necessary and accumulated in rolls. The rolls are kept in storage for a predetermined amount of time to allow the adhesive to cure before use in some applications.

[0005] Although there are many possible types of adhesives not all are suited for use as a laminating adhesive in flexible packaging materials. Flexible packaging lamination adhesives require one or more specific properties such as good adhesion to the materials in each layer, high peel strength, resistance to heat such as from heat sealing or retorting, and resistance to chemically aggressive products. Conventionally, two component polyurethane adhesives have been used as flexible packaging adhesives to provide these properties. Typically, an isocyanate-containing polyurethane prepolymer obtained by the reaction of excess diisocyanate with a polyether and/or polyester containing two or more active hydrogen groups per molecule is used in combination with a second component. The second component is usually a polyether polyol and/or a polyester polyol. The two components are combined just before use and in a predetermined ratio and applied on one of the film surfaces and the coated film is laminated to another substrate.

[0006] Solvent is used as a diluent for some polyurethane laminating adhesives as the viscosity of those adhesives is too high to apply them reliably in liquid form in a roll to roll laminating process. Solventless laminating adhesives (adhesives that can be applied at 100% solids and that do not contain either organic solvents or water) have a distinct advantage in that they can be applied and run at very high line speeds. This is due to the fact that no organic solvent or water has to be removed from the adhesive by

drying. Solvent- or water-based laminating adhesives are limited to an application speed at which the solvent or water can be effectively dried in an oven. Typical line speeds for solvent-based and water-based laminating adhesives are 300 to 600 feet per minute due to the drying restrictions. Solventless adhesives, on the other hand, can be applied at 900 to even 2000 feet per minute, a line speed not possible with solvent-based and water-based laminating adhesives. Solventless laminating adhesives thus have a distinct advantage over solvent-based or water-borne adhesives.

[0007] In order that the proper coating weight of laminating adhesive is applied to the substrate, the adhesive must be “metered down” by transfer rolls to the application web or substrate. This is generally achieved by transferring the adhesive from a “puddle” between two rolls to a second and sometimes third or fourth roll before applying to the substrate. Each subsequent transfer rolls turn at a speed higher than the former roll so that there is less adhesive on each subsequent roll. Since these rolls are rotating at speeds up to 1000 rpm, incomplete transfer of the polyurethane adhesive typically occurs with the formation of adhesive “droplets” that are released into the air around the metering rolls. These adhesive “droplets” are seen as aerosol droplets that are commonly called “adhesive mist”. Adhesive misting is undesirable.

[0008] Another concern for flexible packaging material manufactured for the use as food packaging is safety. The United States Food and Drug Administration has recommended test methods (*Guidance for Industry: Preparation of Premarket Submissions for Food Contact Substances: Chemistry Recommendations*; available on the FDA website) to measure the amount of materials that might migrate from food packaging to food. These and other test methods are well known to those in the art. Unreacted isocyanate monomers from some polyurethane packaging adhesives can react with water to form primary aromatic amines (PAA) that can migrate into the food. This is problematic especially for aromatic isocyanate based adhesives. The reaction of these monomers with moisture in the packaged food turns them into primary aromatic amines, which are carcinogenic and not allowed in food items. A variety of strategies are used to minimize PAA formation. However, these strategies require storage of the completed flexible packaging material in storage until the adhesive components are fully

reacted or reduction of the isocyanate monomer content of the isocyanate prepolymers. These strategies are technically challenging, time consuming and/or expensive.

[0009] Epoxy adhesives have been proposed to replace polyurethane adhesives for use in flexible packaging. However, proposed epoxy adhesives include bisphenol based resins such as bisphenol-A epoxy resin. Bisphenol epoxy resins such as Bisphenol-A resins and Bisphenol-F resins are under scrutiny for their potential to migrate in food contact applications and are being eliminated from consideration as food packaging adhesives. Bisphenol epoxy resins are preferably not used in the presently described compositions.

[0010] Another concern of two component systems is the pot-life. Unless otherwise specifically described pot-life is the time required for the mixed adhesive to double its as mixed viscosity. For example, in a system that is applied at 40°C with an as mixed viscosity of 1000 cps, the pot-life would be the time needed for that mixed adhesive to reach 2000 cps. Typically 2-component polyurethane adhesives have pot-lives of 15-20 minutes. In flexible packaging material lamination once the adhesive viscosity increases to a certain point the machinery must undesirably be shut down and cleaned. In order to maximize pot-life and minimize machinery shutdown and cleaning, special dosing units, so called meter mix dispense units (MMD's) are used to feed freshly mixed adhesive to the application station on an as needed basis. Fast curing adhesives with short pot lives tend to cause more problems in these cases and are not very desirable. Therefore a long pot-life is desired by laminating machine operators.

[0011] Polyurethane adhesives are generally products derived from petroleum such as crude oil or other non-renewable sources. There is a strong and growing interest in using materials made from renewable or sustainable resources to replace their conventional non-renewable counterparts. It is more desirable to use materials made from renewable or sustainable resources that are not part of the human food chain. Sustainability generally refers to using a resource in a manner so that the resource is not depleted or permanently damaged. Renewable refers to using a resource that can be continually replenished. Typically, materials made from, or derived from, sources

such as fossil fuels, petroleum, coal, etc. are not considered to be sustainable or renewable.

[0012] It would be desirable to provide a solvent less laminating adhesive that is free of isocyanates and provides a combination of low viscosity, fast cure, adequate bond strength and workable potlife.

[0013] It would be desirable to provide a solvent less laminating adhesive that reduces concern about PAA formation and provides a combination of low viscosity, fast cure, adequate bond strength and workable potlife.

[0014] It would be desirable to provide a solvent less laminating adhesive comprising sustainable materials that reduces concern about PAA formation and provides a combination of low viscosity, fast cure, adequate bond strength and workable potlife.

Summary:

[0015] The present disclosure provides a two component laminating adhesive comprising Component A and Component B. Component A comprises an amine curing agent. Component B comprises an epoxy composition. Components A and B react when mixed to form a cured adhesive material.

[0016] In one embodiment the aliphatic amine curing agent is a solvent free phenalkamine derived from biorenewable non-food chain raw material sources, for example Cashew Nut Shell Oil (CNSO).

[0017] Flexible packaging adhesives prepared using the disclosed components have some or all of the following properties. They are useful with conventional flexible packaging material production equipment such as meter mix dispensers and transfer roll lamination equipment; can be applied at 100°C or less and preferably about 40°C or less; have a pot-life of about 20 minutes or more to initial viscosity doubling; provide the flexible material with sufficient strength for food packaging use; are resistant to chemicals found in food products; do not contain isocyanates and do not migrate PAA into food products. Preferably, flexible packaging adhesives prepared using the disclosed components also comprise materials from biorenewable sources.

[0018] As used herein percentages are by weight unless otherwise specifically described.

[0019] The disclosed compounds include any and all isomers and stereoisomers. In general, the disclosed compositions may be alternately formulated to comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The disclosed compositions may additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any components, materials, ingredients, adjuvants or species used in the prior art compositions or that are otherwise not necessary to the achievement of the disclosed function and/or objectives.

[0020] When the word "about" is used herein it is meant that the amount or condition it modifies can vary some beyond the stated amount so long as the function and/or objective of the disclosure are realized. The amount of condition so modified can vary by + or – 1 to 10 percent, preferably by + or – 1 to 5 percent and more preferably by + or – 1 percent.

Detailed Description:

[0021] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of ordinary skill in the art. As used herein for each of the various embodiments, the following definitions apply.

[0022] "Alkyl" or "alkane" refers to a hydrocarbon chain or group containing only single bonds between the chain carbon atoms. The alkane can be a straight hydrocarbon chain or a branched hydrocarbon group. The alkane can be cyclic. The alkane can contain 1 to 20 carbon atoms, advantageously 1 to 10 carbon atoms and more advantageously 1 to 6 carbon atoms. In some embodiments the alkane can be substituted. Exemplary alkanes include methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, heptyl, 2,4,4-trimethylpentyl, 2-ethylhexyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-hexadecyl, n-octadecyl and n-eicosyl.

[0023] "Alkenyl" or "alkene" refers to a hydrocarbon chain or group containing one or more double bonds between the chain carbon atoms. The alkenyl can be a straight hydrocarbon chain or a branched hydrocarbon group or a cyclic group. The alkene can contain 1 to 20

carbon atoms, advantageously 1 to 10 carbon atoms and more advantageously 1 to 6 carbon atoms. The alkenyl can be an allyl group. The alkene can contain one or more double bonds that are conjugated. In some embodiments the alkene can be substituted. Exemplary alkenes include C₂-C₁₈-, C₂-C₁₂-, C₂-C₁₀-, C₂-C₈-, C₂-C₆- or C₂-C₄- alkenyl, vinyl, allyl, 1-propen-2-yl, 1-buten-4-yl, 2-buten-4-yl and 1-penten-5-yl.

[0024] "Alkyne" or "alkynyl" refers to a hydrocarbon chain or group containing one or more triple bonds between the chain carbon atoms. The alkyne can be a straight hydrocarbon chain or a branched hydrocarbon group. The alkyne can be cyclic. The alkyne can contain 1 to 20 carbon atoms, advantageously 1 to 10 carbon atoms and more advantageously 1 to 6 carbon atoms. The alkyne can contain one or more triple bonds that are conjugated. In some embodiments the alkyne can be substituted.

[0025] "Alkylene" refers to a divalent linear or branched moiety containing only single bonds between carbon atoms in the moiety and including, for example, C₁-C₁₈-, C₁-C₁₂-, C₁-C₁₀-, C₁-C₈-, C₁-C₆- or C₁-C₄- alkylene. Exemplary alkylenes include methylene, ethylene, propylene, isopropylene, n-butylene, sec-butylene, isobutylene, tert-butylene, n-pentylene, n-hexylene, n-heptylene, 2,4,4-trimethylpentylene, 2-ethylhexylene, n-octylene, n-nonylene, n-decylene, n-undecylene, n-dodecylene, n-hexadecylene, n-octadecylene and n-eicosylene.

[0026] "Amine" refers to a moiety comprising at least one -NHR group wherein R can be a covalent bond, H or hydrocarbyl.

[0027] "Amino alkyl" refers to a moiety comprising one or more amine groups and one or more alkyl groups in any combination.

[0028] "Aryl" or "Ar" or "aromatic" refers to a monocyclic or polycyclic aromatic group. The cyclic rings can be linked by a bond or fused. The aryl can contain from 6 to about 30 carbon atoms; advantageously 6 to 12 carbon atoms and in some embodiments 6 carbon atoms. Exemplary aryls include phenyl, biphenyl, naphthyl, dihydrophenanthrenyl, fluorenyl, phenantrenyl. In some embodiments the aryl is substituted.

[0029] "Cure" refers to both crosslinking and curing. "Crosslinking" is the formation of chemical or physical interactions between molecules. The term "curing" is broader than

the term "crosslinking" and includes the total polymerization process from initiation of the reaction to when the crosslinked adhesive composition is produced.

[0030] "Hydrocarbyl" refers to a group containing carbon and hydrogen atoms. The hydrocarbyl can be linear, branched, or cyclic group. The hydrocarbyl can be alkyl, alkenyl, alkynyl or aryl. In some embodiments, the hydrocarbyl comprises one or more substituents.

[0031] "Oligomer" refers to a defined, small number of repeating monomer units such as 2-5,000 units, and advantageously 10-1,000 units which have been polymerized to form a molecule. Oligomers are a subset of the term polymer.

[0032] "Polymer" refers to any polymerized product greater in chain length and molecular weight than the oligomer. Polymers can have a degree of polymerization of about 20 to about 25000. As used herein polymer includes oligomers and polymers.

[0033] "Substituted" refers to the replacement of a hydrogen atom in any possible position on a molecule by one or more substituent groups. Useful substituents are those groups that do not significantly diminish the disclosed reaction schemes. Exemplary substituents include, for example, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, heteroaryl, heteroalicyclic, aralkyl, heteroaralkyl, (heteroalicyclic)alkyl, protected hydroxyl, aryloxy, acyl, ester, mercapto, alkylthio, arylthio, carbonyl, thiocarbonyl, O-carbamyl, N-carbamyl, O-thiocarbamyl, N-thiocarbamyl, C-amido, N-amido, S-sulfonamido, N-sulfonamido, C-carboxy, protected C-carboxy, O-carboxy, isocyanato, thiocyanato, isothiocyanato, silyl, sulfenyl, sulfinyl, sulfonyl, haloalkoxy, trihalomethanesulfonyl, trihalomethanesulfonamido, amino including mono- and di-substituted amino groups and the protected derivatives thereof. halogen, (meth)acrylate, epoxy, oxetane, urea, urethane, N₃, NCS, CN, NO₂, NX¹X², OX¹, C(X¹)₃, COOX¹, SX¹, Si(OX¹)_iX²_{3-i}, alkyl, alkoxy; wherein each X¹ and each X² independently comprise H, alkyl, alkenyl, alkynyl, aryl or halogen and i is an integer from 0 to 3.

[0034] The disclosed flexible packaging adhesives comprise a substantially homogeneous mixture of Component A, an aliphatic amine curing agent, and

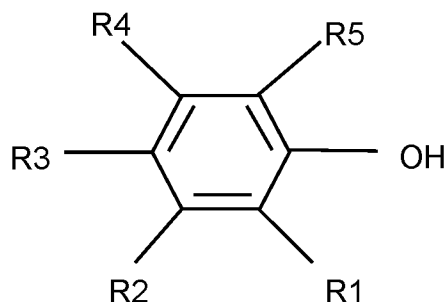
Component B, an epoxy composition. The adhesives are two component compositions wherein Components A and B are stored separately and mixed in a predetermined ratio just before use. Mixing Components A and B initiates a reaction resulting in curing of the composition to an irreversible thermoset state.

Component A

[0035] Component A is an amine curing agent. The amine curing agent comprises a material having amine moieties that, when mixed with an epoxy, will react and cure the epoxy. Amine curing agents include amidoamine curing agents, polyamidoamine curing agents, aliphatic amine curing agents and cycloaliphatic amine curing agents available under the EPICURE name from Hexion; polyamine curing agents; cycloaliphatic curing agents, aromatic amine curing agents and aliphatic amine adduct curing agents available under the ANCAMINE name from Evonik; and phenalkamine curing agents available from Cardolite.

[0036] Preferably Component A comprises phenalkamine curing agents. In some embodiments Component A consists essentially of phenalkamine curing agents and optionally one or more additives but is free of other curing agents. In some embodiments Component A consists of phenalkamine curing agents. Preferred phenalkamine curing agents are a class of Mannich bases obtained by reacting a cardanol-containing extract derived from cashew nutshell liquid, an aldehyde compound, such as formaldehyde, and an amine such as ethylenediamine and diethyltri-amine. The extract from cashew nutshell liquid primarily contains a mixture of cardanol, cardol and related compounds of varying degrees of saturation. These preferred phenalkamine curing agents are materials made from renewable or sustainable resources and are derived from non-food chain sources.

[0037] Preferably the amine curing agent includes a phenalkamine comprising an aryl core with hydrocarbonyl and amine or alkylamine substituents. In one variation phenalkamines have the following structure:

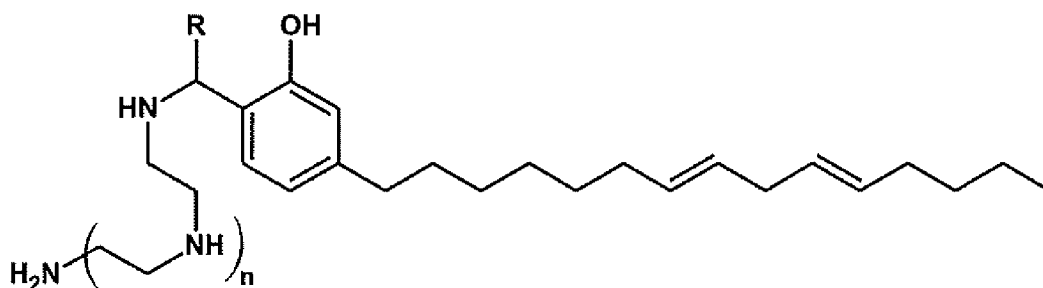


One of R1 to R5 is hydrocarbonyl, preferably alkenyl, more preferably C₅ to C₂₀ alkenyl.

One of R1 to R5 that is not hydrocarbonyl is selected from -CH₂(R)-amino alkyl or -CH₂-CH(NH₂)-R; where R = alkyl, amino alkyl, substituted amino alkyl.

The remainder of R1 to R5 are independently selected from H, alkyl or alkenyl.

[0038] In one preferred embodiment phenalkamines have the following structure.



Phenalkamines

n = 0,1,2,3...

where R is H or hydrocarbonyl, preferably H, alkyl or alkenyl and n is an integer from 1 to about 10, more generally 1 to about 5.

[0039] Component A can have an amine value of about 400 to about 465 mgKOH/g and preferably about 415 to about 430 mgKOH/g. Component A can have a viscosity of about 4000 to about 10000 cps at 25 deg C (Brookfield viscometer) and preferably of about 5000 to about 8000 cps at 25 deg C.

Component B

[0040] Component B comprises one or more epoxy resin(s). Epoxy resins are low molecular weight pre-polymers or higher molecular weight polymers which normally contain at least two epoxide groups. Preferably, the epoxy resins contain 2 to 6 epoxide groups. The epoxide group is also sometimes referred to as a glycidyl or oxirane group. The raw materials for epoxy resin production are typically petroleum derived, although some plant derived sources are becoming commercially available. Epoxy resins comprising aromatic groups such as the Bisphenol A and bisphenol F resins are not preferred for food contact or food packaging applications. Preferably, Component B is free from epoxy resins containing aromatic groups.

[0041] Since epoxy resins are prepolymers or polymers they have a variable chain length resulting from the polymerization reaction used to produce them. High purity grades can be produced for certain applications, e.g. using a distillation purification process.

[0042] An important criterion for epoxy resins is the epoxide group content. This can be expressed as the "epoxy equivalent weight" (EEW), which is grams of resin/mole of epoxy functionality. Component B can have an EEW value of about 135 to about 176 and preferably about 140 to about 170. Component B can have a viscosity of about 300 to about 500 cps at 25 deg C (Brookfield viscometer) and preferably of about 450 to about 500 cps at 25 deg C.

[0043] The amounts of Component A and Component B used in the laminating adhesive systems of this invention will generally be adjusted based on the amine content of Component A and the epoxide content of Component B to provide a fully cured reaction product. Typical Component A to Component B ratios of 5:1 to 1:5 and preferably about 3:1 to 1:3 are found convenient for industrial use.

[0044] The mixture of Component A and Component B when first combined will have a viscosity of about 600 cps to about 4,000 cps (more preferably, about 700 to about 2,000 cps at application temperature. Mixed adhesive viscosities above 5,000 cps at application temperature are difficult or impossible to run on conventional laminating

equipment. Typical application temperatures for flexible packaging lamination are about 35 °C, although higher or lower application temperatures may be useful in some applications.

[0045] Typically, the mixed adhesive will have a pot-life of at least about 20 minutes and more preferably at least about 30 minutes. The viscosity of the mixed adhesive does not increase above about two times the initial viscosity during the pot life after Component A and Component B are mixed and held at a temperature of 40 °C.

[0046] Where appropriate, in addition to Component A and Component B, the two component laminating adhesive may optionally comprise one or more further additives that are conventionally used in flexible packaging laminating adhesives. The additives may, for example, account for up to about 50% by weight of the overall two component adhesive, preferably up to about 30% by weight and more preferably up to about 10% by weight. The additives may be in either of Components A and B. The optional additives which can be used in the context of the present disclosure include solvents, water, catalysts, curing agents, accelerators, plasticizers, stabilizers, antioxidants, light stabilizers, fillers, dyes, pigments, fragrances, preservatives or mixtures thereof.

[0047] The film or films to be coated and adhered to each other using the two component adhesive formulations may be comprised of any of the materials known in the art to be suitable for use in flexible packaging, including both polymeric and metallic materials as well as paper (including treated or coated paper). Thermoplastics are particularly preferred for use as at least one of the layers. The materials chosen for individual layers in a laminate are selected to achieve specific desired combinations of properties, e.g., mechanical strength, tear resistance, elongation, puncture resistance, flexibility/stiffness, gas and water vapor permeability, oil and grease permeability, heat sealability, adhesiveness, optical properties (e.g., clear, translucent, opaque), formability, merchantability and relative cost. Individual layers may be pure polymers or blends of different polymers. The polymeric layers are often formulated with colorants, anti-slip, anti-block, and anti-static processing aids, plasticizers, lubricants, fillers, stabilizers and the like to enhance certain layer characteristics.

[0048] Particularly preferred polymers for use include, but not limited to, polyethylene (including low density polyethylene (LDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), high molecular weight, high density polyethylene (HMW-HDPE), linear low density polyethylene (LLDPE), linear medium density polyethylene (LMPE)), polypropylene (PP), oriented polypropylene, polyesters such as poly (ethylene terephthalate) (PET) and poly (butylene terephthalate) (PBT), ethylene-vinyl acetate copolymers (EVA), ethylene-acrylic acid copolymers (EAA), ethylene-methyl methacrylate copolymers (EMA), ethylene-methacrylic acid salts (ionomers), hydrolyzed ethylene-vinyl acetate copolymers (EVOH), polyamides (nylon), polyvinyl chloride (PVC), poly(vinylidene chloride) copolymers (PVDC), polybutylene, ethylene-propylene copolymers, polycarbonates (PC), polystyrene (PS), styrene copolymers, high impact polystyrene (HIPS), acrylonitrile-butadiene-styrene polymers (ABS), acrylonitrile copolymers (AN), polyamide (Nylon), polylactic acid (PLA), regenerated cellulose films (Cellophane).

[0049] The polymer surface may be treated or coated, if so desired. For example, a film of polymer may be metallized by depositing a thin metal vapor such as aluminum onto the film's surface. Metallization may enhance the barrier properties of the finished laminate. The polymer film surface may also be coated with anti-fog additive or the like or subjected to a pretreatment with electrical or corona discharges, or ozone or other chemical agents to increase its adhesive receptivity. A coating of an inorganic oxide such as SiO_x or AlO_x may also be present on the polymer surface (for example, an SiO_x- or AlO_x-coated PET film).

[0050] One or more layers of the laminate may also comprise a metal film or foil, such as aluminum foil, or the like. The metal foil will preferably have a thickness of about 5 to 100 μm.

[0051] The individual films comprising the laminates can be prepared in widely varying thicknesses, for example, from about 5 to about 200 microns. The films, foils, and laminating adhesive formulation can be assembled into the laminate by using any one or more of the several conventional procedures known in the art for such purpose. For

instance, the adhesive formulation may be applied to the surface of one or both of two films/foils by means of extrusion, brushes, rollers, blades, spraying or the like and the film/foil surfaces bearing the adhesive composition brought together and passed through a set of rollers (often referred to as nip rollers) which press together the film/foils having the adhesive composition between the films/foils. The resulting laminate may be rolled or wound onto a reel for ageing. The adhesive may be applied by conventional techniques; e.g., by a multi-roll application station.

[0052] One way of applying the adhesive composition to a substrate such as a film or foil is through the use of a series of smooth surface rubber and steel transfer rollers on a solventless adhesive laminator. The adhesive components can be mixed using Meter/Mix/Dispense (MMD) equipment capable of automatically measuring and mixing the correct amounts of the components and delivering the resulting mixture to the laminator. The mixed adhesive is deposited on the first two rollers and metered by the remaining rollers in the application station (typically, 3 to 5 rollers). The flow characteristics of the adhesive composition may be improved by heating the first two rollers to a temperature of from about 35 to about 60 degrees C. Typically, the final application roller is heated to a temperature of from about 40 to about 60 degrees C. Modifications of these temperatures may be required depending upon line speed, substrates and roller size.

[0053] The coating weight at which the adhesive formulation can be applied to the surface of a film layer is in the range of about 0.12 to about 3.1 lbs/3000 sq. ft, and more typically about 0.8 to about 1.4 lbs/3000 sq. ft.

[0054] A second film or foil substrate is pressed against the substrate having the adhesive applied thereon by means of one or more nip rollers. Nip temperatures may be adjusted as needed depending upon line speed, thickness of the laminate, reactivity and other characteristics of the adhesive, and the substrates being laminated, but temperatures of from about 45 to about 90 °C are typically suitable.

[0055] It may be desirable to heat the laminate at an elevated temperature (e.g., about 40° C to about 100° C) so as to accelerate full curing of the adhesive composition.

Alternatively, the adhesive composition can be curable at approximately room temperature (e.g., about 20° C to about 25° C) or higher over a period of from about 1 to about 14 days.

[0056] Generally speaking, the adhesive compositions are believed to be largely chemically cured through the reaction of the Component A amine groups and the Component B epoxide groups.

[0057] Adhesives used for bonding films into flexible packaging must have a number of properties to be commercially useful. These properties will change depending on the use for which the flexible packaging is designed. Cured reaction products of the adhesive must have little or no migration from the packaging into the packaged product. Cured reaction products of the laminating adhesive must have minimum room temperature bond strengths to common laminating film materials of 200 to 300 grams/inch for a low stress application. Cured reaction products of the laminating adhesive must have minimum room temperature bond strengths to common laminating film materials of 400 grams/inch or more for a higher stress application. The most preferred result is for the cured reaction products of the laminating adhesive to have sufficient room temperature bond strength to common laminating film materials so that the laminating film fails before the adhesive. Cured reaction products of the laminating adhesive must retain most of this room temperature bond strength to common laminating film materials after exposure to the packaged food product. For some applications the cured reaction products of the laminating adhesive must retain most of this bond strength after exposure to elevated temperatures.

[0058] Laminates prepared in accordance with the present disclosure may be used for packaging purposes in the same manner as conventional or known flexible laminated packaging films. The laminates are particularly suitable for forming into flexible pouch-shaped container vessels capable of being filled with a foodstuff and sealed. For example, two rectangular or square sheets of the laminate may be piled in the desired configuration or arrangement; preferably, the two layers of the two sheets which face each other are capable of being heat-sealed to each other. Three peripheral portions of

the piled assembly are then heat-sealed to form the pouch. Heat-sealing can easily be accomplished by means of a heating bar, heating knife, heating wire, impulse sealer, ultrasonic sealer, or induction heating sealer.

[0059] The foodstuff is thereafter packed in the so-formed pouch. If necessary, gasses injurious to the foodstuff such as air are removed by known means such as vacuum degasification, hot packing, boiling degasification, or steam jetting or vessel deformation. The pouch opening is then sealed using heat. The packed pouch may be heated at a later time.

Examples

[0060] The following materials were used in the examples.

CPP (3 mil) is a 3 mil (0.003 inches) thick film of polypropylene.

Met OPP (65 ga) is a 65 gauge film or oriented polypropylene with a metallized deposit on one face.

PE LL-120 is a 2 mil (0.002 inch) thick film of linear low density polyethylene.

Polyethylene terephthalate (PET) is a typical 48 ga polyester film used for outer layers of food packaging laminations. It can function as support for less robust films, such as aluminum foil. It is often printed on the side facing the interior of the package.

PET Met is 48-gauge polyester with a very thin layer of aluminum, via vacuum vapor deposition

PET-Foil is 48-gauge polyester laminated to 0.0035 ga aluminum foil with a solvent based commercial adhesive

OPP is an oriented polypropylene film of about 75 gauge.

[0061] The following lamination constructions were made and tested.

PET (48 ga)/adhesive/PE LL-120 (2 mil)

PET (48 ga)/adhesive/PET (48 ga)/adhesive/PE LL-120 (2 mil)

PET-Foil

[0062] Laminations were prepared using a Nordmeccanica Labo Combi to coat each of the prepared adhesives at a specified coating weight.

[0063] Viscosity was tested at 25° C using a Brookfield viscometer at 3 rpm with a 31 spindle and a thermosel attachment.

[0064] Bond strength was tested by preparing a flexible packaging laminate material and allowing that material to cure for a desired time. A one inch by 4 inch to 6 inch sample is cut from the pouch and tested for bond strength via a tensile strength tester at room temperature or a desired elevated temperature with failure mode noted. This is a T peel bond strength test with the laminated tail held at 90 degrees to the ends being pulled. Testing was done at room temperature (Regular Bonds) or 158°F (Hot Box Bonds).

[0065] Heat seal bond strength was tested according to ASTM F88 Seal Strength of Flexible Barrier Materials. Generally, a laminated sample is cut into specimens one inch wide by approximately 6-8 inches long. The specimen is folded so that the sealant film is on the inside and the total folded length is 3-4 inches. Form a heat seal in the folded material. Using a tensile tester with a 100 lb. load cell and clamp each leg of the test specimen in the tensile testing machine. Center the specimen laterally in the grips. Align the specimen in the grips so the seal line is perpendicular to the direction of pull. Test the heat seal at a rate grip separation of 8 – 12 inches/min. Test the material to failure and note the force (strength) values and mode of specimen failure.

[0066] Product resistance was tested by preparing a flexible packaging laminate material and allowing that material to cure for a desired time. 4 inch by 4 inch pouches were prepared from the cured laminate and about 30 ml of a test food product (2 gm for the coffee and flavoured coffee samples) was sealed within. The sealed pouch is aged for a specified time at 60 °C. At the end of the aging period a 1 inch by 4 inch to 6 inch sample of a bond area is cut from the pouch and tested for regular bond strength with

failure mode noted. Test food products include water, ketchup, mustard, Thousand Island dressing and 1-1-1 sauce (a 1 to 1 to 1 mixture of ketchup 20 vinegar to vegetable oil).

[0067] Failure modes and their abbreviations are:

Elongation – E; when one or both of the substrates elongates during the test.

SF - Stock Fail; one or both laminating films fail.

P - Peel; when the laminate is allowed to separate the entire length of the test strip without either of the two substrates tearing or breaking.

SS - Stock Split; when either of the two substrates fails after the first inch of the test strip

MT - Metal Transfer; the metallized layer pulls off of the originally metalized film and remains bonded to the other film.

Z – Zipper; when the failure has an alternating high strength, low strength, high strength, low strength mode

P-MT -Peel and Metal Transfer;

P/E-N -Peel and Elongation Neck;

P/E/N -SS-Peel and Elongation Neck and Stock Split)

P/Z – Peel and Zipper

Amine Component A

[0068] Ultra LITE 2009SF, available from Cardolite Co. was used as Component A.

Physical properties : viscosity at 25 deg C = 5589 cps, weight per gallon = 8.54 lbs/gallon, amine value= 424 mgKOH/g, color = <2 Gardner, and appearance is light yellow liquid.

Epoxy Component B

[0069] In a 1000 mL reactor equipped with thermometer, mechanical stirrer, reflux condenser and nitrogen inlet, was charged 372.7g of Loctite Liofol LA 8600, available from Henkel Corporation, (EEW 135-150). Stirring was started and the reactor temperature was set to 35°C to 50°C to facilitate mixing. At temperature add 559.1g of Epalloy 8240, available from Emerald Performance Materials – CVCThermost Specialties (EEW 164-176) and 68.2g of Silquest A-1871, available from Momentive Performance Materials. The materials were mixed for about 45 minutes to a homogeneous state. The mixture was cooled to about 25° C and discharge into a container. Component B had a viscosity at 25°C of about 492 cps, a weight per gallon of about 9.7498 lbs per gallon and a clear color.

Example 1

[0070] A mixed non-isocyanate, solvent-free, two component adhesive was made by mixing epoxy Component B (typical EEW, 140-170 range) with amine Component A (typical amine value 415-430 mgKOH/g range) at ambient temperature at a mix ratio 2.7 parts by weight Component B to 1 part by weight Component A for a balanced stoichiometric ratio. The adhesive mixture was used at an application temperature of 25°C, a coating weight of 1.1 lbs./ream and a nip temperature of 25°C to bond samples of PET (48 ga)/PE LL-120(2 mil); PET (48 ga)/PET (48 ga)/PE LL-120(1 mil); and PET /foil.

[0071] Stock failure T peel bond strength, hot box bond strength, heat seal bond strength and product resistance testing was done on the bonded laminates after 24 hours cure at ambient temperature. These tests were repeated after 14 days cure. Results are shown in the Tables below.

Example 1 Bond Strength of Non-Isocyanate Solvent-Free Adhesive						
	Regular Bonds		Hot Box (158 F)		Heat Seal	
	24 Hr.	14 Day	24 Hr.	14 Day	24 Hr.	14 Day
PET (48 ga)/PE LL-120 (2 mil)	450(SF)	394(SS)	250(P)	110(P)	4321(SF)	3104(SF)
PET (48 ga)/PE LL-120 (1 mil)	528(SS)	368(SF)	185(P)	123(P)	4973(SF)	5144(SF)
PET (48 ga)/Foil (1 mil)	420(SS)	433(SF)	64(P)	121(P)	NA	NA
Met OPP (65 ga)/OPP (75 ga)	225(P)	269(P-MT)	38(P)	158(P)	NA	NA
PET-Foil/CPP (3 mil)	765(P)	367(P)	112(P)	403(P)	5345(SF)	7053(SF)

[0072] The PET-Foil/adhesive/CPP (3 mil) lamination had a strong peel bond strength within 24 hours of cure at ambient temperature and maintained the peel bond strength when tested after 14 days cure. Further, this lamination also had a desirable stock failure mode for heat seal bonds tested after 24 hours of cure time and maintained this heat seal bond performance after 14 days cure.

[0073] The Met OPP (65 ga)/adhesive/OPP (75 ga) had a peel and peel metal transfer failure mode for bond strength after 24 hours cure at ambient temperature and maintained this bond strength when tested after 14 days cure.

Example 1 Product Resistance of Non-Isocyanate Solvent-Free Adhesive						
	Day	Water	Ketchup	Mustard	Thousand Island	1-1-1 sauce
PET (48 ga)/PE LL-120 (2 mil)	9	196(SS)	303(SS)	281(SS)	266(SS)	261(SS)
	17	230(SF)	387(SF)	325(SF)	340(SS)	310(SS)

[0074] During product resistance testing the bonds maintained high strength and desirable stock failure mode for the regular bonds.

Example 2

[0075] The solvent-free adhesive made in Example 1 was used. The adhesive was coated onto films at an application temperature of 25°C, a coating weight of 1.3 lbs./ream and a nip temperature of 25°C and the films were laminated. The laminated samples were tested after curing. Results are shown in the Tables below.

Example 2 Bond Strength of Non-Isocyanate Solvent-Free Adhesive						
	Regular Bonds		Hot Box (158 F)		Heat Seal	
	24 Hr.	14 Day	24 Hr.	14 Day	24 Hr.	14 Day
PET (48 ga)/PE LL-120 (2 mil)	738(SF)	519(SF)	207(P)	212(P)	5597(SF)	8842(SF)
PET (48 ga)/PE LL-120 (1 mil)	565(SS)	444(SS)	153(P)	137(P)	4619(SF)	6920(SF)
PET (48 ga)/Foil (1 mil)	514(SS)	476(SF)	71(P)	271(P)	NA	NA
Met OPP (65 ga)/ OPP (75 ga)	239(P)	510(SS)	45(P)	163(P)	NA	NA
PET-Foil/CPP (3 mil)	772(P)	4257(P)	84(P)	357(P)	4732(SF)	5758(SF)

[0076] Desirable stock failure modes were obtained for regular bonds of the PET (48 ga)/adhesive/PE LL-120 (2 mil) and PET (48 ga)/adhesive/PE LL-120 (1 mil) laminations after 24 hours of cure at ambient temperature. This regular bond performance was maintained after 14 days of cure at ambient temperature.

[0077] PET (48 ga)/adhesive/Foil (1 mil) laminations exhibited desirable stock failure modes for regular bonds after 24 hours of cure at ambient temperature. These results were maintained after 14 days cure.

[0078] PET-Foil/adhesive/CPP (3 mil) laminations achieved strong regular bond strength after 24 hours of cure at ambient temperature and maintained this performance when tested after 14 days cure. Heat seal bonds for this lamination had a stock failure mode after 24 hours of cure at ambient temperature and maintained this performance after 14 days cure.

[0079] Met OPP (65 ga)/adhesive/ OPP (75 ga) laminations achieved acceptable regular bond strength after 24 hours of cure at ambient temperature. These laminations had an improved regular bond strength and desirable stock split failure mode after 14 days cure.

Example 2 Product Resistance of Non-Isocyanate Solvent-Free Adhesive						
	Day	Water	Ketchup	Mustard	Thousand Island	1-1-1 sauce
PET (48 ga)/PE LL-120 (2 mil)	9	31(P)	34(P)	68(P)	17(P)	71(P)
	17	64(P)	215(SS)	190(SS)	166(SS)	65(P)

[0080] During product resistance testing after 9 days of exposure the bonds exhibited low strength and poor product resistance, especially with water, Thousand Island and 1-1-1 sauce. The strengths improved after 17 days exposure.

Example 3

[0081] The solvent-free adhesive made in Example 1 was used. The adhesive was coated onto films at an application temperature of 25°C a coating weight of 1.5 lbs./ream and a nip temperature of 25°C and the films were laminated. The laminated samples were tested after curing. Results are shown in the Tables below.

Example 3 Bond Strength of Non-Isocyanate Solvent-Free Adhesive						
	Regular Bonds		Hot Box (158 F)		Heat Seal	
	24 Hr.	14 Day	24 Hr.	14 Day	24 Hr.	14 Day
PET (48 ga)/PE LL-120 (2 mil)	516(SF)	443(SS)	185(P)	164(P)	6366(SF)	7462(SF)
PET (48 ga)/PE LL-120 (1 mil)	477(P/E)	506(SF)	156(P)	142(P)	5048(SF)	5968(SF)
PET (48 ga)/Foil (1 mil)	371(SS)	429(SF)	92(P)	402(P)	NA	NA
Met OPP (65 ga)/ OPP (75 ga)	262(P)	539(SS)	38(P)	157(P)	NA	NA
PET-Foil/CPP (3 mil)	848(P)	346(SS)	102(P)	371(P)	2372(SF)	4541(SF)

[0082] The PET (48 ga)/adhesive/PE LL-120 (2 mil) and PET (48 ga)/adhesive/PE LL-120 (1 mil) laminations exhibited stock failure modes in the regular bond test after 24 hours of cure at ambient temperature and maintained this desirable performance after 14 days cure.

[0083] The PET (48 ga)/adhesive/Foil (1 mil) laminations exhibited stock split failure mode in the regular bond test after 24 hours of cure and after 14 days cure. These regular bond test results indicate stock failure rather than adhesive failure.

[0084] The PET-Foil/adhesive/CPP (3 mil) lamination achieved strong peel bond strength after 24 hours of cure at ambient temperature and maintained this performance after 14 days cure. Further, in heat seal bond tests the failure mode was stock failure after 24 hours of cure at ambient temperature and after 14 days cure.

[0085] The Met OPP (65 ga)/adhesive/ OPP (75 ga) lamination exhibited peel failure mode in the regular bond test after 24 hours cure at ambient temperature and exhibited an improved stock split failure mode when tested after 14 days cure.

Example 3 Product Resistance of Non-Isocyanate Solvent-Free Adhesive						
	Day	Water	Ketchup	Mustard	Thousand Island	A-1 sauce
PET (48 ga)/PE LL-120 (2 mil)	9	38(P)	40(P)	38(P)	24(P)	81(P)
	17	61(P)	228(SS)	165(SS)	147(SS)	59(P)

[0086] During product resistance testing after 100 hours at 60 deg. C the bonds exhibited low strength and poor product resistance, especially water, Thousand Island and 1-1-1 sauce.

Example 4

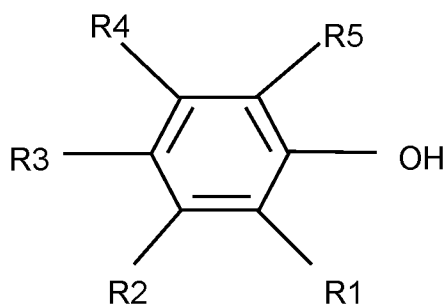
[0087] The solvent-free adhesive made in Example 1 was used. The adhesive was coated onto films at an application temperature of 25°C, a coating weight of 1.1 lbs./ream and a nip temperature of 25°C. The laminated samples were tested after curing. Results are shown in the Table below.

Example 4 Bond Strength of Non-Isocyanate Solvent-Free Adhesive						
	Regular Bonds		Hot Box (158 F)		Heat Seal	
	24 Hr.	14 Day	24 Hr.	14 Day	24 Hr.	14 Day
PET (48 ga)/PE LL-120 (2 mil)	752(SF)	740(SF)	50(P)	793(SF)	4990(SF)	6258(SF)

[0088] The PET (48 ga)/adhesive/PE LL-120 (2 mil) laminate had high strength and desirable stock failure mode in the regular bond testing after 24 hours of cure at ambient temperature and maintained this performance after 14 days cure. The heat seal bond testing also had the desirable stock failure mode after 24 hours of cure and 14 days cure.

What is claimed is:

1. A two component, flexible packaging laminating adhesive comprising:
a component A including a curing agent comprising one or more amines prepared from sustainable resources that are derived from non-food chain sources and optionally one or more additives; and
a component B comprising an epoxy resin free of aromatic groups and optionally one or more additives.
2. The two component, flexible packaging laminating adhesive of claim 1 wherein all of the amines in component A consist of amines prepared from sustainable resources that are derived from non-food chain sources.
3. The two component, flexible packaging laminating adhesive of claim 1 or 2 wherein one or more of the amines in component A are a phenalkamine.
4. The two component, flexible packaging laminating adhesive of any of claims 1 to 3 wherein all of the amines in component A consist of phenalkamine.
5. The two component, flexible packaging laminating adhesive of any of claims 1 to 4 wherein one or more of the amines in component A comprise a structure:



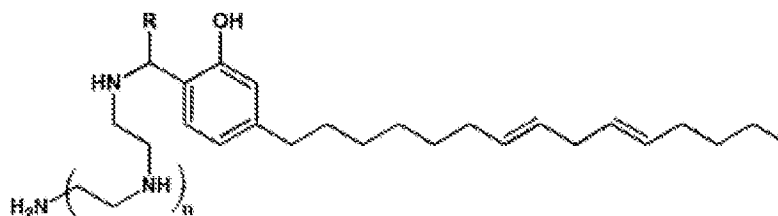
wherein one of R1 to R5 is hydrocarbyl, or alkenyl, or C₅ to C₂₀ alkenyl;
one of R1 to R5 that is not hydrocarbyl is selected from -CH₂(R)-amino alkyl or

$-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{R}$; where R is selected from alkyl, amino alkyl, substituted amino alkyl; and

the remainder of R1 to R5 are independently selected from H, alkyl or alkenyl.

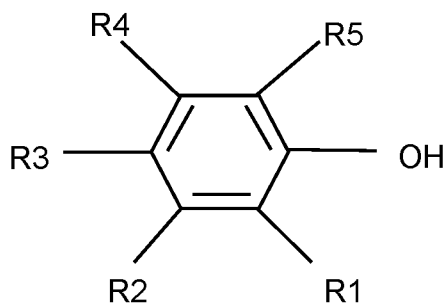
6. The two component, flexible packaging laminating adhesive of any of claims 1 to 5 wherein the one of R1 to R5 that is hydrocarbyl is C_5 to C_{20} alkenyl.

7. The two component, flexible packaging laminating adhesive of any of claims 1 to 5 wherein one or more of the amines in component A comprises a structure



wherein n is an integer from 1 to 10.

8. The two component, flexible packaging laminating adhesive of any of claims 1 to 7 wherein all of the amines in component A consist of a structure:



wherein one of R1 to R5 is hydrocarbyl, or alkenyl, or C_5 to C_{20} alkenyl;
one of R1 to R5 that is not hydrocarbyl is selected from $-\text{CH}_2(\text{R})$ -amino alkyl or $-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{R}$; where R is selected from alkyl, amino alkyl, or substituted amino alkyl; and

the remainder of R1 to R5 are independently selected from H, alkyl or alkenyl.

9. A flexible packaging laminate comprising a first film layer; a second film layer adjacent the first film layer; and a mixture of the two component, flexible packaging laminating adhesive of claim 1 disposed between the first film layer and the second film layer.
10. The flexible packaging laminate of claim 9 comprising the first film layer; the second film layer adjacent the first film layer and cured reaction products of the mixed flexible packaging laminating adhesive bonding the first film layer to the second film layer.
11. The flexible packaging laminate of claim 9 or 10 wherein component A wherein all of the amines in component A consist of amines prepared from sustainable resources that are derived from non-food chain sources.
12. The flexible packaging laminate of any of claims 9 to 11 wherein all of the amines in component A consist of phenalkamine.
13. The flexible packaging laminate of any of claims 9 to 12 wherein component A consists of one or more phenalkamine curing agents.
14. A method of making a flexible packaging laminate comprising:
 - providing a component A including a curing agent comprising one or more amines prepared from sustainable resources that are derived from non-food chain sources, and optionally one or more additives;
 - providing a component B comprising an epoxy resin free of aromatic groups, and optionally one or more additives;
 - mixing component A and component B to form a mixed flexible packaging laminating adhesive;
 - providing a first film having a first surface;

disposing the mixed flexible packaging laminating adhesive over at least portions of first surface;

providing a second film having a second face;

disposing the second face onto the adhesive disposed on the first face; and

curing the mixed flexible packaging laminating adhesive to bond the first face to the second face.

15. The flexible packaging laminate of claim 14 wherein all of the amines in component A consist of amines prepared from sustainable resources that are derived from non-food chain sources.

16. The flexible packaging laminate of claim 14 or 15 wherein component A comprises a phenalkamine curing agent.

17. The flexible packaging laminate of any of claims 14 to 16 wherein component A consists of one or more phenalkamine curing agents.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2020/021379**A. CLASSIFICATION OF SUBJECT MATTER****C09J 163/00(2006.01)i, C08G 59/50(2006.01)i, B32B 7/12(2006.01)i, B32B 27/08(2006.01)i, B32B 37/12(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)

C09J 163/00; B32B 027/38; C08G 59/50; C08K 3/36; C08K 320; C08L 63/00; C08L 6302; C09D 163/00; B32B 7/12; B32B 27/08; B32B 37/12

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords:adhesive, amine, curing agent, epoxy, flexible

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0561048 A2 (HUGHES AIRCRAFT COMPANY) 22 September 1993 abstract; claims 1-3; page 2	1-3,9-11,14-16
X	US 6262148 B1 (CHENG, C.-W. F. et al.) 17 July 2001 claims 1, 17; column 1, line 15-18; column 11, lines 60-65; column 12, lines 60-63; column 13, lines 15-17	1-3,9-11,14-16
A	US 2015-0240068 A1 (YAN, L. et al.) 27 August 2015 claims 1, 18; paragraphs [0007], [0008], [0040]-[0042]	1-3,9-11,14-16
A	US 2015-0284608 A1 (SIKA TECHNOLOGY AG) 08 October 2015 claims 1, 9, 11, 12	1-3,9-11,14-16
A	US 2004-0197563 A1 (KYE, J.) 07 October 2004 the whole document	1-3,9-11,14-16



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

"D" document cited by the applicant in the international application

"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

30 June 2020 (30.06.2020)

Date of mailing of the international search report

30 June 2020 (30.06.2020)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2020/021379

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-8, 12, 13, 17
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2020/021379

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0561048 A2	22/09/1993	DE 69229262 T2 EP 0561048 A3 EP 0561048 B1 JP 06-017024 A JP 2685399 B2 US 5367006 A	20/01/2000 01/03/1995 26/05/1999 25/01/1994 03/12/1997 22/11/1994
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